Surface-ligand-induced crystallographic disorder–order transition in oriented attachment for the tuneable assembly of mesocrystals

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In the crystallisation of nanomaterials, an assembly-based mechanism termed ‘oriented attachment’ (OA) has recently been recognised as an alternative mechanism of crystal growth that cannot be explained by the classical theory. However, attachment alignment during OA is not currently tuneable because its mechanism is poorly understood. Here, we identify the crystallographic disorder-order transitions in the OA of magnetite (Fe₃O₄) mesocrystals depending on the types of organic surface ligands on the building blocks, which produce different grain structures. We find that alignment variations induced by different surface ligands are guided by surface energy anisotropy reduction and surface deformation. Further, we determine the effects of alignment-dependent magnetic interactions between building blocks on the global magnetic properties of mesocrystals and their chains. These results revisit the driving force of OA and provide an approach for chemically controlling the crystallographic order in colloidal nanocrystalline materials directly related to grain engineering.

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The assembly of nanometric building blocks into self-limited periodic structures is key to forming natural and artificial materials and in their structure-induced emergent properties. In the field of mesocrystal crystallisation, during which the building blocks regularly tile into discernible single crystals, an assembly-based growth mechanism referred to as ‘oriented attachment’ (OA) has entered into the spotlight as a new model for explaining the creation of crystallographically ordered structures with emergent functionalities that cannot be explained by the classical nucleation and growth theory, occurring via ion-by-ion accretion. In OA, crystal growth proceeds as building-block nanocrystals (BNCs) adhere to each other in the same crystallographic order; this mechanism is widely observed in the formation of various natural and chemically synthesised nanomaterials such as metal oxides (e.g., iron oxides, TiO2), ceramics (PbSe), and even metals (Au). Accordingly, OA has advanced our understanding of the growth of complex hierarchical and anisotropic nanostructures as well as the evolution of microstructural features, including twins, stacking faults, and grain boundaries.

Therefore, discovering an unknown rule in crystallisation via OA into mesocrystals is an important goal, particularly in studying the nonclassical crystallisation of iron oxides to control their magnetic properties and tailor them for promising applications in biomedicine and electronics. Several groups successfully proposed the thermodynamic contribution of the volume free energy of BNC formation to the phase transformation into final magnetite (Fe3O4)-phase nanoparticles and to size-predictable nanoparticle synthesis by interpreting the kinetics of the colloidal assembly of Fe3O4 BNCs. Recently, another group proposed a new OA pathway for the growth of hematite (α-Fe2O3) via interface-driven nucleation and attachment, in which primary particles nucleate and attach at a distance of ~2 nm from the parent mesocrystal in the presence of a surface ligand, namely, oxalate.

Despite these contributions, it remains unknown how the BNCs are crystallographically aligned during OA and whether the BNC alignment is chemically controllable by overcoming the confined order of OA. Concomitantly, another unanswered question is how the magnetic properties of mesocrystals vary with the crystallographic order of the BNCs. The magnetic properties of disordered and ordered nanocrystalline materials are theoretically well understood. However, experimentally elucidating this effect remains challenging because the crystallographic order of intra-mesocrystal grains has never been successfully controlled during chemical synthesis.

This study demonstrates that the crystallographic alignment between BNCs with truncated octahedral shapes can be tuned during the OA of Fe3O4 mesocrystals by coordinating different surface ligands, including acetate, polyacrylate, and Mg2+-adsorbed polyacrylate on the BNCs. The experiments and density functional theory (DFT) calculations presented herein reveal that the tilting rule of BNCs is guided by the reduction in the surface energy anisotropy and surface deformation commensurate to the coordination of different surface ligands, which could not be predicted using generic interparticle interactions following the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory. BNC alignment significantly influences inter-BNC magnetic interactions, resulting in different collective magnetic behaviours of individual Fe3O4 mesocrystals and their magnetic chains.

Results

Crystallisation of Fe3O4 mesocrystal. We synthesised Fe3O4 mesocrystals using the modified polyol method and observed their crystallisation process via ex situ transmission electron microscopy (TEM) (Fig. 1). Specifically, we reacted a mixture of sodium acetate (hydroxyl ion source) dissolved in ethylene glycol and iron chloride hexahydrate (ferric ion source) dissolved in H2O for 15 min at room temperature and subsequently for

![Fig. 1 Control of Fe3O4 mesocrystal crystallisation pathway via OA. a TEM images and b SAED patterns of Fe oxyhydroxide intermediates and Fe3O4 mesocrystals at different reaction times. c Crystallisation pathway of Fe3O4 mesocrystals including stepwise transformation (dotted line) and OA (solid line). d HR-TEM image at the boundary between crystalline Fe3O4 (Region 1) and the poorly crystalline Fe oxyhydroxide intermediate phase (Region 2) and corresponding FFT images.](https://doi.org/10.1038/s41467-022-28830-7)
210 min at 200 °C (see Methods), yielding Fe₃O₄ mesocrystals. TEM observations reveal that the Fe₃O₄ mesocrystals did not form directly from ions but rather formed through a stepwise transformation while consuming a ferric oxyhydroxide intermediate as a precursor for Fe₃O₄ growth (Fig. 1a–d). At the beginning of the reaction (t = 0.5 h), a broad ring diffraction pattern appeared in the selected area electron diffraction (SAED) images at d-spacings of 0.265 and 0.153 nm, indicating the formation of poorly crystalline ferric oxyhydroxide with short-range order (Figs. 1b and 2a and Supplementary Fig. 1)²¹. We also verified that the oxidation state of Fe in this intermediate was the ferric state (Fe³⁺), through the electron energy-loss spectroscopy (EELS) of the Fe L₃ edge with a peak at 711.8 eV (Supplementary Fig. 1)²². After t = 1.5 h, diffraction spots corresponding to Fe₃O₄ gradually appeared, with the main peak attributed to the [311] plane with a d-spacing of 0.253 nm. By t = 3.5 h, the intermediate phase had been entirely consumed, leading to the growth of Fe₃O₄ mesocrystals with a uniform size of 153 ± 11 nm (Fig. 2b, c). The Fe₃O₄ mesocrystals that initially formed in the intermediate matrix had a broad size distribution, but this distribution gradually narrowed with increasing reaction time (Fig. 2b). In addition, the average Fe₃O₄ mesocrystal diameter increased with increasing initial [Fe³⁺] content, in agreement with growth via OA (Supplementary Fig. 2)²⁸.

The polymorphism of ferric oxyhydroxide as an intermediate significantly affects the crystallisation mechanism of Fe₃O₄ mesocrystals¹⁷,¹⁸,²³–²⁵. We recently identified two Fe₃O₄ crystallisation pathways starting from either lepidocrocite or goethite and revealed that Fe₃O₄ mesocrystals grew via OA only in the former case²³. These pathways are competitively responsible for Fe₃O₄ growth and can be selectively regulated according to the initial [OH⁻]/[Fe³⁺] ratio. In this study, we chemically controlled Fe₃O₄ mesocrystals such that they grow through a single crystallisation pathway via OA (Supplementary Figs. 3–5 and Supplementary Note 1).

As shown in the high-resolution (HR) TEM image (Fig. 1d), at t = 1.5 h, the fast Fourier transform (FFT) pattern of a nanogranular Fe₃O₄ mesocrystal comprising assemblies of smaller BNCs (Region 1) exhibits a spot diffraction pattern, indicating that the BNCs have almost identical orientations. In contrast, the polycrystalline ring pattern at the periphery of the nanogranular mesocrystal (Region 2) is attributed to the random orientation of Fe₃O₄ BNCs formed in the lepidocrocite intermediate. This secondary structure, in which the primary particles are assembled in a specific crystallographic order in the range from hundreds of nanometres to micrometres, is characteristic of mesocrystals. These mesocrystalline structures typically form through the colloidal assembly of BNCs.

Tunable crystallographic order in OA. We examined the morphologies and crystallographic orientations of individual single mesocrystals coordinated with different surface ligands (Fig. 3), which included acetate (denoted in sample labels as ‘ac’), polycrylate (‘pa’), and Mg²⁺-adsorbed polycrylate (‘mg’) as model moieties that can coordinate on the Fe₃O₄ BNC surface as a monolayer during the reaction (see Methods).

Through a surface analysis using Fourier transform infrared (FT-IR) spectroscopy, X-ray photoelectron spectroscopy (XPS), and thermogravimetric–differential thermal analysis (TG-DTA), we confirmed that the ligand densities for polycrylate (1.92 ligand nm⁻²) and Mg²⁺-adsorbed polycrylate (2.57 ligand nm⁻²) on BNCs were close to the maximum ligand-to-surface ratio for the coordinated monolayer (2.4–2.7 ligand nm⁻²), whereas that for the ac-coordinated surface (2.42 ligand nm⁻²) was much lower than the theoretical maximum value (9 ligands nm⁻²) required to sufficiently fill the BNC surface (Supplementary Fig. 6 and Supplementary Table 1)²⁶. In the FT-IR results, the average shifts of the Mg 1s XPS peak (Supplementary Figs. 6 and 8)²⁸.
direction, resulting in a single-crystal-like spot diffraction pattern (Fig. 3a). When polyacrylate was grafted onto the BNC surface, the diffraction spots were stretched owing to the slight misalignment between BNCs (Fig. 3b). Furthermore, when Mg\(^{2+}\) was attracted to the negatively charged polyacrylate, the BNCs did not exhibit regular alignment, thus forming a polycrystalline ring pattern because of their random orientations (Fig. 3c). The ‘orientation factor’ derived from the azimuthal profile of every single mesocrystal diffraction in the (311) plane decreased when polyacrylate was grafted onto the BNC surface, and reached a minimum value upon the injection of Mg\(^{2+}\) (Fig. 3d, Supplementary Fig. 9 and Supplementary Note 3). This decrease in the orientation factor indicates a discrepancy in the tiling of the BNCs during aggregative OA.

The BNCs were 4 nm truncated octahedrons predominantly formed by [100] and [111] facets (Supplementary Fig. 10). Atomic-resolution high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), HR-TEM, and the corresponding FFT images obtained along the [001] and [011] zone axes indicated that the Fe\(_3\)O\(_4\)-truncated octahedron BNCs were single crystals with the inverse spinel structure, and Fe atoms (expectedly) occupied the octahedral and tetrahedral sites (Supplementary Fig. 10). We observed BNC tiling along the same [001] zone axis (Fig. 5a–c). In the ac-MCs, the BNCs completely packed together with coherent orientational ordering that minimised the [111] facets while forming eight [111]-to-[111] and four [100]-to-[100] facet-to-face contacts per BNC (Fig. 5a). The pa-MCs exhibited the same tiling rule as the ac-MCs, but the

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**Fig. 3 Disorder-order transition in the crystallographic alignment in mesocrystals during OA.** a–c Morphological and microstructural analyses of Fe\(_3\)O\(_4\) mesocrystals with different crystallographic orders in BNC tiling depending on the surface ligand: acetate (ac) (a), polyacrylate (pa) (b), and Mg\(^{2+}\)-adsorbed polyacrylate (mg) (c). Bright-field (BF)-TEM images display a representative shape for each mesocrystal, and the SAED pattern was acquired from the single mesocrystal in the TEM images. Dark-field (DF)-STEM images describe the change in the outline of single mesocrystals.

**Fig. 4 Quantitative analyses of crystallographic alignment.** a Orientation factor obtained from the azimuthal profile of the SAED pattern of a single mesocrystal at a constant distance corresponding to the (311) plane. b Crystallite sizes calculated using the Debye-Scherrer equation and measured from the HR-TEM images. c Size distribution of each sample measured from 50 mesocrystals in the TEM images. Error bars in panels (a) and (b) indicate standard deviations.
adjacent BNCs were tilted by approximately 2°, resulting in a stretched spot in the collective FFT pattern (Fig. 5b and Supplementary Fig. 11). Upon adding Mg\textsuperscript{2+}, adjacent BNCs randomly clustered with a tilt angle of 14°, making it difficult to determine a consistent tiling rule (Fig. 5c and Supplementary Fig. 11).

The degree of BNC alignment can influence grain formation in mesocrystals. In all samples, the BNCs measured via TEM were approximately 4 nm with similar morphologies, regardless of the type of ligand (Fig. 4b and Supplementary Fig. 10). However, the grain size measured via X-ray diffraction (XRD) decreased with the misalignment induced by polyacrylate and Mg\textsuperscript{2+} ions (Fig. 4b and Supplementary Fig. 12). When the reaction time was 10 h, the ac-MCs stopped growing after 3.5 h, and coarsening occurred between the BNCs thereafter, leading to the collapse of the nanogranular morphology and formation of larger grains (Supplementary Fig. 13). Interestingly, coarsening proceeded along the perfectly aligned region, and the crystallite sizes measured by XRD were maintained during coarsening (Fig. 2c and Supplementary Fig. 13). In the pa-MC cases, however, the BNCs were not coarsened, even at 10 h postreaction, and the nanogranular morphology was

![Fig. 5 Local BNC alignment within a mesocrystal. a–c HR-TEM (left) images and FFT patterns (right) of ac-MCs with the ordered state (a), pa-MC with the intermediate state (b), and mg-MC with the disordered state (c). The yellow dotted boxes indicate the region with the [001] zone axis. Three FFT patterns were acquired from each BNC having the same numbering in the HR-TEM images. The tilt angle between adjacent BNCs was measured using the auxiliary crosses connecting (110) planes in each FFT pattern; solid lines: BNC #1, dash–single dotted line: BNC #2, and dotted line: BNC #3. Overlaid crosses and schematics were reconstructed based on each FFT pattern as a visual aid.](#)
maintained because of the misalignment between the BNCs (Supplementary Fig. 13).

**Crystallographic-order-dependent magnetic property.** The degree of crystallographic ordering of BNCs within a mesocrystal can influence the inter-BNC magnetic coupling, thus resulting in a variation in the collective magnetic properties of the mesocrystal. The saturation magnetisation ($M_s$), blocking temperature ($T_B$), and magnetic coercivity ($H_c$) of the Fe$_3$O$_4$ mesocrystals decreased as the BNCs became misaligned (Fig. 6a, b, Supplementary Fig. 14 and Supplementary Table 4). The disordered BNC alignment in the mesocrystals represented superparamagnetic behaviour with $T_B=216$ K (Fig. 6a). Given that Fe$_3$O$_4$ mesocrystals can be regarded as nanocystalline systems composed of different grain sizes and orientations depending on the BNC alignment, their magnetic properties are imparted by the distribution of the magnetic anisotropy of grains and exchange coupling between grains, which can be expressed as $F = A\left\{\nabla m(r)\right\}^2 + K_{\text{loc}}\left\{\left[m(r) \cdot \nabla m(r)\right]\right\}^2 - \gamma$. In this equation, $A$, $K_{\text{loc}}$, $m(r)$, and $\nabla m(r)$ are the free energy, exchange stiffness, local anisotropy constant, local reduced magnetisation ($M(r)/M_0$), and unit vector of the local easy axis, respectively (Fig. 6d). Furthermore, the magnetic moments of the grains were coupled to each other through exchange interactions on the scale of a few nanometres. Therefore, ac-MCs with BNCs that are aligned in the same direction can have the strongest anisotropy and exchange interactions, thereby increasing $M_s$, $T_B$, and $H_c$. When the mesocrystals had disordered grains smaller than 10 nm because of BNC misalignment, the local anisotropy varied with the position, thus resulting in random anisotropy, attenuating the exchange coupling, and decreasing $M_s$, $T_B$, and $H_c$.19

To examine how the interactions between mesocrystals depend on the BNC alignment, we arranged mesocrystals in a one-dimensional (1-D) nanochain under an external magnetic field of 160 kA m$^{-1}$ (Fig. 6c, e and Supplementary Fig. 15). Interestingly, the ac-MCs aligned along the <111> easy axis of the magnetocrystalline anisotropy owing to the interaction anisotropy, which induces the uniaxial anisotropy of nanocrystals due to magnetostatic coupling between mesocrystals (Fig. 6c). In contrast, the mesocrystals with misaligned BNCs did not exhibit a particular orientation (Supplementary Fig. 15). We also explored the angular dependence of the $H_c$ behaviour in the nanochains by varying the angle between the chain axis and magnetic field (Fig. 6c). The coercivity of the magnetic chains arranged in the <111> direction showed a pronounced dependency on this angle, with a minimum at $\theta=0^\circ$ and maximum at $\theta=90^\circ$. This result agrees with the theoretical prediction of the chain-of-spheres model and magnetic chains formed by magnetotactic bacteria.33–35 However, this angle dependency tended to diminish as the BNCs became disordered. Finally, the nanochains of mg-MCs showed an isotropic magnetic coercive force for all field angles, indicating that the magnetostatic interaction was not sufficiently strong to induce anisotropy along the nanochain axis; thus, the nanochain behaved like an isolated superparamagnetic mesocrystal (Fig. 6d).

**Driving force guiding BNC tiling rule.** The driving force guiding the assembly of colloidal nanocrystals is generally explained by interparticle interactions using the DLVO theory (Fig. 7a and Supplementary Note 5).20 This pair interaction potential shows the energy barrier balanced by the attractive and repulsive forces between BNCs and suggests their collision kinetics. The nanoscale interactions occurring in our system can be described by van der Waals, electrostatic, and magnetic dipole–dipole forces. In our system, the Debye screening lengths ($\kappa^{-1}$) were estimated to be $0.64$, $0.65$, and $0.54$ nm for the ac-MCs, pa-MCs, and mg-MCs, respectively. Therefore, the surface-charge-induced repulsion had little effect on the overall interaction potential. Furthermore, considering the superparamagnetic BNCs commensurate with extremely small sizes (less than 10 nm), magnetic Keesom interactions can be ignored in our case. Therefore, the attractions between BNCs dominated the overall potential through the van der Waals interaction, thereby forming a barrierless interaction potential regardless of the type of surface ligand and leading to preferential assembly between the BNCs (Fig. 7a). Despite the generality of the DLVO theory, this surface-ligand-induced variation in the BNC alignment cannot be rationalised based on traditional pairwise interactions.

To better understand the factors governing alignment variation induced by different ligands, we examined the surface energy and ligand binding energy considering the ligand configurations on the {111}, {100}, and {110} planes by performing DFT calculations (Fig. 7b, c, Supplementary Figs. 16–18, and Supplementary Note 5). The surface energies of unpasivated Fe$_3$O$_4$ for {100}, {110}, and {111} were 0.51, 4.24, and 1.12 eV nm$^{-2}$, respectively (Table 1). Consistent with the significantly high energy of the {110} facet according to the DFT calculations, experimentally observing the {110} facets via TEM was more challenging than observing the {100} and {111} facets (Supplementary Fig. 10).

Concurrently, the binding affinity of all ligands to the {111} facets is also more substantial than that to the {100} facets, which can relax the anisotropic surface energies ($\gamma_{\text{110}} < \gamma_{\text{100}} > 0$) by passivating the dangling bonds (Table 1). For acetate, the binding energy ratio of the {111} and {100} facets was 1.46 ($E_{\text{b,111}}/E_{\text{b,100}}$), which is insufficient to alleviate the surface energy anisotropy, resulting in a crystallographically ordered BNC alignment that minimises the surface energy by eliminating the {111} facets rather than the {100} ones (Fig. 7b). With polycrystals, the binding energy to all facets notably increased, although the $E_{\text{b,111}}/E_{\text{b,100}}$ ratio was 1.40, thereby maintaining the regularity of the acetate-like tiling rule (Fig. 7b). Meanwhile, the carboxylate of the surface ligands coordinated by bidentate bridging on each BNC facet distorted the positions of the Fe and O atoms and created a zigzag topography, which was prominent on the polycrystalline-grafted surfaces (Fig. 7c). This topography hindered the perfect coherence in the attachment between facets and slightly decreased the orientation factor, as determined in the TEM observations. In the mg-MCs, Mg$^{2+}$ ions could bridge the unbound free carboxylate of polycarboxylic and O on the Fe$_3$O$_4$ surface, which agreed with the decreased electrokinetic potential (Fig. 7c and Supplementary Fig. 7). The Mg$^{2+}$-ion-induced distortion in the configuration of acrylate coordination on Fe$_3$O$_4$ increased the difference in binding energy between the {111} and {100} facets, with an $E_{\text{b,111}}/E_{\text{b,100}}$ ratio of 1.98, thus suppressing the anisotropic surface energies and disorder in the tiling rules of BNC attachment (Fig. 7b).

Generic facet formation and the growth of single-crystal nanoparticles were driven by surface energy minimisation following the Wulff construction in the classical theory (Fig. 7d).36,37 Considering that the volume free energy is negligible during the aggregative OA process accompanied by a constant number of BNCs, the BNC tiling rule to form thermodynamically stable aggregates is governed by the surface energy. These results indicate that the disorder–order transitions in the BNC alignment were induced by surface ligand coordination, which resulted in variations in the anisotropic surface energy and surface distortion of the BNCs. Consequently, similar to self-assembly, when BNCs have anisotropy in surface energy, the
**Fig. 6 Magnetic properties of mesocrystals and their 1-D nanochains depending on the BNC alignment.**

**a** Zero-field-cooling (ZFC)/field-cooling (FC) magnetisation curves.

**b** $H_c$ plot of Fe$_3$O$_4$ mesocrystals depending on the crystallographic order in BNC alignment. $H_c$ behaviour of the nanochains as a function of the angle $\theta$ between the axial directions of the nanochains and the direction of the applied magnetic field. Each point is the average of three different measurements; the error bars denote the standard deviations.

**d** Effects of inter-BNC magnetic interactions on the magnetic behaviour of mesocrystals and their nanochains. Single arrows indicate the local magnetocrystalline anisotropy. BF-TEM image of a 1-D nanochain composed of Fe$_3$O$_4$ mesocrystals with aligned BNCs (ac-MCs). The ac-MCs are arranged in the direction of the magnetic field (160 kA m$^{-1}$). The solid and dotted double arrows indicate the [111] and [311] directions of the Fe$_3$O$_4$ unit crystal derived from the FFT analysis. The scale bars in the FFT images represent 5 nm$^{-1}$.
Fig. 7 Driving force guiding the variation in the BNC alignment during OA. a Theoretical model of the pair interaction potential between BNCs as a function of the inter-BNC distance calculated by the extended DLVO theory, considering van der Waals attraction, electrostatic repulsion, and magnetic dipole-dipole interactions. b Surface energy ratio of unpassivated BNCs and ratio of the binding energies of surface ligands for the \{111\} and \{100\} facets, as calculated by DFT. c Side view of the BNC surface conformation and surface ligand simulated by DFT calculations after relaxation. Relaxed slab structure of BNC before and after surface ligand coordination on the \{001\} and \{111\} facets. The blue, black, white, red, and orange spheres indicate Fe, C, H, O, and Mg atoms, respectively. The red dotted auxiliary lines illustrate the surface distortion relative to the unpassivated Fe$_3$O$_4$ surface. d Classical facet overgrowth and nonclassical regular tiling processes.
Table 1 Calculated surface energies and ligand binding energies for the different facets of Fe₃O₄.

| Facet | Surface energy (eV nm⁻²) | Binding energy (eV per molecule) |
|-------|--------------------------|---------------------------------|
|       | ac-MC | pa-MC | mg-MC |
| (100) | 0.51 | 3.84 | 8.19 | 7.49 |
| (110) | 4.24 | 3.40 | 23.64 | 11.81 |
| (111) | 1.12 | 5.11 | 11.49 | 14.86 |

assembled structure follows trends that expose low-energy facets or eliminate high-energy facets.38,39

Discussion

In summary, the crystallisation and growth of Fe₃O₄ mesocrystals can be chemically controlled into a single pathway via OA. Upon OA, the coordination of different surface ligands, namely, acetate, polyacrylate, and Mg²⁺-adsorbed polyacrylate, altered the crystallographic order of the BNC tiling rule, thereby producing mesocrystals with different grain structures. BNC alignment significantly affected the inter-BNC and intermesocrystal magnetic interactions (via exchange coupling and dipole–dipole interactions, respectively), resulting in different collective magnetic behaviours in individual Fe₃O₄ mesocrystals and their magnetic chains. We then revealed that the tunable alignment of BNCs is guided by the facet-dependent surface energy of BNCs and changes in the surface energy after ligand coordination. These results help elucidate the driving force guiding the OA of Fe₃O₄ and a fundamental magnetic model for mesocrystal assembly with different microstructural orders. This work provides a starting point for the grain engineering of nanocrystalline materials based on control of the crystallisation process in natural and synthetic systems, as well as relevant practical applications.

Methods

Chemicals. Iron chloride hexahydrate (FeCl₃·6H₂O, ≥97%, Sigma-Aldrich, Korea), NaOAC (≥98.5%, Sigma-Aldrich, Republic of Korea), sodium acetate (NaAc, 97%, Sigma-Aldrich, Republic of Korea), magnesium chloride hexahydrate (MgCl₂·6H₂O, ≥99%, Sigma-Aldrich, Republic of Korea), and ethylene glycol ([C₂H₄(OH)]₂, ≥99%, Alfa Aesar, Republic of Korea) were used as received without further purification. Deionised water was obtained using a Millipore Direct-Q UV 3.

Chemical control of crystallisation pathways of multigrain Fe₃O₄ mesocrystals. We used a modified polyol method to synthesise the Fe₃O₄ mesocrystals. This method has been extensively employed to produce metal and metal oxide mesocrystals of various sizes.40 We employed iron chloride hexahydrate (FeCl₃·6H₂O) as a Fe³⁺ ion precursor, and used NaOAC and deionised water (Millipore Direct-Q UV 3) as the hydroxyl ion sources. Ethylene glycol was used as a solvent and reducing agent. We prepared solution 1 by dissolving FeCl₃·6H₂O in deionised water, and solution 2 by dissolving NaOAC in 50 mL of ethylene glycol under aN-or jerk sonication for 10 min. We adjusted the concentrations of FeCl₃·6H₂O and NaOAC with each solution to analyse the changes in the crystallisation pathways according to the OH⁻/Fe³⁺ ratio. To analyse the effects of NaOAC on the crystallisation pathway, 6, 10, and 15 mmol of NaOAC were dissolved in 50 mL of ethylene glycol for solution 2, whereas 2 mmol of FeCl₃·6H₂O was dissolved in 150 mL of H₂O for solution 1. To produce mesocrystals only through pathway 1, we prepared solution 1 with 2 mmol of FeCl₃·6H₂O in 150 mL of H₂O, and solution 2 containing 6 mmol of NaOAc in 50 mL of ethylene glycol. To produce mesocrystals only through pathway 2, 1 mmol of FeCl₃·6H₂O was dissolved in 200 mL of H₂O for solution 1, and 3 mmol of NaOAc was dissolved in 50 mL of ethylene glycol. In a typical synthesis process, after preparing solutions 1 and 2, we recorded XRD patterns in a PANalytical XPert PRO MPD with a Cu Ka radiation source (λ = 1.5406 Å) at the Korea Basic Science Institute, Seoul Western Center. We recorded XRD patterns in a φ-2θ geometry from 20° to 80° using a 45 kV and 40 mA for assembly. The average grain size was calculated from the (311) XRD peak of Fe₃O₄ using the Scherrer equation after fitting the profiles of the samples with a pseudo-Voigt function and correcting for instrumental broadening.

Surface characterisation. The amount of surface ligands on BNCs was analysed by conducting TG-DTA (TA Instrument, SDT Q600) under Ar flowing at 100 mL min⁻¹. Vacuum-dried samples were mounted onto a holder and heated from room temperature to 500 °C at a ramp rate of 10 °C min⁻¹. Considering the weight change (%) and temperature differences (°C mg⁻¹), the ligand densities of acetate, polyacrylate, and Mg²⁺-adsorbed polyacrylate were determined using the following equation: η(Ligand) = \frac{\text{mass of the sample before TGA}}{\text{mass of the sample after TGA} \times \text{weight of a surface ligand unit}}. The data were obtained from the TG curves of Fe₃O₄ mesocrystals with different surface ligands in the ATR mode with a diamond crystal window. Vacuum-dried samples were mounted onto the ATR crystal and then measured at a resolution of 2 cm⁻¹ in the range of 4000–4000 cm⁻¹. We collected XPS (Thermo Scientific, K-Alpha³) profiles with a monochromated Al Kα X-ray source operating at 1486.6 eV. A survey scan including the photoemission features from all elements was collected with a pass energy of 200 eV in 1.0 eV eV intervals, and detailed scans of narrow elemental regions (Fe 2p, O 1s, C 1s, and Mg 1s) were recorded at 50 eV in 0.1 eV intervals. All energy-loss regions in the narrow scan spectra were fitted using Shirley background functions. We performed atomic absorption spectrometry (Thermo Scientific, iCE 3500) and inductively coupled plasma optical-emission spectrometry (Thermo Scientific, iCAP 6500 Duo) to determine the relative
chemical compositions of Mg$_2$Fe$^{2+}$ and Fe$^{2+}$/Fe$^{3+}$, respectively, in the mesocrystals coordinated with Mg$^{2+}$-adsorbed polyacrylate. Dynamic light scattering and zeta-potential measurements were conducted using the Zetasizer Nano ZS90, Malvern Instruments, with diluted samples dispersed in 0.5 mL of deionised water.

**Magnetic property characterisation.** We analysed the magnetic properties of the powder samples with different crystallographic orders by measuring the magnetisation curves $M(H)$ and zero-field-cooling (ZFC)/field-cooling (FC) curves using a vibrating sample magnetometer (Microsense, EV9) and a physical property measurement system (PPMS, Quantum Design, PPMS-14) equipped with a vibrating sample magnetometer. The magnetisation curves $M(H)$ of Fe$_3$O$_4$ mesocrystals with different BNC alignments were measured at 300 K using an applied field of up to 1559 kA m$^{-1}$. We performed the ZFC/FC measurements using the PPMS in the sweep mode with a temperature variation rate of 10 K min$^{-1}$. In detail, all samples were cooled to 4 K from room temperature without applying an external field ($H_{ex} = 0$), and the magnetisation of the mesocrystals was collected with increasing temperature up to 400 K in a field of 40 kA m$^{-1}$ (ZFC). Subsequently, the samples were cooled to 4 K again under the same external field strength, and the magnetisation was measured by the same process. To examine the angular dependence of the $H_{c}$ behaviours of 1-D Fe$_3$O$_4$ nanochains, we measured the magnetisation curves $M(H)$ of each nanochain with different BNC alignments using the EV9 vibrating sample magnetometer equipped with a rotating holder. Specifically, we dispersed different types of Fe$_3$O$_4$ mesocrystals with different BNC alignments in ethanol at a concentration of 0.01 mg mL$^{-1}$, and then dropped 10 μL of the solution on a 6.4 × 6.4 mm$^2$ oxidised Si wafer substrate under an external magnetic field of 160 kA m$^{-1}$. To ensure that only mesocrystal–mesocrystal magnetic interactions in the nanochain affected the magnetisation, we maintained a large inter-nanochain distance, and ensured that each nanochain was composed of only one row of mesocrystals, thus minimising nanochain–nanochain magnetic interactions.

**Data availability**

The data that support the findings of this study are available from the corresponding author upon request. Source Data are provided with this paper.

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**Author contributions**

B.C.P. and M.J.K. contributed equally to this study. B.C.P., M.J.K., and Y. Keun K. designed and conceived the experiments. B.C.P., M.J.K., T.M.K., M.S.K., and H.E.F.T.
optimised the synthesis conditions of Fe3O4 mesocrystals. B.C.P., M.J.K., T.M.K., and M.S.K. analysed the microstructure of the Fe3O4 mesocrystals. B.C.P., M.J.K., and G.W.K. analysed the magnetic properties of the mesocrystals and their chain. B.C.P., M.J.K., and Y. Kwang K. conducted the theoretical modelling and DFT calculations. B.C.P. and M.J.K. wrote the manuscript after discussion with all other authors. Y. Keun K. supervised the entire project.

Competing interests
The authors declare no competing interests.

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