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# Macromolecular Ligand Engineering for Programmable Nanoprism Assembly

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| Cite This: J. Am. Chem. Soc. 2021, 143, 16163–16172 |                    |  | Read Online             |                          |
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**ABSTRACT:** Ligands play a central role for the energetics and kinetics of nanocrystal assembly. Yet, the precise and simultaneous manipulation of ligands to dictate assembly outcome has proven difficult. Here, we present macromolecular ligand-engineering strategies to control, characterize, and model four molecular parameters of grafted polymer chains: chain length, chain dispersity, grafting density, and chain distribution. Direct ligand-exchange between nanoprisms and polymers functionalizes facets selectively and produces patchy nanocrystals. We develop a generalizable two-step ligand-exchange approach for the independent control of the two emergent brush parameters, brush thickness and brush softness. The resultant polymer-grafted prismatic nanocrystals with programmable ligand brushes self-assemble into thin-film superstructures



of different wallpaper symmetries and faceted supracrystals. Our experiments are complemented by coarse-grained computer simulations of nanoprisms with directional, facet-specific interactions. This work paves the way for the precision synthesis of polymer–nanocrystal hybrid materials and enables the further refinement of theoretical models for particle brush materials.

## INTRODUCTION

Colloidal nanocrystals (NCs) interact with their surrounding primarily through surface ligands. Ligands are necessary not only to control nucleation and growth of NCs and impart colloidal stability but also to mediate NC assembly into ordered superstructures in which ligand-ligand attractions can be the dominant force behind cohesion.<sup>1</sup> Superstructure phase behavior can be tuned by utilizing the interplay between NC geometry and free energy contributions from surface ligands.<sup>1-9</sup> For example, varying ligand-to-core size ratio of spherical NCs induces a transition from the close-packed facecentered cubic lattice to the more open body-centered cubic lattice.<sup>2,5,9</sup> This transition exploits the preference of the ligands to maximize conformational entropy and attractions with neighboring NCs. Particle shape as a design parameter already unlocked a rich diversity of superstructures with distinctive electronic, photonic, and mechanical properties, as predicted with computer simulations<sup>10,11</sup> and realized experimentally by harnessing van der Waals (vdW),<sup>12-18</sup> electrostatic,<sup>19-21</sup> hydrogen bonding,<sup>22</sup> and DNA base pairing<sup>23,24</sup> interactions. Besides ligand length, grafting density and spatial distribution of ligands have been exploited as tuning parameters to direct quasi-spherical NCs into superstructures with long-range translational and orientational order.<sup>4,25</sup> However, precise ligand engineering to achieve orthogonal control of multiple ligand parameters and to dictate assembly outcome has proven difficult for many NC systems.

Polymer-grafted nanocrystals (PGNCs), also known as "hairy nanoparticles", promise a vast parameter space for materials design through the molecular-level control of entropic and enthalpic contributions to NC interactions.<sup>5,26–33</sup> Significant progress has been made on the synthesis of unary and binary spherical PGNC assemblies and in the development of sophisticated models to describe the collective deformation of ligands during assembly.<sup>5,30,34-36</sup> By contrast, predicting and programming the phase behavior of shape-anisotropic PGNCs at high densities where many-body effects emerge from the interplay of NC shape with its ligand brush remains difficult.<sup>37</sup> Here, we develop macromolecular ligand-engineering strategies to control the ligand variables chain length, chain dispersity, grafting density, and chain distribution. We choose triangular nanoprisms because of their high aspect ratio and strong variation in local surface curvature, ranging from sharp tips to atomically flat basal planes. Direct ligand-exchange with polymers produces patchy nanoprisms that assemble into thin-film superstructures with diverse wallpaper symmetries. Coarse-grained computer simulations of hard and attractive

Received: July 13, 2021 Published: September 22, 2021



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**Figure 1.** Synthesis and characterization of PS-grafted  $Gd_2O_3$  triangular nanoprisms. (a and b) Representative AC-HAADF-STEM images of a single triangular nanoprism viewed along the [001] zone axis. (c) Normalized GPC traces of different PS-Br samples and the corresponding number-averaged molecular weight  $M_n$ . (d) Schematic of the direct ligand-exchange method. (e–g) TEM image (e) and schematic illustrations (f and g) of self-assembled PS-grafted nanoprism superstructures showing coexisting horizontally lying and vertically standing domains with different nearest-neighbor distances. (h and i) FTIR spectra (h) and TGA results (i) of as-made nanoprisms, pure PS–PEHA ligands, and PS-grafted nanoprisms obtained using the direct ligand-exchange method. Scale bars: (a) 5, (b) 1, and (e) 50 nm.

nanoprisms guide us to develop a generalizable two-step ligand-exchange method, which is distinct from the common grafting-to method for PGNC synthesis. We demonstrate the independent control of ligand chain and ligand brush parameters and create programmable thin-film superstructures and faceted supracrystals.

## EXPERIMENTAL SECTION

Synthesis of Nanocrystals, Polymeric Ligands, and Polymer-Grafted Nanocrystals.  $Gd_2O_3$  triangular nanoprisms were synthesized through the thermal decomposition of gadolinium acetate in the presence of oleic acid and oleylamine.<sup>38</sup> Pentaethylenehexamine-terminated polystyrene (PS–PEHA) ligands were synthesized in a two-step reaction. In the first step, bromine-terminated polystyrene was synthesized by using activators regenerated by electron transfer atom transfer radical polymerization (ARGET ATRP).<sup>39,40</sup> In the second step, the bromine end group was converted to PEHA. Two grafting-to methods, namely, direct ligand-exchange and two-step ligand-exchange, were used to functionalize NCs with PS-PEHA ligands. Further details on materials synthesis and characterization are provided in the Supporting Information (SI). Calculations of the vdW interactions between NC cores and between interdigitating ligands are detailed in the SI.

Assembly of Polymer-Grafted Triangular Nanoprisms into Ordered Superstructures. Nanoprisms were assembled by using the liquid–air interfacial assembly method, which involves drying a solution of nanoprisms on top of an immiscible ethylene glycol liquid subphase.<sup>5,41</sup> Ordered superstructures were also prepared by drying PS-grafted nanoprisms directly on Si substrates. Details are described in the SI.

**DFT Calculations of Ligand Binding on Gd<sub>2</sub>O<sub>3</sub> Nanoprisms.** Density-functional theory (DFT) calculations were performed using the projector augmented wave (PAW) method implemented with the Vienna *ab initio* simulation package (VASP).<sup>42</sup> The Perdew–Burke– Ernzerhof (PBE) approximation was used to describe the exchange and correlation functionals. The plane-wave cutoff energy was set to 400 eV, the Hellmann–Feynman force on each atom was smaller than 0.01 eV Å<sup>-1</sup>, and the total energy converged to  $10^{-5}$  eV for structural optimization. Gd<sub>2</sub>O<sub>3</sub> was modeled by a 2 × 2 supercell, and a vacuum space of 20 Å was added between adjacent supercells. Gd<sub>2</sub>O<sub>3</sub> (001) and (100) surfaces were modeled by a five-atomic-layer slab and a sixatomic-layer slab, respectively. Details on DFT calculations are provided in SI.

**Transmission Electron Microscopy (TEM) Image Processing and Analysis.** A flowchart describing TEM image processing and analysis procedure is shown in Figure S18. Raw TEM images were processed by using the open-source software ImageJ to identify particles contours and locate centroids. Custom written MATLAB scripts were used to calculate the radial distribution function g(r) as well as bond-orientational order parameters and particle orientational order parameters. Details are provided in the SI.

**Densest Packing Calculation and Monte Carlo Simulation with the Hard Spherotriangle Model.** Spherotriangles are the Minkowski sum of a triangle and a disk. We evaluated their densest packings analytically as described in the SI. Hard particle Monte Carlo simulations were performed using the HPMC package in HOOMDblue.<sup>43</sup> Simulations were initialized in the pmg phase and conducted in the isochoric ensemble with flexible shear and aspect ratio changes enabled using the boxMC updater to minimize finite-size effects. Phase maps were generated by analyzing the local symmetry of all particles at the end of each simulation. Further details are provided in the SI.

Molecular Dynamics Simulation with the Attractive Triangle Model. We modeled the interaction between two triangular nanoprisms covered with ligand brushes using the Derjaguin approximation. This approximation evaluates the interaction of two bodies by integrating an isotropic pair potential. We chose the Morse potential  $U_{\text{pair}}(r) = U_0(e^{-2\alpha(r-r_m)} - 2e^{-\alpha(r-r_m)})$ , which introduces the dimensionless parameter  $S = (\alpha I)^{-1}$ , which we term the softness of the ligand brush, the location of the minimum  $r_m \approx 2r_D$ , and the attraction strength  $U_0$ . We can express the effective interaction U of two nanoprism as a double integral computed over the surface of both shape A and shape B,

$$U = \oint_{A} d\mathbf{r}_{A} \oint_{B} d\mathbf{r}_{B} U_{pair} (|\mathbf{r}_{B} - \mathbf{r}_{A}|)$$

We solved this integral numerically and stored it in precomputed three-parameter tables. Simulations were performed with an in-house molecular dynamics code. Simulations were initialized in the pmg phase and ran at a fixed simulation box volume. The aspect ratio of the simulation box was kept variable by including Monte Carlo box update moves. The system was slowly thermalized to the desired temperature with a Bussi–Donadio–Parrinello thermostat. A complete discussion of the attractive triangle model is given in the SI.

#### RESULTS AND DISCUSSION

Synthesis and Characterization of Polymer-Grafted Nanoprisms. Gd<sub>2</sub>O<sub>3</sub> triangular nanoprisms were synthesized through the thermal decomposition of gadolinium acetate in the presence of oleic acid (OA) and oleylamine (OLAM).<sup>38</sup> The nanoprisms are highly anisotropic with a thickness of 1.2  $\pm$  0.1 nm and an edge length of triangular basal planes tunable between 15 and 25 nm (Figure 1a and Figure S1). TEM image estimated the radius of curvature of nanoprism vertices to be  $1.1 \pm 0.2$  nm. Top-view aberration-corrected scanning TEM (AC-STEM) images of a single nanoprism revealed a honeycomb arrangement of Gd atoms (Figure 1b). We attribute these Gd<sub>2</sub>O<sub>3</sub> nanoprisms to the hexagonal La<sub>2</sub>O<sub>3</sub>type crystal phase (space group  $P\overline{3}m1$ , a = 3.86 Å, c = 5.25 Å) rather than the previously reported cubic phase (space group Ia3).44 This assignment is supported by powder X-ray diffraction (PXRD) data (Figures S2 and S3).

As-synthesized nanoprisms preferentially self-assemble into linear stacks, maximizing face-to-face contact between nanoprisms as a result of vdW attractions from interdigitated alkyl ligands and between Gd<sub>2</sub>O<sub>3</sub> cores (Figures S4–S6). Narrowly dispersed pentaethylenehexamine-terminated polystyrene (PS-PEHA) ligands of a wide range of molecular weights were synthesized using atom transfer radical polymerization (ATRP) (Figure 1c and Tables S1 and S2).<sup>39</sup> We prepared polymer-grafted nanoprisms by direct ligand-exchange between alkyl-capped nanoprisms and PS-PEHA (Figure 1d and Table S3). Afterward, the nanoprisms became insoluble in aliphatic solvents such as hexane, indicating the successful grafting of PS-PEHA. Fourier-transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA) were employed to analyze ligand composition.<sup>45</sup> The presence of aromatic C-H and COO<sup>-</sup> stretching vibrations suggests that these nanoprisms have mixed alkyl and PS ligands (Figure 1h).46-Incomplete ligand-exchange is also manifested from the multistep mass loss of TGA for as-made alkyl-capped and PS-grafted nanoprisms (Figure 1i and Figure S7).

The difficulty in achieving complete ligand-exchange could arise from the strong binding of OA/OLAM ligands to the flat basal planes, which promotes their stabilization and expression during nanoprism growth. We tested this hypothesis by evaluating the binding affinity of OA and OLAM on different  $Gd_2O_3$  crystal planes using density-functional theory (DFT) calculations (Table S4). We found that oleate has higher binding energies compared to OA and OLAM, showing that it is the primary ligand for as-synthesized nanoprisms. DFT calculations also suggest that oleate binds more strongly to the (001) basal planes than the (100) side planes of nanoprisms. A probable cause for this is a higher density of Gd<sup>3+</sup> ions on the (001) surface. Both bridging and chelating bidentate modes of oleate are predicted to be favorable on the (001) basal planes, which is supported by the FTIR results (Figure 1h and Figure S8). By contrast, only the bridging bidentate mode is stable on the (100) side planes (Table S4).

Collectively, our DFT calculations suggest that PS-PEHA preferentially displaces alkyl ligands on the sides of nanoprisms during ligand-exchange, producing patchy nanoprisms. Indeed, such chemical patchiness is confirmed by experimental results (Figure 1e-g and Figures S9 and S10). Specifically, the faceto-face distance measured from the vertically standing stacks of PS-grafted nanoprisms was only marginally larger than that of alkyl-capped nanoprisms  $(4.3 \pm 0.2 \text{ vs } 3.6 \pm 0.2 \text{ nm})$ . This trend persisted for a wide range of PS chain lengths, suggesting a sparse coverage of PS on the basal planes of nanoprisms. In contrast, the nearest-neighbor edge-to-edge distance measured from horizontally lying PS-grafted nanoprism stacks was larger and increased monotonically with PS chain length (vide infra). We ruled out separate populations of PS- and alkyl-capped nanoprisms by conducting ligand-exchange at different PS-tonanoprism molar ratios and by performing multiple superstructure preparations to ensure reproducibility in the orientation-dependent nearest-neighbor spacing. Taken together, PS-grafted Gd<sub>2</sub>O<sub>3</sub> nanoprisms afforded by direct ligand-exchange represent shape-anisotropic, patchy PGNCs whose interaction can be tuned by PS chain length.

Assembly of Polymer-Grafted Nanoprisms into Ordered Superstructures. A two-dimensional tiling of equilateral triangles has neighbors in opposite orientations. Gliding and shear along lattice directions can induce transitions from the hexagonal wallpaper symmetry p6m to the lower symmetries p2 and pmg (Figure S11).<sup>49</sup> As the polymer chain length increases, the ligand brush becomes



**Figure 2.** Structural diversity in self-assembled superstructures of PS-grafted  $Gd_2O_3$  triangular nanoprisms. (a) Schematic illustration of a pmg-type superstructure with vertical stacks of nanoprisms. (b–h) Experimental phase diagrams (b) and TEM results of superstructures self-assembled from large (23.5 nm edge length) and small (17.0 nm edge length) nanoprisms grafted with PS–PEHA ligands. For each superstructure in (c–h), representative TEM images are shown on the left with nanoprisms edge length and ligand molecular weight indicated. FFT and WAED patterns are on the upper right and lower right, respectively. (i) Average vertex-to-edge (blue) and edge-to-edge (red) distances in pmg-type superstructures of nanoprisms grafted with PS–PEHA ligands of different molecular weights  $M_n$ . The nearest-neighbor distances of 4.5 nm Au nanocrystals grafted with the same PS–PEHA ligands are also shown (yellow). (j–m) Radial distribution functions of different superstructures computed from TEM images. Insets are structure sketches and polar diagrams of bond and triangular nanoprism orientations. Scale bars: (c–f) 100 nm and (g, h) 50 nm. FFT patterns: 0.05 nm<sup>-1</sup>. WAED patterns: 2 nm<sup>-1</sup>.

more malleable. Furthermore, nanoprisms may respond strongly to constraints from their neighbors, resulting in significant nonadditive interparticle interactions.<sup>37</sup>

We assembled PS-grafted nanoprisms by the slow drying of a toluene solution on top of ethylene glycol (EG).<sup>5,41</sup> The resultant superstructures are arrays of short stacks of aligned nanoprisms with distinct wallpaper symmetries (Figure 2a). We found that the ratio of ligand length to nanoprism edge length is the key parameter to traverse the phase diagram

(Figure 2b). Large nanoprisms (edge length: 23.5 nm) grafted with 1.8 kDa PS produced superstructures with the p2 symmetry, similar to alkyl-capped nanotriangles (Figure 2c).<sup>50</sup> When the same nanoprisms were grafted with 2.6 kDa PS ligands, p6m-type superstructures were obtained (Figure 2d). Both superstructures showed long-range translational and orientational order, as evidenced by sharp spots on the fast Fourier transform (FFT) and wide-angle electron diffraction (WAED) patterns (Figure 2c,d). P2-type superstructures

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**Figure 3.** Particle shape and ligand brush softness explain the phase behavior of PS-grafted triangular nanoprisms. (a) Analysis of densest packings of spherotriangles under symmetry constraints. For the pmg phase, we distinguish horizontal translation only (light blue) and a staggered variant, which is denser (dark blue). (b) Phase diagram of the hard spherotriangle model at  $\phi \leq 0.9$ . Lines are guides to the eye. (c) Color map of the pairwise interaction potential between two attractive triangles in opposite orientations as a function of the relative translation vector (x, y), normalized to attraction strength  $U_0$ . (d) Schematic illustration of the ligand brush around a nanoprism, highlighting the rounding parameter  $R = r_D/(l + r_D)$  and the softness parameter *S*. (e) Energy per surface area of the ligand brush as a function of nanoprism distance for edge-to-edge (e–e) and vertex-to-vertex (v–v) contact, normalized to keep the edge-to-edge curves constant. (f) Phase diagram of the attractive triangle model at  $\phi = 0.9$ , S = 0.01. The p2-type superstructure (green diamonds) appears in two separated regions ① and ②. Symbols as in (b).

dominated again as the molecular weight of PS–PEHA ligands increased to 3–6 kDa (Figure 2e). A new phase with pmg symmetry coexisted with the p2 phase over this molecular weight range (Figure S12). It is characterized by alternating rows of antiparallel nanoprisms, featuring both edge-to-edge and edge-to-vertex neighbor contacts, and became dominant with PS–PEHA ligands of 8–14 kDa for large nanoprisms (Figure 2f and Figure S12) and with PS–PEHA ligands of 3–6 kDa for small nanoprisms (edge length: 17.0 nm, Figure 2b and Figures S13 and S14). Upon further increase of the ligand chain length, the orientational order of the nanoprism stacks started deteriorating (Figure 2g).

Statistical image analysis of pmg-type superstructures revealed a larger edge-to-edge distance than edge-to-vertex distance over a wide range of PS-PEHA ligand lengths. Furthermore, the edge-to-vertex distance was consistently smaller than the brush thickness when the same PS-PEHA ligands were grafted onto spherical Au NCs (radius: 2.2 nm, Figure 2i, Figures S16, S17, and S22, and Table S5). These results show that the polymer brush thickness is sensitive to the curvature of the grafting surface. Chain tilt and redistribution of ligands away from the contact area can further reduce osmotic repulsion between ligand brushes and densify the superstructure. With even longer PS-PEHA ligands, a hexagonal plastic phase was realized, as evidenced by hexagonal spots on the FFT pattern and simultaneous diffraction rings on the WAED pattern (Figure 2h). Although analogous structure transitions occur for large and small

nanoprisms, we did not observe the p6m-type superstructure in the latter system (Figure 2b). Our shortest PS-PEHA ligands (1.8 kDa) might already be too long to stabilize the p6m phase. To quantify the degree of ordering of nanoprism assemblies, we tracked the center positions and orientations of nanoprism stacks (Figure 2j-m and Figures S18-S20). Sharp peaks of the radial distribution function g(r) manifest the long-range translational order of p2, p6m, and pmg superstructures, with the p6m structure having the shortest nearest-neighbor distance. All three superstructures feature two distinct triangle orientations and antiparallel alignment between nearest neighbors (insets of Figure 2j-m and Figure S21).

**Simulations of Polymer-Grafted Nanoprisms.** We probed the phase behavior of nanoprisms with coarse-grained computer simulations. Our strategy was to gradually add complexity to the model until it reproduces all observations. The simplest model considers nanocrystals as hard particles that arrange to optimize the utilization of the available space. The translation of this model into a mathematical problem is the search for the densest packings of identical shapes. Because of the ligand brush, the shape of Gd<sub>2</sub>O<sub>3</sub> nanoprisms is best approximated by spherotriangles with rounding parameter  $R = r_D/(l + r_D)$ , which are constructed by sweeping a disk of radius  $r_D$  (the ligand brush thickness) along a triangle (the inorganic core) of edge length *l*.

We evaluated the densest packing of spherotriangles analytically as a function of rounding (Figure 3a and Figure S23). At R = 0, triangles fill space with wallpaper group p6m.



Figure 4. Programing superstructure symmetry through independent tuning of ligand length and grafting density. (a) Scheme of the two-step ligand-exchange process. (b-d) TGA results for nanoprisms grafted with 3.4 (b), 2.6 (c), and 1.8 kDa (d) PS-PEHA. (e-p) Representative TEM images of superstructures self-assembled from  $Gd_2O_3$  triangular nanoprisms (23.5 nm edge length) grafted with different PS-PEHA ligands at varying grafting densities. (q) Experimental phase diagram of superstructures. (r) Average edge-to-edge distances for different superstructures as a function of ligand length and grafting density. (s) Average edge-to-edge distances for p2-type (from k-m) and p6m-type (from n-p) superstructures upon increasing ligand length. (t) Representative SEM image of p6m-type faceted supercrystals composed of PS-grafted nanoprisms. Scale bars: (e) 100 nm, inset of (h), 0.05 nm<sup>-1</sup>; (t) 5  $\mu$ m, inset, 100 nm. TEM images (f-p) share the same scale bar as image (e) and FFT patterns in (i-p) share the same scale bar as inset of (h).

For R > 0, a phase with symmetry p2 appeared, followed by pmg symmetry near R = 0.4. Finally, at R = 1, the hexagonal disk packing, a limiting case of the plastic phase, is reached. Next, we included entropic contributions with hard particle Monte Carlo simulation.<sup>11</sup> Simulations of this hard spherotriangle model (HSM) were initialized from different starting configurations and continued at a constant packing density  $\phi$ up to convergence (Figure S24–25). The HSM phase diagram (Figure 3b) predicts the enhanced stability of the highsymmetry phase p6m for  $\phi = 0.8-0.9$  and a robust plastic phase for rounded particles at  $\phi \leq 0.85$ . The stability of the low-symmetry phases p2 and pmg is reduced. Overall, the HSM explains the phase sequence p6m  $\rightarrow$  p2  $\rightarrow$  pmg  $\rightarrow$ plastic in Figure 2b, highlighting the importance of steric effects for superstructure formation in the limit of long alkyl ligands.

It remains to explain the second appearance of the p2-type superstructure for native alkyl and short PS–PEHA ligands. In this limit, the HSM breaks down, and vdW attractions of ligand brushes must be modeled explicitly. We described ligand-induced interactions with the Derjaguin approximation, which, however, is not accessible directly with standard molecular simulation techniques.<sup>51,52</sup> Instead, we evaluated surface integrals numerically and precomputed forces and energies in tables. This attractive triangle model (ATM) captures the rounding effect of ligand brushes automatically and yields the full orientation-dependent, anisotropic vdW pair potential (Figure S26). The pair potential map for a fixed relative

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orientation (Figure 3c) confirms that attraction is strongest when ligands interact over a large area (edge-to-edge contact) and weakest when the interaction area is small (vertex-tovertex contact). Besides the dimensionless brush parameter rounding R, which relates to ligand brush thickness, the ATM has the dimensionless brush parameter S (Figure 3d). We term this parameter as the softness of the ligand brush because it describes the sharpness of the transition from steric repulsion to vdW attraction in the pair potential map and is related to the width of the ligand brush boundary. Energy per surface area of the ligand brush decreases with increasing S for vertexto-vertex contact compared to edge-to-edge contact (Figure 3e), predicting that superstructures prefer vertex-to-vertex contacts as the ligand brush softens. Such contacts dominate in the p2 phase.

We test the stability of the p2 and p6m phases with molecular dynamics simulations of the ATM. We fix the softness at a low value S = 0.01 to simulate near the hard particle limit. Figure 3f shows the phase behavior as a function of rounding R and attraction strength  $U_0$ . Because vdW attractions increase as solvent leaves the sample, we increased  $U_0$  to model the drying process. The lower limit  $U_0/k_BT = 0.2$ corresponds to nanoprisms during the early stage of drying. Our simulations suggest that the p6m phase transforms into a p2 phase (region ② in Figure 3f) as drying proceeds toward  $U_0 \gg k_BT$ . This energetically favored p2 phase persists and gradually extends toward a higher rounding with increasing softness (Figures S27–S29). A second, entropically favored p2 phase (region ① in Figure 3f) coincides with the p2 phase found in the HSM (Figure 3b).

Programming Superstructure Symmetry through Independent Control of Ligand Length and Grafting Density. The phase diagram of nanoprism softness versus vertex rounding from simulation predicts that, for ligand brush thickness in the range 1.2-2.6 nm, it is possible to tune the relative stability between p2-type and p6m-type superstructures by controlling the softness of ligand brush, with p2 becoming more favorable with increasing softness (Figure S27). To test these predictions, we developed a two-step ligand-exchange method that removes the native alkyl ligands before polymer grafting (Figure 4a). In the first step, the alkylating agent triethyloxonium tetrafluoroborate ( $Et_3OBF_4$ ) was used to strip the hydrocarbon ligands of as-made Gd<sub>2</sub>O<sub>3</sub> nanoprisms.<sup>53,54</sup> Near-complete ligand removal was evidenced by the greatly diminished intensity of C-H stretching vibrations on FTIR and the significantly reduced mass-loss from TGA (Figure 4b-d and Figure S30). In the second step, reacting ligand-stripped nanoprisms with PS-PEHA at different molar ratios produced a library of PGNCs. TGA results revealed that the PS grafting density increased monotonically with the feeding grafting density, albeit at a decreasing grafting efficiency, and reached values as high as two chains per nm<sup>2</sup> with PS-PEHA of 1.8-3.4 kDa (Figure S31 and Table S6). Dense polymer brushes, including those on the basal planes of nanoprisms, were further manifested by the large interprism spacings determined from vertically standing stacks (Figure S32). These results show that our two-step method overcomes key challenges associated with the common grafting-to method, with which the ligand grafting density is difficult to control and to quantify with TGA due to mixed ligands. Twostep ligand exchange also extends the range of grafting densities through the optimal utilization of ligand binding sites on the NC surface.

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Superstructure symmetry depends markedly on PS-PEHA grafting density (Figure 4e-p). At low grafting densities below 0.6 chains per nm<sup>2</sup>, disordered assemblies resulted after drying the nanoprism solution atop of EG (Figure 4e-g). At intermediate grafting densities, the p2-type superstructures became dominant, and its degree of ordering improved with increasing grafting density (Figure 4h-m and Figure S33). At high grafting densities above 1.6 chains per nm<sup>2</sup>, extended p6m-type superstructures were obtained (Figure 4n-p and Figure S34). As summarized in the phase diagram in Figure 4q, this grafting-density-dependent amorphous-to-p2-to-p6m structural transition pathway was independent of PS-PEHA molecular weight in the range 1.8-3.4 kDa, in excellent agreement with the phase behavior predicted by the ATM (Figure S27). Quantitative TEM image analysis revealed that the edge-to-edge distance between nearest-neighbor nanoprisms increases monotonically with grafting density as well as with the chain length of PS-PEHA ligands, further attesting the successful formation of dense polymer brushes with programmable softness and brush thickness (Figure 4r,s and Figures S35 and S36). Greater angular offsets between the triangle edges and the direction normal to the largest periodicity for p2-type superstructures with increasing ligand length (Figure S37) indicate a preference to maximize the overlapping area between opposing edges.

An important advantage of the two-step grafting-to method is the reduction of ligand brush disorder by the near-complete elimination of mixed ligand brushes. Previous simulations showed that ligand ordering and grafting density strongly affect ligand-induced attraction.<sup>52</sup> Therefore, we hypothesized that purely PS-grafted nanoprisms can assemble not only into extended thin-films but also into discrete supracrystals. Indeed, we discovered well-faceted supracrystals after the slow drying of a toluene solution of nanoprisms on top of silicon substrates (Figure 4t). Top-view and cross-sectional SEM images revealed unprecedented translational and orientational registry of nanoprisms (Figure S38). The local p6m symmetry amplified into a hexagonal prismatic faceting of the supracrystals. Although PS-grafted nanoprisms prepared by direct and two-step ligand-exchange methods both assembled into p6m-type superstructure on top of EG, the former did not produce ordered supracrystals when drying directly on Si substrates (Figure S39). These control experiments underscore the significance of managing ligand composition and spatial distribution for multiscale control of PGNC superstructure growth. Finally, disordered films were obtained with PS-PEHA ligands longer than 6 kDa (Figure S40). In these cases, the low polymer grafting density on the nanoprism basal planes due to greater steric hindrance might not cause sufficient attraction to favor the formation of linear nanoprism stacks during assembly.

## CONCLUSION

In conclusion, we developed macromolecular ligand-engineering strategies to control, characterize, and model polymer ligand brushes on NC surfaces. Patchy and densely grafted shape-anisotropic NCs with programmable ligand brush thickness and softness were synthesized. We assembled polymer-grafted triangular prismatic NCs into diverse thinfilm superstructures with different wallpaper symmetries and into faceted supracrystals. The simulations of hard and attractive particles highlighted the diversity and complexity of PGNC assemblies achievable by tailoring the interplay

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between entropy and short-range attractions through ligandengineering. Our modular approaches apply to diverse combinations of polymeric ligands bearing versatile end functionalities and colloidal NCs for which mild stripping of native ligands has become routine. Thus, a vast parameter space spanned by size, shape, composition, ligand chemistry, and topology of PGNC building blocks can be leveraged to realize the potential of nanostructured hybrid materials by design.

### ASSOCIATED CONTENT

#### **1** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c07281.

Discussions of detailed experimental and simulation methods, FTIR peak assignments and spectral analysis, calculations of pairwise van der Waals interactions and ligand-ligand interactions, density functional theory calculations, TEM image processing and analysis, calculation of densest packings, determination of the hard spherotriangle phase diagram, and coarse-grained simulations of attractive triangles, scheme of synthetic pathway, figures of TEM and SEM images, size distribution histograms, powder XRD pattern, unit cell and structure models, distance-dependent pairwise vdW interactions, TGA results, FTIR spectra, line profile, tapping-mode AFM image, height profile, schematic illustration of distinct planar wallpaper symmetries, radial distribution functions, flowchart of general image processing and analysis procedure, exemplary data illustrating the particle contour-finding and centroiddetection process, plot of triangle centroids obtained, exemplary polar histograms, geometric constructions used, coordinate polygons obtained, phase diagram of the attractive triangle model, and plot of grafting efficiency versus feeding grafting density, and tables of synthetic parameters, summaries of experimental parameters used, and summary of binding energies (PDF)

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## Author Contributions

<sup>§</sup>Y.L., M.K., Y.W., and Y.Z. contributed equally to this work.

## Funding

Y.L., Y.W., Y.Z., B.Z., J.C., and X.Y. acknowledge support from the U.S. National Science Foundation through award DMR-2102526. M.K. and M.E. acknowledge support from the German Research Foundation (DFG) through the Collaborative Research Center CRC 1411.

## Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The authors are thankful to Dr. Huisheng Zhang for help with DFT calculations. The authors would like to thank Indiana University Nanoscale Characterization Facility and Electron Microscopy Center for access of instrumentation. Computational resources and support provided by Erlangen Regional Computing Center (RRZE) are gratefully acknowledged.

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