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Probing the Consequences of Cubic Particle Shape and Applied Field on Colloidal Crystal Engineering with DNA

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Abstract: In a magnetic field, cubic Fe_3O_4 nanoparticles exhibit assembly behavior that is a consequence of a competition between magnetic dipole-dipole and ligand interactions. In most cases, the interactions between short hydrophobic ligands dominate and dictate assembly outcome. To better tune the face-to-face interactions, cubic Fe_3O_4 nanoparticles were functionalized with DNA. Their assembly behaviors were investigated both with and without an applied magnetic field. Upon application of a field, the tilted orientation of cubes, enabled by the flexible DNA ligand shell, led to an unexpected crystallographic alignment of the entire superlattice, as opposed to just the individual particles, along the field direction as revealed by small and wide-angle X-ray scattering. This observation is dependent upon DNA length and sequence and cube dimensions. Taken together, these studies show how combining physical and chemical control can expand the possibilities of crystal engineering with DNA.

Superlattices of magnetic nanoparticles (NPs) have enabled studies of the magnetic morphogenesis of materials,^[1,2] microrobots,^[3,4] and nanoscale magnetic phenomena.^[5–9] Typically, when assembled in a magnetic field, the structures of these superlattices result from a balance of surface ligand and magnetic dipole coupling interactions.^[10,11] Anisotropic NPs, such as cubes, introduce directionality to these interactions and provide an opportunity to control structure and investigate complex colloidal arrangements. The majority of studies on the assembly of cubic, magnetic NPs have been carried out on NPs surface-modified with hydrophobic ligands.^[11-16] Their preferred axis of magnetization, or easy axis, is along the $\langle 111\rangle_{Fe_3O_4}$ direction (the $\langle 111\rangle$ crystallographic direction of magnetite) which corresponds to the diagonal of the cube.^[11] In most studies, a magnetic field is applied to either a solution of magnetic nanocubes during

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b supporting information and the offerb identification number(s) for the author(s) of this article can be found under: https://doi.org/10.1002/anie.202012907. solvent evaporation-induced assembly or a highly concentrated solution of nanocubes to induce superlattice assembly.^[17] In both cases, face-to-face interactions from surface ligands compete with corner-to-corner field-induced dipoledipole interactions to control the structure of the resulting superlattices. These surface ligands, which are typically the stabilizing agents introduced during colloidal synthesis, provide little to no control over particle spacing, neighboring particle coordination number, or interaction strength. DNA offers an opportunity to tailor these surface interactions to control the possible structures obtainable with cubic Fe_3O_4 NPs.

As a surface ligand, DNA is a powerful tool for controlling the assembly of colloidal crystals.^[18-20] When densely arranged on a NP core, this results in a programmable atom equivalent (PAE).^[20,21] Here, the length, base pair (bp) specificity, and backbone flexibility of the DNA strands are molecular knobs that can be tuned to achieve different crystal symmetries and habits.^[21-24] In addition, the composition and shape of the NP core can be varied independently from the DNA shell.^[25-28] Recent work has investigated the use of external stimuli to influence colloidal crystal growth of spherical, DNA-coated Fe₃O₄ NPs. This work found that applying magnetic fields to the magnetic PAEs resulted in the formation of elongated nanostructures,^[29] highlighting the unique ability of DNA to separate the interactions of dipoledipole coupling and DNA hybridization interactions to form high-aspect ratio structures with tailored crystal symmetry. However, the effect of nanoscale anisotropy on these interactions could not be investigated as spherical PAEs were used. Here, the assembly of cubic Fe₃O₄ PAEs was investigated with and without an applied magnetic field as a function of DNA design and cubic NP size. We show that the innate anisotropy of cubic PAEs enables orientation control of the NPs across multiple length scales.

Cubic Fe₃O₄ NPs were synthesized by the controlled thermal decomposition of iron oleate in the presence of sodium oleate and oleic acid.^[11,30] The cubes had an average edge length of 21.4 ± 1.9 nm as determined by transmission electron microscopy (TEM) analysis (Figure 1b). The NPs were then transferred into the aqueous phase using a multicatechol polymer containing functional azide groups that covalently binds to the NP surface, displacing the native oleate ligands (Figure 1a).^[31] Once the polymer-coated NPs were stabilized in buffer, PAEs were synthesized by reacting dibenzylcyclooctyne (DBCO)-terminated DNA with the azide groups on the polymer.^[25]

Ligand exchange of the cubic Fe_3O_4 NPs was confirmed by Fourier-transform infrared spectroscopy (FTIR) where the

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Figure 1. a) Schematic of the synthesis of cubic Fe₃O₄ PAEs. The original oleate ligands are replaced with an azide functionalized multi-catechol polymer to transfer the NPs from the organic (hexanes) to the aqueous phase. DBCO-terminated DNA is then reacted with the azide groups and linker strands are hybridized to those anchor strands to form the final PAE construct. b) TEM image of the \approx 22-nm edge-length cubes. Scale bar = 100 nm. c) FTIR spectra of the oleate-coated and multi-catechol polymer-coated cubes. d) DLS data reveal size increases upon DNA attachment and subsequent linker hybridization.

removal of oleate from the cube's surface was confirmed by the disappearance of the symmetric carboxylate stretching peak around 1412 cm⁻¹ (Figure 1c). Attachment of the catechol polymer was confirmed by the relative change in intensity of the surface bound C-O stretch of the catechol around 1280 cm⁻¹ and the azide stretch at ≈ 2100 cm⁻¹. Importantly, the particle edge length and morphology were retained after ligand exchange, as seen via TEM (Figure S1). Additionally, particles of this size are expected to be on the edge of superparamagnetic magnetization behavior.^[32,33]

To understand how Fe₃O₄ NPs assemble without external stimuli or DNA, oleate-capped NPs were assembled via solvent destabilization in hexane. Under such conditions, these particles form ordered, simple cubic (SC) symmetry superlattices (Figure 2a,b) due to strong magnetic coupling and face-to-face van der Waals interactions. To separate the magnetic coupling from surface anisotropy, we looked to assemble the 22-nm cubic Fe₃O₄ PAEs (Fe₃O₄ cubes with 22 nm edge length functionalized with DNA). To do so, 66 bp linker strands of DNA (\approx 22 nm in length) were hybridized to the anchor strands on the particle's surface. These linker strands possess an unhybridized sticky end region with a complementary bp sequence designed to form superlattices with body centered cubic (bcc) symmetry.^[34] The length of these strands triples the hydrodynamic diameter of the particle construct as compared to the polymer passivated cubic Fe₃O₄ NPs as evidenced by dynamic light scattering (DLS) measurements (Figure 1 d). This significant increase in effective diameter leads to a more isotropic arrangement of DNA. The resulting decrease in particle anisotropy is expected to cause the cubic PAEs to assemble as spherical PAEs.[35] Consistent with this assumption, when slow cooled ($0.01 \,^{\circ}\mathrm{C\,min^{-1}}$), the cubes assembled into the expected *bcc* symmetry structures, as confirmed by small-angle X-ray scattering (SAXS; Figure 2d). A population of rhombic



Figure 2. a) STEM image of assemblies of oleate coated 22-nm nanocubes. Scale bar = 500 nm. b) Oleate capped Fe₃O₄ PAEs assembled without an applied magnetic field form a SC symmetry as seen via experimental and simulated SAXS patterns. STEM HAADF images of 22-nm nanocube PAE assemblies grown under c) 0 and e) 3800 G magnetic fields. Scale bars = 1 μ m. d) Assemblies of particles grown under 0 and 3800 G magnetic fields possess *bcc* symmetry as seen by a comparison of their SAXS patterns to a simulated pattern.

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dodecahedra superlattices form from this symmetry and shape design, as expected but not observed before for cubic PAEs (Figures 2 c, S2). This result agrees with literature precedent that even though the core is anisotropic, the nature of the DNA shell controls the crystal symmetry.^[35] In an attempt to study how the length and specificity of DNA ligands affect assembly, shorter lengths of DNA (24 bp) and different DNA sticky end designs (self-complementary and shorter and longer lengths) were tested. However, these did not result in highly ordered assemblies (Figure S3) potentially due to stronger coupling at shorter distances or more nearest neighbors, which frustrate the packing and prevent crystal-linity.

Since the cubes with the 66 bp DNA design assembled with the same symmetry as spheres, we hypothesized that a similar series of morphologies would form after assembly in a field, consistent with what has been observed with spherical particles.^[29] When slowed cooled as before, the morphology of the resulting crystals varied as a function of magnetic field strength from more isotropic clusters (0 G; Figure 2c), to aligned crystals (140 G; Figure S5), and finally to defined, smooth rods (3800 G; Figure 2e). The rod shape indicates that the superlattices are macroscopically aligned with respect to the applied magnetic field. SAXS data suggest that the symmetry of each superlattice is the same regardless of the field strength (Figure 2d). These results indicate that the DNA shell dictates both the morphology and symmetry of superlattices grown in magnetic fields, as observed for spherical PAEs. Consequently, we sought to understand whether the cubic PAEs are randomly oriented with respect to the superlattice unit cell or whether the external field induces shape orientation.

The orientation of cubic NPs is expected to be random if assembled with long DNA and without an applied field.^[35] With the application of a magnetic field during growth, we hypothesized that the cubes will preferentially orient within the unit cell. To probe this hypothesis, superlattices were studied by SAXS, which provides information about superlattice symmetry as well as details on particle orientation and shape registry across the lattice.^[28] The orientation of NPs makes a substantial contribution to the intensities of higher order reflections from the superlattice.^[36] For instance, the {332}, {422}, and {510}/{431} reflections of simulated SAXS patterns show changes in intensity due to changes in the orientation of the constituent cubes (Figure 3a). To determine if the cubes in the superlattices were oriented, the experimental SAXS patterns for samples assembled with and without a magnetic field were compared with the simulated ones. First, to see if a field applied after superlattice formation changes the orientation of the cubes, SAXS patterns were collected for these crystallized samples placed both outside and inside a magnetic field during the measurements. While little difference was observed between the cases (Figure S6), the SAXS patterns measured in a field were compared to simulated patterns due to their higher quality. The intensities of the experimental peaks for each field strength do not match the data when the $\langle 100\rangle_{Fe_3O_4}$ of the cubes is parallel to the $(100)_{SL}$ ((100) direction of the superlattice unit cell) or when randomly oriented (Figure 3a,b). Rather, closer agreement is



Figure 3. a) SAXS patterns from samples grown under 0 and 3800 G. Both patterns were acquired for crystallized superlattices suspended in a magnetic field (3800 G) during the SAXS measurement. Simulated SAXS patterns of (from the top down) $\langle 100 \rangle_{Fe_{3}O_{4}} || \langle 100 \rangle_{SL}$, disordered cube orientation, and $\langle 111 \rangle_{Fe_{3}O_{4}} || \langle 100 \rangle_{SL}$. b) Models of unit cells with different cube orientations.

observed with the simulated patterns when the cubes are oriented such that the $\langle 111 \rangle_{Fe_3O_4}$ points along the $\langle 100 \rangle_{SL}$ (Figure 3 a,b). However, a cube with this orientation can be rotated along its $\langle 111 \rangle_{Fe_3O_4}$ axis to give equivalent simulated patterns (Figure S7), leaving its exact orientation ambiguous. Even so, the superlattice grown under a field is more oriented along this axis than the no field sample, as indicated by the intensity of the {332} peak (Figure 3 a). This observation indicates that DNA interactions alone lead to a degree of shape orientation, and importantly, an applied field during growth further aligns the cubes.

While the field strength has little influence on particle orientation, it should influence the overall crystallographic alignment of the superlattices in a field. To study the superlattice crystallographic alignment, the cubic Fe₃O₄ PAE crystals grown inside and outside a magnetic field were placed back in a field during SAXS measurements (Figure S8). A clear orientation alignment along the $\langle 111 \rangle_{SL}$ with the field direction is observed for both samples grown inside (3800 G, Figures 4b,d, S9) and outside a field (0 G, Figure S10b,c). This alignment is in contrast to what is observed for spherical Fe₃O₄ PAE crystals with bcc symmetry which have their $\langle 100 \rangle_{SL}$ oriented along the field direction.^[29] The alignment in a field also contrasts with what observed for oleate coated cubes with SC symmetry, where the $\langle 100 \rangle_{SL}$ is oriented along the field direction and $\langle 100\rangle_{Fe_3O_4}\,|\,|\,\langle 100\rangle_{SL}$ (Figure S11, see SI for details). This indicates that the underlying cubic shape of the PAEs impacts the crystallographic alignment of the superlattice.

To determine if there is a specific orientation of the cubic NPs in the PAE superlattices, wide-angle X-ray scattering (WAXS) data were collected in situ for superlattices sus-

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Figure 4. a) 2D WAXS and b) 2D SAXS patterns of samples slow-cooled in a 3800 G field and then suspended in a field to study the alignment of the atomic crystals. c) Schematic depicting the rod morphology and the parallel alignment of the $(100)_{Fe_3O_4}$ and $(111)_{SL}$ directions along the rod under an applied magnetic field. d) Intensity distribution along the {400} reflection from WAXS (top) and the {200} reflection from SAXS (bottom) vs. azimuthal angle. e) Orientation factor (f_2) values calculated from the intensity distribution along the {200} reflection from the 2D SAXS patterns for 22-nm and 10-nm cubic PAEs assembled into bcc symmetry structures at different field strengths.

pended in a field. WAXS allows for the alignment of the atomic crystals of each NP to be observed.^[37-40] When azimuthally plotting the intensity profile along the {400} reflection of magnetite for crystals grown in a 3800 G field, there is higher intensity along 0° and 90° (Figure 4a,d), indicating alignment of the $\langle 100\rangle_{Fe_3O_4}$ along the field direction. This indicates that $\langle 100 \rangle_{Fe_3O_4} || \langle 111 \rangle_{SL}$, as both axes align along the magnetic field direction (Figure 4c). By increasing the interparticle distance and changing the symmetry of the superlattice through the DNA design, the dipole-dipole coupling between cubes is lowered as compared to oleate ligands, yet the superlattice still shows an alignment of the $\langle 100 \rangle_{\text{Fe}_{2}O_{4}}$ along the field direction. The reason for alignment is not due to a complex array of dipole orientations for closely interacting cubes but rather due to the energetically favorable alignment of individual cubes in a field (see SI for details). The modularity of DNA-mediated assembly in turn enables further investigation of how field strength and relative PAE size affect their crystallographic alignment.

To address this issue, different magnetic field strengths were applied during crystallization, and cubic particles with different edge lengths were assembled. Higher field strengths and larger cubes are expected to show increased orientation along a superlattice crystallographic direction. We analyzed the intensity of the {200} reflection from the 2D SAXS patterns to find the orientation factor (f_2) which enabled the comparison of the degree of orientation for each system (see SI for details). Alignment of the $\langle 111 \rangle_{SL}$ along the field direction occurs at several field strengths (1000, 2000, and 3800 G) for 10-nm cubic Fe_3O_4 PAEs assembled with 24 bp linker strands, highlighting the shape effect across length scales (Figures 4e, S12, S13). No alignment occurs for the PAEs assembled without a field, suggesting that an applied field is critical to influence particle orientation and therefore alignment of smaller particles. Although 10-nm cubic PAE superlattices have a smaller surface-to-surface spacing (linker strands with 24 bp instead of 66 bp), the strength of the dipole scales with the volume; therefore, the 22-nm cubes exhibit stronger coupling across all applied field strengths. This manifests in a higher orientation factor at all field strengths for these PAEs. Furthermore, as the magnetic field strength is increased (0, 140, 500, 1000, and 3800 G), crystals of 22-nm cubic Fe₃O₄ PAEs generally show an increasing degree of alignment (Figures 4e, S14). Samples grown without an applied field consist of more single domain crystal habits than samples grown at lower fields (Figure S5) and thus can more freely move to align to the field in solution. This ability to tune the

degree of crystalline alignment is not possible with other ligand systems that have less controlled crystallization conditions and interaction tunability.

Taken together, these studies show that using DNA as a ligand allows for cubic Fe₃O₄ NPs to assemble with a symmetry and orientation that cannot be achieved with non-specific, oleate ligands. Consequently, even when the lattice symmetry and interparticle spacing are changed, the NP core affects orientation across length scales. Although further study is needed to determine exactly how magnetic dipole coupling produces such a result, this work lays the framework for the structural characterization and material synthesis needed to explore other shapes and symmetries in magnetic NP colloidal crystallization and their effect on crystallographic alignment in magnetic fields. Importantly, this study expands the structural space to design crystals with specific orientations and symmetries for the evolving field of nano-magnetism and related applications.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: crystal engineering · DNA · magnetic materials · nanoparticles · self-assembly

- M. Hu, H.-J. Butt, K. Landfester, M. B. Bannwarth, S. Wooh, H. Thérien-Aubin, ACS Nano 2019, 13, 3015–3022.
- [2] C. A. Brisbois, M. Tasinkevych, P. Vázquez-Montejo, M. Olvera de la Cruz, Proc. Natl. Acad. Sci. USA 2019, 116, 2500–2505.
- [3] J. Yu, B. Wang, X. Du, Q. Wang, L. Zhang, Nat. Commun. 2018, 9, 3260-3269.
- [4] X. Yan, Q. Zhou, M. Vincent, Y. Deng, J. Yu, J. Xu, T. Xu, T. Tang, L. Bian, Y.-X. J. Wang, K. Kostarelos, L. Zhang, *Sci. Robot.* **2017**, *2*, eaaq1155.
- [5] P. J. Santos, R. J. Macfarlane, J. Am. Chem. Soc. 2020, 142, 1170– 1174.
- [6] L.-M. Wang, A. Qdemat, O. Petracic, E. Kentzinger, U. Rücker, F. Zheng, P.-H. Lu, X.-K. Wei, R. E. Dunin-Borkowski, T. Brückel, *Phys. Chem. Chem. Phys.* **2019**, *21*, 6171–6177.
- [7] B. J. Frankamp, A. K. Boal, M. T. Tuominen, V. M. Rotello, J. Am. Chem. Soc. 2005, 127, 9731–9735.
- [8] J. Chen, A. Dong, J. Cai, X. Ye, Y. Kang, J. M. Kikkawa, C. B. Murray, *Nano Lett.* **2010**, *10*, 5103–5108.
- [9] A. Fernández-Pacheco, R. Streubel, O. Fruchart, R. Hertel, P. Fischer, R. P. Cowburn, *Nat. Commun.* 2017, 8, 15756.
- [10] K. J. M. Bishop, C. E. Wilmer, S. Soh, B. A. Grzybowski, *Small* 2009, 5, 1600-1630.
- [11] G. Singh, H. Chan, A. Baskin, E. Gelman, N. Repnin, P. Král, R. Klajn, *Science* 2014, 345, 1149–1153.
- [12] C. Jiang, C. W. Leung, P. W. T. Pong, Nanoscale Res. Lett. 2016, 11, 189.
- [13] A. Ahniyaz, Y. Sakamoto, L. Bergström, Proc. Natl. Acad. Sci. USA 2007, 104, 17570–17574.
- [14] C.-J. Chen, R.-K. Chiang, Y.-R. Jeng, J. Phys. Chem. C 2011, 115, 18142–18148.

- [15] E. Wetterskog, A. Klapper, S. Disch, E. Josten, R. P. Hermann, U. Rücker, T. Brückel, L. Bergström, G. Salazar-Alvarez, *Nanoscale* 2016, 8, 15571–15580.
- [16] S. Mehdizadeh Taheri, M. Michaelis, T. Friedrich, B. Förster, M. Drechsler, F. M. Römer, P. Bösecke, T. Narayanan, B. Weber, I. Rehberg, S. Rosenfeldt, S. Förster, *Proc. Natl. Acad. Sci. USA* 2015, *112*, 14484–14489.
- [17] T. Wang, X. Wang, D. LaMontagne, Z. Wang, Z. Wang, Y. C. Cao, J. Am. Chem. Soc. 2012, 134, 18225–18228.
- [18] C. A. Mirkin, R. L. Letsinger, R. C. Mucic, J. J. Storhoff, *Nature* 1996, 382, 607–609.
- [19] D. Nykypanchuk, M. M. Maye, D. van der Lelie, O. Gang, *Nature* 2008, 451, 549–552.
- [20] S. Y. Park, A. K. R. Lytton-Jean, B. Lee, S. Weigand, G. C. Schatz, C. A. Mirkin, *Nature* 2008, 451, 553–556.
- [21] R. J. Macfarlane, B. Lee, M. R. Jones, N. Harris, G. C. Schatz, C. A. Mirkin, *Science* **2011**, *334*, 204–208.
- [22] A. J. Senesi, D. J. Eichelsdoerfer, K. A. Brown, B. Lee, E. Auyeung, C. H. J. Choi, R. J. Macfarlane, K. L. Young, C. A. Mirkin, *Adv. Mater.* 2014, *26*, 7235–7240.
- [23] E. Auyeung, T. I. N. G. Li, A. J. Senesi, A. L. Schmucker, B. C. Pals, M. Olvera de la Cruz, C. A. Mirkin, *Nature* **2014**, *505*, 73– 77.
- [24] S. E. Seo, M. Girard, M. Olvera de la Cruz, C. A. Mirkin, *Nat. Commun.* 2018, 9, 4558–4558.
- [25] Y. Zhang, F. Lu, K. G. Yager, D. van der Lelie, O. Gang, Nat. Nanotechnol. 2013, 8, 865–872.
- [26] M. R. Jones, R. J. Macfarlane, B. Lee, J. Zhang, K. L. Young, A. J. Senesi, C. A. Mirkin, *Nat. Mater.* 2010, *9*, 913–917.
- [27] C. Zhang, R. J. Macfarlane, K. L. Young, C. H. J. Choi, L. Hao, E. Auyeung, G. Liu, X. Zhou, C. A. Mirkin, *Nat. Mater.* **2013**, *12*, 741–746.
- [28] M. N. O'Brien, M. R. Jones, B. Lee, C. A. Mirkin, Nat. Mater. 2015, 14, 833–839.
- [29] S. S. Park, Z. J. Urbach, C. A. Brisbois, K. A. Parker, B. E. Partridge, T. Oh, V. P. Dravid, M. Olvera de la Cruz, C. A. Mirkin, *Adv. Mater.* **2019**, *32*, 1906626.
- [30] M. V. Kovalenko, M. I. Bodnarchuk, R. T. Lechner, G. Hesser, F. Schäffler, W. Heiss, J. Am. Chem. Soc. 2007, 129, 6352–6353.
- [31] W. Wang, X. Ji, H. B. Na, M. Safi, A. Smith, G. Palui, J. M. Perez, H. Mattoussi, *Langmuir* 2014, *30*, 6197–6208.
- [32] Q. Li, C. W. Kartikowati, S. Horie, T. Ogi, T. Iwaki, K. Okuyama, *Sci. Rep.* **2017**, 7, 9894.
- [33] S. Singamaneni, V. N. Bliznyuk, C. Binek, E. Y. Tsymbal, J. Mater. Chem. 2011, 21, 16819–16845.
- [34] R. J. Macfarlane, M. R. Jones, A. J. Senesi, K. L. Young, B. Lee, J. Wu, C. A. Mirkin, *Angew. Chem. Int. Ed.* **2010**, *49*, 4589–4592; *Angew. Chem.* **2010**, *122*, 4693–4696.
- [35] M. N. O'Brien, M. Girard, H.-X. Lin, J. A. Millan, M. Olvera de la Cruz, B. Lee, C. A. Mirkin, *Proc. Natl. Acad. Sci. USA* 2016, *113*, 10485–10490.
- [36] A. J. Senesi, B. Lee, J. Appl. Crystallogr. 2015, 48, 1172-1182.
- [37] J. J. Choi, K. Bian, W. J. Baumgardner, D.-M. Smilgies, T. Hanrath, *Nano Lett.* **2012**, *12*, 4791–4798.
- [38] M. Corricelli, D. Altamura, M. L. Curri, T. Sibillano, D. Siliqi, A. Mazzone, N. Depalo, E. Fanizza, D. Zanchet, C. Giannini, M. Striccoli, *CrystEngComm* **2014**, *16*, 9482–9492.
- [39] R. Li, K. Bian, T. Hanrath, W. A. Bassett, Z. Wang, J. Am. Chem. Soc. 2014, 136, 12047–12055.
- [40] R. Li, K. Bian, Y. Wang, H. Xu, J. A. Hollingsworth, T. Hanrath, J. Fang, Z. Wang, *Nano Lett.* **2015**, *15*, 6254–6260.

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Communications



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Probing the Consequences of Cubic Particle Shape and Applied Field on Colloidal Crystal Engineering with DNA



Assembly of magnetic nanoparticles results from a competition between dipole and surface interactions. To modulate these forces, cubic Fe_3O_4 nanoparticles were functionalized with DNA to

explore the assembly behavior in a magnetic field. X-ray scattering elucidates that orientation is controlled across length scales due to the altered arrangement of particles.