Self-Assembly of One-Dimensional Nanocrystal Superlattice Chains Mediated by Molecular Clusters

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S *Supporting Information*

ABSTRACT: Self-assembly of nanocrystal (NC) building blocks into mesoscopic superstructures with well-defined symmetry and geometry is essential for creating new materials with rationally designed properties. Despite the tremendous progress in colloidal assembly, it remains a fundamental challenge to assemble isotropic spherical NCs into one-dimensional (1D) ordered superstructures. Here, we report a new and general methodology that utilizes molecular clusters to induce the anisotropic assembly of NCs in solution, yielding polymer-like, single-NC-wide linear chains comprising as many as ~1000 close-packed NCs. This cluster-assisted assembly process is applicable to various metallic, semiconductor, and magnetic NCs of different sizes and shapes. Mechanistic investigation reveals that the solvent-induced association of clusters plays a key role in driving the anisotropic assembly of NCs. Our work opens a solution-based route for linearly assembling NCs and represents an important step toward the bottom-up construction of 1D ordered NC superstructures.

Driven by recent advances in colloidal synthesis and assembly,[1] the past decade has witnessed the emergence of diverse self-assembled nanocrystal (NC) superstructures.[2] One notable example is long-range ordered arrays of close-packed NCs, also known as NC superlattices,[1] which are of great importance for both fundamental studies and techno-logical applications.[3] To date, 3D superlattices consisting of single- or multicomponent NCs are routinely achievable by the conventional self-assembly process induced by solvent evapo-ration.[1,4] The recently developed liquid–air interfacial assembly technique also allows the growth of 2D NC superlattice membranes over large areas.[5] 1D ordered arrays of NCs are intriguing for photonic, optoelectronic, and sensing applica-tions, owing to their unique 1D geometry in combination with the coupling interactions of periodically separated NCs.[6] However, unlike their 2D and 3D counterparts, there has been little success reported on the self-assembly of 1D ordered NC superstructures.[7]

The assembly challenges associated with 1D NC assembly are mainly due to the lack of directional interactions arising from the isotropic nature of spherical NCs.[6a] As a result, external assistance is usually needed in order to achieve linear organization of NCs.[8] Over the past few years, much effort has been devoted to exploring the anisotropic assembly of NCs,[9–11] aiming to develop a general approach that enables the 1D organization of colloidal NCs over long distances. It has been reported that the intrinsic magnetic-dipole moment is capable of inducing the linear assembly of NCs in the presence of a magnetic field,[9] yet this strategy is only applicable to certain types of magnetic NCs. The linear arrangement of NCs can also be realized with the aid of templates such as litho-graphically patterned surfaces[10] and rolled sheets.[11] However, these methods usually suffer from either low yields or short-range NC ordering. The concept of colloidal polymerization has also been exploited in growing NC longer chains through a process that mimics molecular polymerization.[12] This strategy is particularly attractive as it offers an opportunity to design the architectures of NC chains by a molecular approach.[13] Although the conceptual viability has been demonstrated,[14] existing polymerization methods typically yield intrinsically flexible, quasi-1D NC chains.

Here, for the first time we report that molecular clusters can induce the linear organization of NCs in solution, enabling 1D NC superlattice chains having lengths extending several micrometers. We show that conventional hydrophobic colloidal NCs, regardless of the NC composition, size, and shape, exhibit an unusual anisotropic assembly behavior when incubated in hexane in the presence of molecular clusters such as lead sulfate ($PbSO_4$). Extensive structural characterization reveals that the resulting NC arrays are encapsulated by a half-cylindrical cluster shell, which provides fixation and stabilizes NC chains in hexane. It is hypothesized that the solvophobicity and solvophilicity balance dictates the evolution of such uniquely structured NC chains.

$PbSO_4$ clusters used in the present work are ligated by oleylamine (OAm) and are synthesized by reaction of lead chloride or lead oleate with a number of alkyl-ammonium sulfate compounds (see Methods and Figure S1 in Supporting Information for details). Various monodisperse colloidal NCs stabilized by oleic acid (OA) and/or OAm are synthesized by the corresponding literature methods.[15] The OA-capped Fe_3O_4 NCs[15a] are chosen as a model system to demonstrate the linear assembly process. NC superlattice chains are obtained by simply introducing $PbSO_4$ clusters into a hexane solution containing NCs followed by incubation without disturbing for a

particular time. It should be noted that the addition of a small amount of OAm can greatly accelerate the chain growth process, making it complete within 30 min. Starting with NC and cluster random mixtures, we observe the emergence of short chains of 2–6 NCs within the first 5 min of incubation (Figure S2), which gradually evolve into longer chains with time (Scheme 1).

Scheme 1. Schematic Illustration of the Self-Assembly Process of 1D NC Superlattice Chains in Solution in the Presence of Molecular Clusters[a]
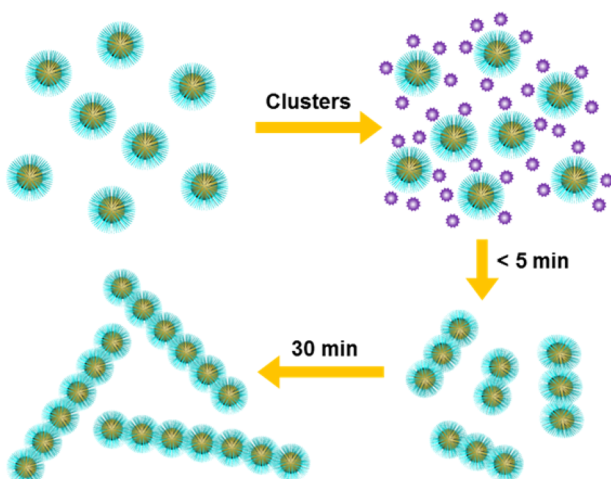
[a]For simplicity, molecular clusters are not included in NC chains.

Figure 1a shows a low-magnification transmission electron microscopy (TEM) image of the product self-assembled from 15 nm Fe_3O_4 NCs, illustrating the straightness and bundling of polymer-like linear chains. Scanning electron microscopy (SEM, Figure 1b) and high-magnification TEM (Figure 1c) reveal that most chains consist of a single line of close-packed NCs, displaying a 1D superlattice structure extending several micrometers in length. The uniform interparticle spacing is further verified by the intensity profile acquired along the chain length (Figure 1c, inset). The average interparticle distance is ~2.2 nm, consistent with the existence of OA ligands at NC surface. Typical chain lengths are in the range of 1–5 μm, while extremely long but flexible chains with lengths exceeding 18 μm, corresponding to ~1000 close-packed NCs, are also observed in some cases (Figure 1d,e). It is worth mentioning that the chain growth process is reversible by varying the incubation medium. Namely, dispersing the preformed NC chains in chloroform disassociates chains into NC and cluster mixtures, which can be reassembled into chains when the incubation solvent is switched back to hexane (Figure S3). This result strongly suggests that the incubation medium has a profound effect on the anisotropic assembly of NCs. In addition to hexane, other types of nonpolar solvents such as toluene and octane can also be used as the incubation media for chain growth.

A close inspection of individual chains by high-resolution TEM (HRTEM) indicates that Fe_3O_4 NC arrays are embedded within a polymer-like shell (Figure 2a), which undulates along the chain length to conform to NCs, resulting in a peapod-like structure. Atomic-resolution, aberration-corrected TEM is performed to further elucidate the structure of NC chains. Figure 2b shows a representative high-angle annular dark-field
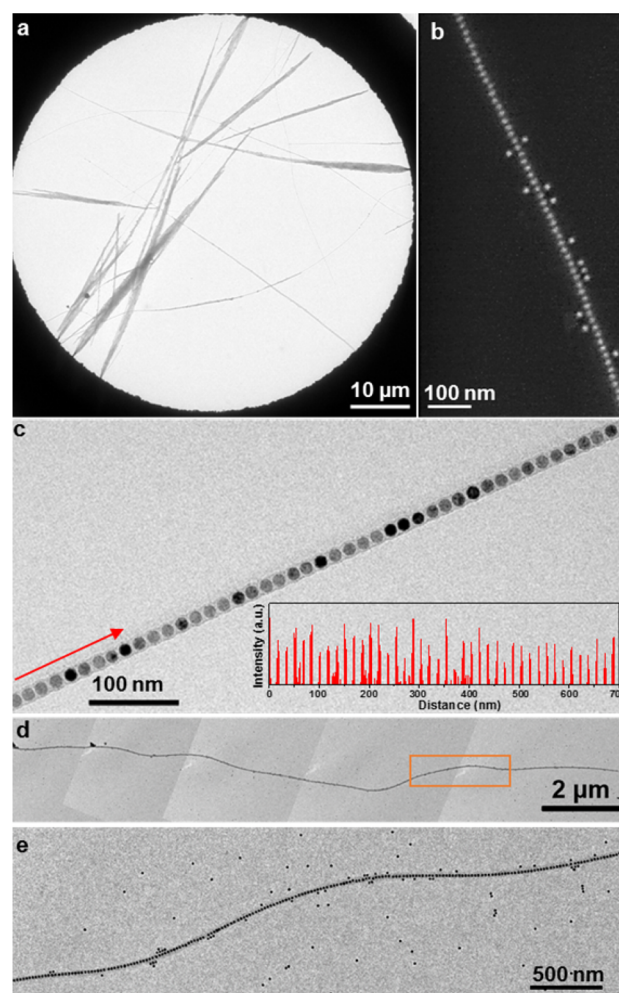
Figure 1. (a) Low-magnification TEM image of the product self-assembled from 15 nm Fe_3O_4 NCs. (b) Representative SEM image of a single NC chain. (c) High-magnification TEM image of a segment of a straight NC chain and the corresponding intensity profile (inset) along the chain length (indicated by the arrow). Evenly spaced interparticle spacing (~2.2 nm) indicated by the intensity profile suggests a 1D superlattice structure exhibited by the NC chain. (d) Representative TEM image of an ultralong NC chain. TEM image was obtained by combining five TEM images taken along the chain length. (e) High-magnification TEM image of the region indicated in (d).
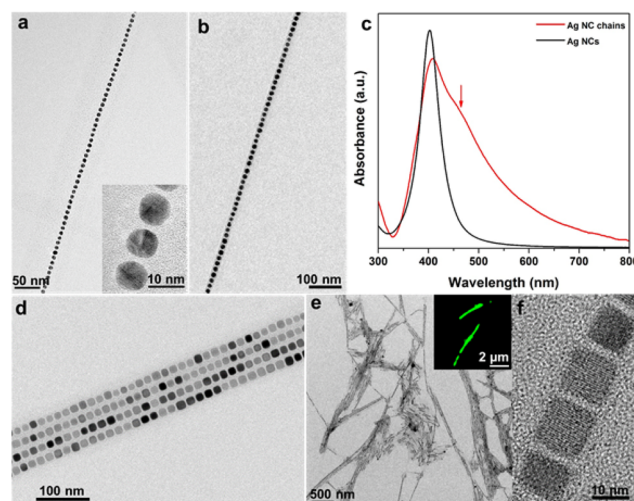
scanning TEM (HAADF-STEM) image, clearly revealing the existence of a cluster shell surrounding NC arrays with a separation of ~2 nm between them. The undulated feature of cluster shells is indicative of strong interactions between clusters and NCs, presumably originating from the van der Waals (vdW) attractions between the long-chain organic ligands (i.e., OAm and OA) stabilizing the two components. Energy-dispersive X-ray spectroscopy and elemental mapping (Figure 2c) establish the uniform distribution of Pb and S with an atomic ratio of ~1:1.05, confirming that the shell is composed of $PbSO_4$ clusters. Such shell-encapsulated NC arrays display remarkable mechanical robustness, as most chains remain intact after 10 min of vigorous sonication despite the release of a small fraction of NCs. Interestingly, the NC dislocation reveals that the cluster shell exhibits a tubular morphology (Figure S4a), which is also consistent with the Pb and S elemental mapping profiles seen in Figure 2c. We also observe in some cases that the empty shell completely unrolls
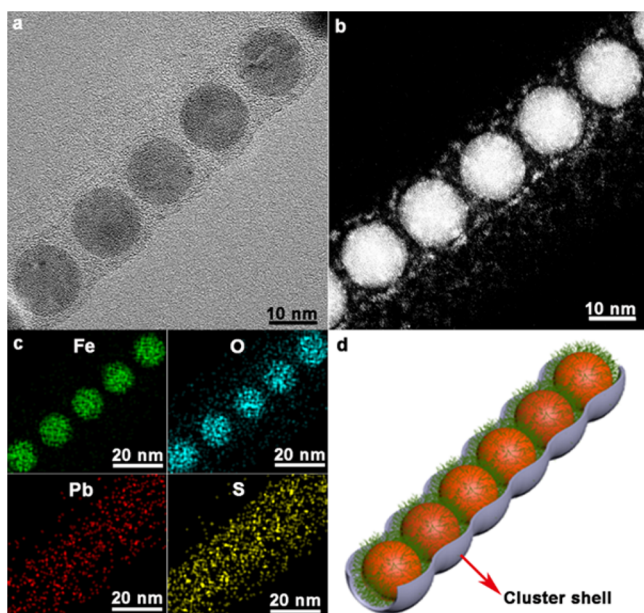
Figure 2. (a) HRTEM image of a segment of a single Fe_3O_4 NC chain. (b) Representative HAADF-STEM image of a single chain, revealing the existence of a cluster shell surrounding NC arrays. (c) Elemental mapping of the same chain segment as shown in (b). (d) Schematic of a single NC chain, illustrating the encapsulation of NC arrays by a half-cylindrical cluster shell.

Figure 3. (a) Low- and high-magnification (inset) TEM images of Au NC chains. (b) Representative TEM image of a single Ag NC chain. (c) Absorption spectra of Ag NCs and Ag NC chains. The red arrow indicates the longitudinal plasmon band arising from the coupling interactions of close-packed Ag NCs. (d) TEM image of chains self-assembled from 13 nm PbS nanocubes. (e) Low-magnification TEM and HRTEM (f) images of chains composed of 11 nm $CsPbBr_3$ nanocubes. Inset in (e) shows an optical image of $CsPbBr_3$ NC chains under a laser beam.

to form a narrow ribbon, and comparison of the ribbon width and the NC diameter indicates that the original tubular shell is partially opened (Figure S4b), resembling a half cylinder as schematically illustrated in Figure 2d. Notably, the partial exposure of the embedded NCs in this unique architecture leads to structural anisotropy across the chain width, which is further corroborated by tilted TEM experiments (Figure S5). It is also interesting to note that increasing the cluster concentration results in thicker cluster shells without changing their half-cylindrical morphology (Figure S6).

Of particular significance is that this cluster-mediated linear assembly strategy is general for a variety of NCs with different sizes and shapes. Figure 3a,b shows TEM images of plasmonic chains self-assembled from 7 nm Au[15b] and 14 nm Ag[15c] NCs, respectively. The absorption peak of Au NC chains is red-shifted by ~10 nm relative to that of free Au NCs (Figure S7), presumably due to the enhanced plasmon coupling between NC repeat units.[16] More pronounced coupling is observed in Ag NC chains, as evidenced by the emergence of a low-energy shoulder at ~465 nm (Figure 3c), which could be ascribed to the longitudinal plasmon band arising from the strong coupling of 1D NC arrays.[17] Besides spherical NC building blocks, anisotropic NCs such as PbS[15d] (13 nm, Figure 3d) and $CsPbBr_3$[15e] (11 nm, Figure 3e,f) nanocubes can also be linearly assembled under the same conditions, further demonstrating the versatility of the approach. It is interesting to note that NC chains composed of perovskite $CsPbBr_3$ NCs are highly luminescing under a laser beam (Figure 3e, inset), suggesting that the optical properties of $CsPbBr_3$ NCs are largely retained during the chain growth process. It is also worth mentioning that $PbSO_4$ is not the only cluster that can induce the linear assembly of NCs. Our preliminary studies show that the OAm-ligated $(CdSe)_{13}$ clusters[18a] can also be used to direct the linear organization of NCs in solution (Figure S8). Although further optimization of the self-assembly conditions is needed to

achieve longer chains with a higher yield, the successful 1D arrangement of NCs suggests that a variety of molecular clusters developed previously[18b] might also be suitable for inducing the linear assembly of NCs.

Having established the structure of NC superlattice chains as well as the generality of the approach, we turn our attention to the driving forces that induce the self-assembly of NC chains. The fact that chain growth is independent of the constituent NCs rules out the magnetic or electric dipole–dipole interactions as the main driving forces. Additionally, colloidal NCs capped with OA and/or OAm are known to be fully dispersible in hexane, such that they cannot assemble spontaneously in solution. Therefore, the molecular clusters introduced must play a critical role in driving the linear assembly of NCs. To further elucidate the role of clusters, control experiments are carried out by incubating $PbSO_4$ clusters alone in hexane under otherwise identical conditions. A cloudy suspension containing white precipitates is observed after 30 min of incubation (Figure S9a). As indicated by TEM and small-angle X-ray diffraction, the precipitates are composed of lamellar ribbons with a dimension of ~400 × 60 nm (Figure S9b,c). Lamellar mesostructures self-assembled from clusters have been commonly observed previously,[18a] the formation of which might be explained by an amine-bilayer templating mechanism. Nonetheless, the precipitated ribbons observed in our work suggest that hexane is a poor solvent for $PbSO_4$ clusters. Accordingly, $PbSO_4$ clusters have a tendency to associate to minimize the surface energy of the system when dispersed in hexane. We surmise that upon the introduction of $PbSO_4$ clusters into the NC solution, the solvent-induced association of clusters induces the co-assembly of NCs because of the strong interactions between the two components. The preferential end-on attachment of NCs and clusters, which is responsible for chain growth, is likely governed by the subtle interplay between nanoscale attractive and repulsive forces (e.g., vdW and poor solvency attractions vs steric repulsions),[19]

yet further work is needed to elucidate the underlying mechanisms. With regards to the organization of $PbSO_4$ clusters in the presence of NCs, one could reasonably expect that the formation of tubular shells surrounding NCs rather than flat ribbons is energetically more favorable, because the embedded NCs could effectively screen unfavorable interactions between clusters and hexane. In this context, the eventual evolution of a half-cylindrical cluster shell surrounding NC arrays could be reflective of a balance between solvophobicity and solvophilicity, considering that individual chains are amphiphilic, that is, the cluster shells and the exposed NCs are solvophobic and solvophilic, respectively.

In summary, our studies have established a new and general methodology that utilizes molecular clusters to induce the anisotropic assembly of NCs in solution, enabling 1D, single-NC-wide superlattice chains extending several micrometers in length. Access to such chainlike superstructures provides an unprecedented opportunity for exploring unidirectional charge and energy transport through 1D ordered NC arrays, which is essential to the development of various NC-based optical and electrical devices. Given the generality of the approach, we anticipate that in the future multifunctional chains with a higher level of structural complexity can be realized by modular assembly of distinct types of NCs.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b00055.

   Experimental details and data (PDF)

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Notes
The authors declare no competing financial interest.

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