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Letter

Molecular Additives as Competitive Binding Agents to Control Supramolecular-Driven Nanoparticle Assembly

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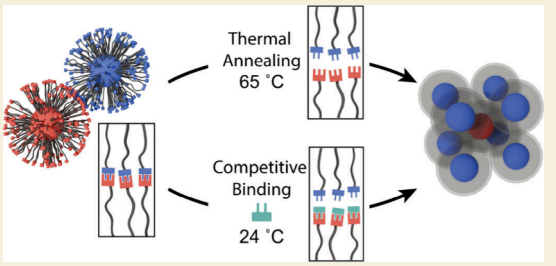
ABSTRACT: Colloidal nanoparticle assembly methods can produce intricate superlattice structures and often use knowledge of atomic crystallization behaviors to guide their design. While this analogy has enabled multiple routes to programming colloidal crystallization thermodynamics, fewer tools or strategies exist to manipulate nanoparticle superlattice growth kinetics in a controlled manner. Here we investigate how small-molecule additives can be used to modulate the thermodynamics and kinetics of supramolecular-chemistry-driven nanoparticle assembly. Specifically, we introduce monovalent binding agents into the superlattice growth solution that compete with the multivalent interparticle bonding interactions driving particle assembly, thereby altering interparticle bond strength by reducing the number of bridging complexes formed between particles. In this manner, the assemblies can be steered to avoid kinetic traps and crystallize into faceted single crystals under isothermal conditions, alleviating the need for precise thermal control that has conventionally been required to produce large, faceted crystals in prior assembly methods.



KEYWORDS: *self-assembly, colloidal crystal, supramolecular chemistry, competitive binding, crystallization, reorganization*

Colloidal nanoparticle superlattices share many structural analogies to traditional atomic crystals, and thus the field of nanoparticle assembly has significantly benefitted from knowledge gained from studies of atomic crystallization.[1−9] Despite the large differences in length, time, and energy scales associated with the formation of atomic and nanoparticle lattices, many crystal structural features (e.g., favored crystal unit cell geometries, and equilibrium crystallite shapes and surface facets) are often mirrored across these material types.[10−15] These structural similarities have provided insights that enable the intentional programming of nanoparticle superlattice unit cell symmetry. However, the processing pathways used to control colloidal crystal growth remain limited compared to the complex thermal or chemical methods used to modulate atomic crystallization.[16−18] The most successful strategies for nanoparticle superlattice assembly typically use simple slow phase transitions (e.g., slow cooling or solvent evaporation), where reducing assembly rate is the main design handle used to increase crystal size or improve crystal quality.[19−25] Although such approaches can indeed make large and well-faceted structures, relying on just slow thermal transitions to control crystallization potentially limits the ability to modify crystal design parameters like crystallite size, shape, or surface faceting.[26−28] Moreover, the extended amount of time required for these processes to generate large single crystals makes them more challenging for multi-parameter investigations of crystal growth and structure−property relationships, or integration into technological applications.[7,29]

An alternate strategy to modulate crystallization rate is the use of monofunctional additives as crystal "capping agents"—atomic or molecular species that dynamically bind to the exposed sites on a crystal surface. These additives affect crystallization via multiple mechanisms including slowing down nucleation, passivating select crystal facets, and promoting dynamic bond exchange.[30−32] Modulating atomic or molecular crystal growth with capping agents has led to improvements in crystal quality and enabled control over crystal shapes and sizes.[33−39] Some initial examples have demonstrated that these design principles can also be used for colloidal assemblies driven via DNA hybridization.[40−43] However, fundamental questions remain about how to effectively design both the molecular additives and the assembly conditions necessary to regulate crystallization. Despite the ubiquity of this strategy in atomic or molecular crystal growth, it is not necessarily straightforward that the use of capping agents on colloidal crystal growth will replicate all aspects of crystal growth observed in their atomic or molecular counterparts, as colloidal building blocks often use multivalent and dynamic supramolecular interactions for assembly. In

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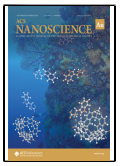

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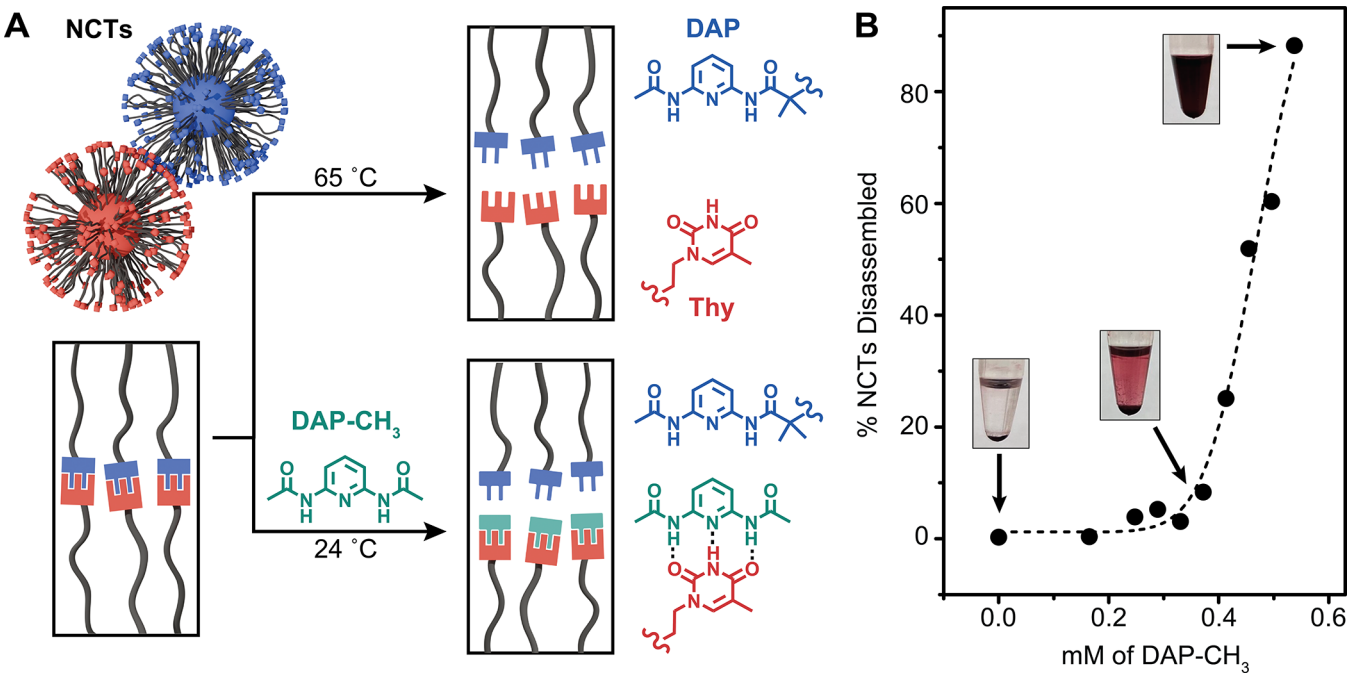

Figure 1. (A) NCTs in this study consist of gold nanoparticles functionalized with polystyrene brushes that terminate in either DAP (blue) or Thy (red) complexes. The assembly state of NCTs can be controlled by heating the assemblies above the melting transition or by adding competitive binding agents (DAP-CH_3, green). (B) Increasing the amount of DAP-CH_3 present during NCT assembly results in higher concentrations of NCTs that remain disassembled in solution, since DAP-CH_3 competes with DAP-NCTs for binding with Thy-NCTs.

other words, molecular capping agents typically compete 1:1 with molecular crystals' building blocks for attachment to the growing crystals' surfaces, but when they are used to modulate colloidal crystal growth, they will instead compete with multivalent and dynamic binding interactions between nanoparticles. Thus, the "competition" between monovalent binding agents and multivalent crystal building blocks is disproportionate, which potentially has serious implications for the fundamental thermodynamics and kinetics of crystallization. Systematic fundamental investigations into these factors are necessary to more precisely modulate the kinetics of colloidal crystal growth.

Here we study the effects of small molecule additives on the crystallization of Nanocomposite Tectons (NCTs), which are nanoparticle building blocks consisting of inorganic particle cores grafted with polymer chains that terminate in supramolecular binding groups (Figure 1). NCTs assemble via multivalent supramolecular bonding interactions, and the addition of monovalent binding agents decreases the multivalency of NCT bridging interactions by competitively binding with the supramolecular moieties that drive NCT assembly. We demonstrate that this competition alters the thermodynamics of multivalency-driven NCT assembly in a fundamentally different manner than simply weakening each supramolecular complex (e.g., by increasing system temperature, or changing the solvent environment). As a result, these binding agents widen the thermal window over which NCTs can crystallize, and even enable rapid NCT crystal formation at room temperature for systems that typically require significantly elevated temperatures to escape kinetically trapped arrangements. Moreover, because the amount of capping agent can be controlled volumetrically, it is possible to more finely tune the assembly kinetics compared with traditional methods that use heat, since equilibration with an external bath can be slow, and heating blocks (though easy to use) can be imprecise or subject to fluctuations.[23,44] These findings suggest that competitive binding agents represent a valuable alternative approach for self-assembly compared to conventional thermal annealing strategies. The mechanistic understanding achieved here enables better design principles to push multivalency-driven nanoscale assemblies out of kinetically trapped states, resulting in better precision over colloidal crystallization.

RESULTS AND DISCUSSION

NCTs in this work were constructed by grafting gold nanoparticles with polystyrene (PS) brushes, where each PS chain terminated in a supramolecular binding group—either a derivative of diaminopyridine (DAP) (specifically 2,6-bis-(acylamino)pyridine), or thymine (Thy) (Figure 1). DAP and Thy form complementary hydrogen bonding pairs, and thus DAP- and Thy-NCTs rapidly assemble via multivalent interactions when combined.[45,46] Under typical assembly conditions, each of these DAP-Thy complexes is dynamic, but the collective NCT-NCT bonds are typically irreversible under ambient conditions due to the high local concentration of hydrogen bonding groups confined between NCTs. Because each individual DAP-Thy bond is dynamic, we hypothesized that the collective strength of NCT-NCT bonds could be controlled by adding small molecules that competitively bind with the particle-tethered supramolecular groups, thereby lowering the number of bridging complexes between NCTs.

To test this hypothesis, 2,6-bis(acetamido)pyridine (DAP-CH_3) was synthesized as a competitive binding agent and combined with solutions containing DAP- and Thy-NCTs (18 nm gold nanoparticle cores, 11 kDa PS brushes; solutions contained 16.6 nM each of DAP- and Thy-NCTs) (Figure 1A). Varying amounts of DAP-CH_3 were added to these solutions, which were then equilibrated at 24 °C for ~75 min. As the amount of DAP-CH_3 increased, the equilibrium state of

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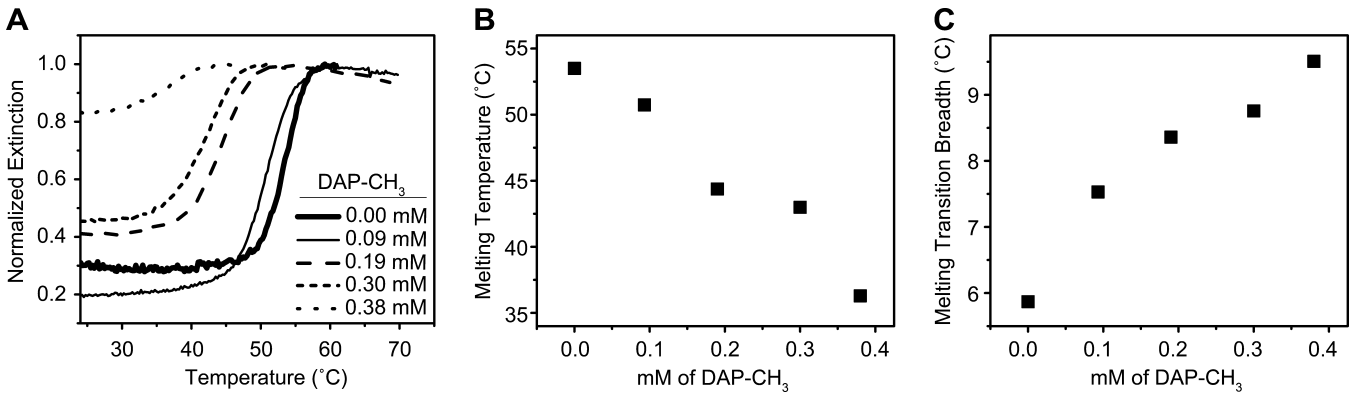

Figure 2. (A) Melting curves of NCT assemblies formed in the presence of varying concentrations of binding agents show a decrease in thermodynamic stability as indicated by (B) reduction in melting temperature. (C) Binding agents decrease the number of bridging complexes between particles, which results in a broadening of the melting transition.

the NCTs did indeed transition from entirely assembled to entirely dissociated, though in a nonlinear manner (Figure 1B). Below ~0.37 mM of DAP-CH_3 (23 equiv of DAP-CH_3 relative to the total number of DAP groups bound to NCTs), there was only a slight increase in the number of dissociated NCTs at equilibrium with increasing amounts of DAP-CH_3. Above this value, however, there was a significant increase in the number of dissociated NCTs with increasing DAP-CH_3, such that nearly all NCTs were dissociated at ~0.58 mM (~36 equiv). For a detailed discussion on considering the effects of DAP-CH_3 as a function of molar concentration of DAP-CH_3 versus the stochiometric ratio of DAP-CH_3 to the number of Thy end groups, we direct the readers to the Supporting Information. We hypothesize that a large excess of DAP-CH_3 groups is necessary to induce NCT disassembly because of the high degree of multivalency in NCT-NCT bonds. More simply, tethering DAP and Thy groups to the surface of the NCTs via polymer chains ensures that the local concentration of these groups is always large, and each NCT-NCT bond consists of numerous DAP-Thy connections. Moreover, the high local concentration of DAP and Thy groups enables rapid reformation of DAP-Thy connections whenever an interparticle DAP-Thy complex dissociates. Thus, since NCTs can only diffuse away from an assembly once all of its intraparticle DAP-Thy connections are broken simultaneously, a large excess of free DAP-CH_3 is necessary to out-compete all the bridging complexes and induce particle disassembly.

Notably, the dissociated particles could be reassembled by adding toluene, as the addition of toluene dilutes the concentration of DAP-CH_3, but does not affect the local concentration of particle-bound DAP and Thy groups. Cycles of complete disassembly and reassembly could therefore be induced by adjusting the concentration of DAP-CH_3 between 0.58 mM and 0.16 mM, respectively (Figure S6). These assembly and disassembly transitions in response to DAP-CH_3 concentration mimic the response of NCTs to temperature, which is typically the design handle used to control particle assembly kinetics to enable crystal formation. To further demonstrate that DAP-CH_3's effects on NCT assembly are driven by dynamic binding to the NCT supramolecular groups, the same experiments were performed using a DAP-based binder with greater steric hindrance around the hydrogen bonding groups. The bulky groups on these modified DAP molecules decrease the DAP-Thy association constant by a factor of approximately 2 compared to DAP-CH_3 (Figure S7). As a result, they were unable to induce NCT dissociation, even at 2.5x the concentration of DAP-CH_3 that enabled complete disassembly. These data further indicate that the molecular capping agent facilitates dynamic reorganization of the supramolecular bonds between NCTs.

Based on these experiments, we hypothesized that DAP-CH_3 modifies NCT assembly by adjusting the multivalency of their bonding interactions. However, DAP-CH_3 may also be reducing the strength of each individual DAP-Thy interaction. Polar solvent environments weaken hydrogen bonds, and prior work has shown that the addition of polar molecules lowers the stability of NCT assemblies in a manner similar to DAP-CH_3 as described in the above experiments.[46,47] It is important to distinguish between these two mechanisms as they can have significant impacts on the kinetics of NCT reorganization and the protocols required to induce crystallization. Specifically, systems with highly multivalent binding interactions possess a sharp dependence of binding strength on temperature. In practice, slow cooling through this sharp transition is necessary for crystallization since reorganization can only take place within this small temperature window.[43] Modulating NCT assembly thermodynamics by reducing multivalency should therefore better enable crystallization than simply lowering monovalent bond strength, as it would be expected to widen the thermal window over which crystallization occurs.

To determine whether competitive binding agents reduce multivalency or the strength of individual DAP-Thy complexes, the thermally induced melting transitions of NCT assemblies were measured in the presence of varying concentrations of DAP-CH_3. As the concentration of DAP-CH_3increased, the melting temperature lowered and, more importantly, broadened (Figure 2). This increase in breadth indicates that the DAP-CH_3 groups are indeed competing with the NCT-bound DAP groups, reducing the collective binding strength of NCT interactions by lowering multivalency. These effects are further confirmed by control experiments where the binding strength between NCTs was modified via the addition of anisole (a polar solvent). The addition of anisole also lowered NCT melting temperatures, but without significant changes to the thermal transition breadth (Figure S8). Collectively, these melting curve measurements indicate that competitive binding agents should permit NCT reorganization over a wider temperature range compared to methods that alter the strength of individual bridging complexes.

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Without molecular additives, NCT reorganization is achieved by heating the system near its melting transition, thereby enabling the rapid dynamic exchange of DAP and Thy bonds.[45,48] Given the data presented above, we hypothesized that DAP-CH_3 could similarly disrupt NCT bonds, thereby facilitating isothermal NCT reorganization. To investigate this hypothesis, small-angle X-ray scattering (SAXS) was used to characterize the crystallinity of assemblies formed in the presence of varying concentration of DAP-CH_3 at 24 °C. While NCTs assembled at this temperature without any DAP-CH_3 formed arrays with limited long-range order, systems assembled in the presence of DAP-CH_3 formed CsCl-type lattices, the predicted equilibrium crystal symmetry for this NCT design (Figure 3A).[45,49] The crystallinity of these superlattices (as determined from Scherrer analysis, Figure 3B) increased concomitantly with added DAP-CH_3 up to 0.37 mM of DAP-CH_3—the "onset point" observed in Figure 1B.

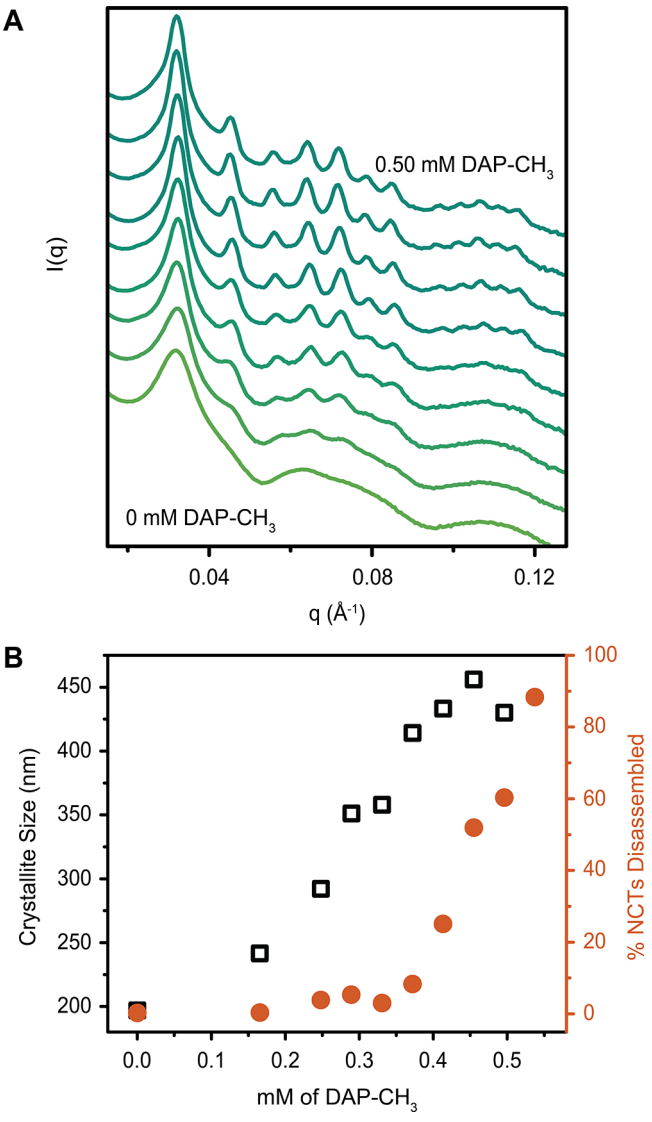

Figure 3. SAXS patterns of assemblies formed at 24 °C from increasing concentration of DAP-CH_3 showing continuous improvement in crystallinity up to 0.37 mM. Beyond this concentration, only minimal changes to crystallinity were observed, although the weakened NCT interactions resulted in significant loss in assembly yield.

Above this concentration, further increases in the concentration of DAP-CH_3 produced only minimal improvements in crystal quality but with decreasing fraction of NCTs in the assembled state. It is important to note that the melting temperature of assemblies formed in the presence of 0.37 mM DAP-CH_3 was 36 °C, and this assembly took place at room temperature (24 °C), well below this thermal transition. In contrast, forming assemblies with similar crystal quality via the addition of anisole was only possible under conditions that also resulted in a large percentage of NCTs fully dissociating from the assemblies (thus lowering the yield of crystals) (Figures S9, S10). These data indicate the mechanism by which molecular additives facilitates dynamic exchange of individual DAP-Thy bonds between particles has significant implications on the conditions under which superlattices can be formed.

To further determine how different design parameters influence the DAP-CH_3's effects on colloidal crystal growth, NCT superlattices were assembled using nanoparticles with different inorganic particle core sizes and polymer lengths. Changing these design parameters alters the enthalpic and entropic factors that contribute to the stabilization of these superlattices (e.g., local concentration of supramolecular groups, the entropic penalty for constricting bound polymer chains), which alters the multivalency of NCT interactions. Indeed, prior work has demonstrated that larger nanoparticle cores can be more difficult to crystallize via slow cooling, as their higher degrees of multivalency result in narrower thermal windows.[43] However, when DAP-CH_3 was added to NCTs of different diameters (12, 20, and 31 nm) and different polymer lengths (6, 11, and 18 kDa), all assemblies were able to form superlattices, even at 24 °C. Additionally, trends in the melting temperature further confirm the role of DAP-CH_3 in modulating crystal growth by altering multivalency (Figure S11). Specifically, increasing NCT particle core sizes necessitated higher concentrations of binding agents to achieve optimum crystallinity (Figure 4A), while increasing polymer brush length lowered the threshold concentration of DAP-CH_3 required to form high quality superlattices (Figure 4B). These trends are consistent with predictions based on the hypothesis that DAP-CH_3 is modulating multivalency, as increased particle sizes and polymer lengths have previously been shown to increase and decrease NCT multivalency, respectively.[46]

Finally, although DAP-CH_3 binding agents are able to form highly ordered superlattices at room temperature, SEM images of the resulting assemblies showed aggregates with ordered nanoparticle arrays but no distinct crystal habits (Figure S12). We attribute this observation to the highly flexible and multivalent nature of NCT bonding interactions, which increases the tolerance of the assemblies to crystal defects like grain boundaries or nonideal surface faceting; this effect has been previously documented in NCTs and other multivalent systems.[48,50] We predicted that using the concentration of binding agents to dial in the appropriate degree of multivalency during nucleation and growth would allow the crystals to avoid these kinetically trapped states and form faceted single crystals (Figure 5A). To test this hypothesis, a set of NCTs was incubated with large quantities of DAP-CH_3 (0.58 mM, sufficient to keep all NCTs dissociated), then incrementally diluted with toluene via a syringe pump. Using this protocol, single crystal Wulff constructions (rhombic dodecahedron-shaped crystallites) were observed for a wide range of rates of toluene addition

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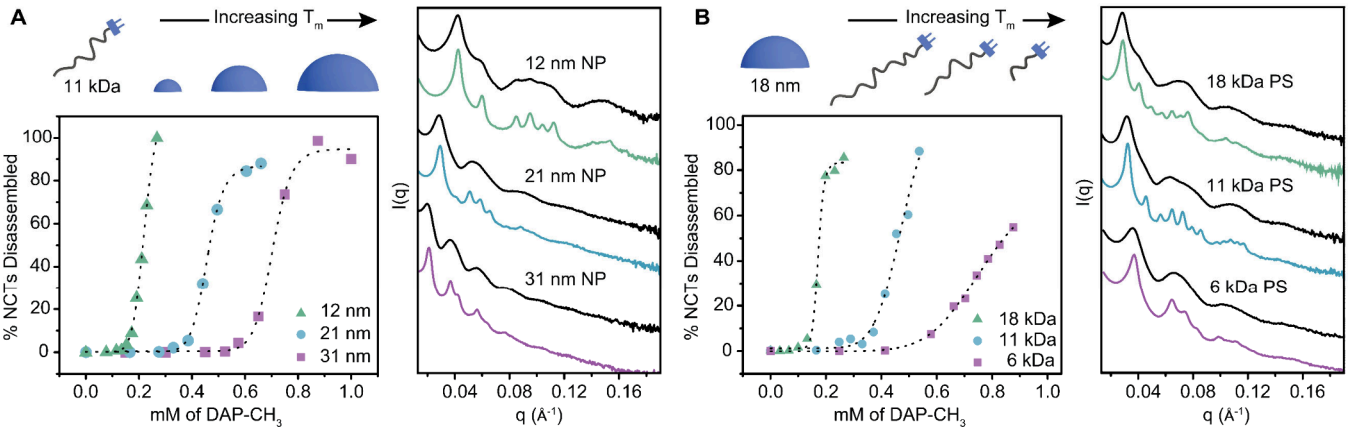

Figure 4. Binding agents (DAP-CH_3) enable crystallization of superlattices at 24 °C from NCTs with (A) varying particle sizes and constant polymer length and (B) varying polymer lengths and constant particle size. NCTs that assemble with higher degrees of multivalency (i.e., NCTs with larger particle diameters or lower polymer lengths) require higher concentrations of binding agents to disrupt assembly and achieve the highest quality superlattices. SAXS diffraction patterns in black represent assemblies formed without binding agent, while patterns in other colors correspond to assemblies formed using binding agents with optimum crystallinity and highest assembly yield.

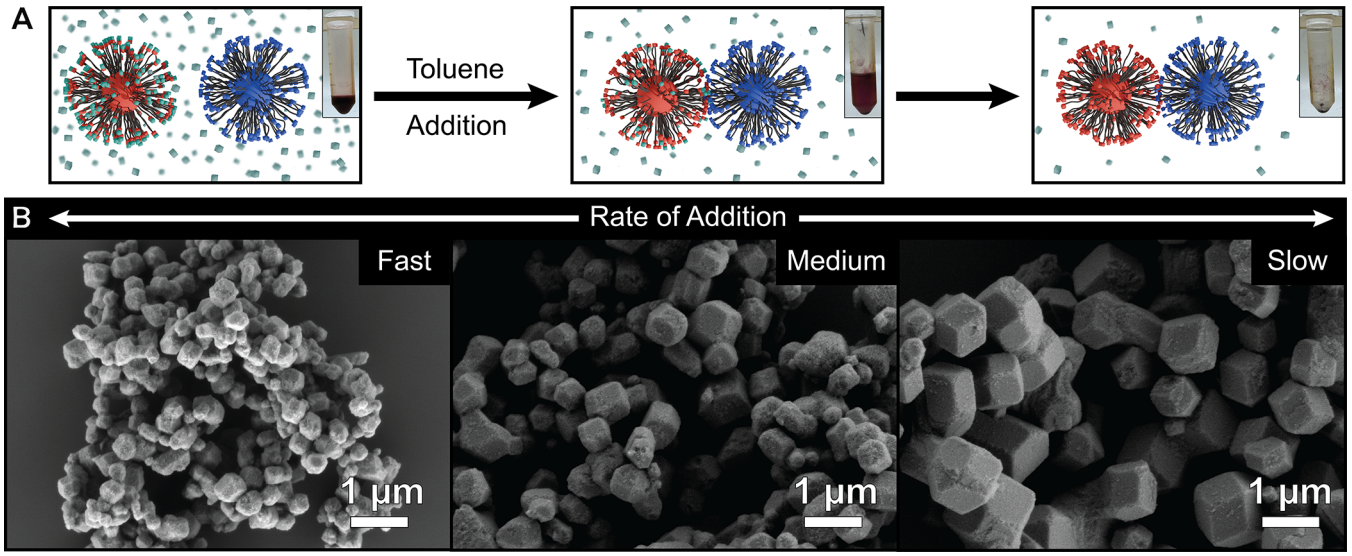

Figure 5. Faceted single crystals are formed when NCT binding strength is continuously reduced over time. (A) Diluting the concentration of binding agents with toluene addition induces NCT assembly. (B) Larger single crystals result from slower addition rates (64, 8, and 1 μL/min, from left to right).

(Figure 5B). Furthermore, faster toluene addition rates yielded smaller sized crystallites, indicating that slowly increasing the number of available binding groups in NCTs in this manner can indeed suppress nucleation in the same manner as slowly cooling through the systems' thermal transition. We predict that the use of molecular competitive binding agents will therefore be a useful tool in further developing strategies to assemble nanoparticle superlattices, especially in situations where thermal control is challenging or imprecise due to heat diffusion or inaccurate temperature measurement and heating tools, as well as systems with even higher multivalency with steep melting windows.

CONCLUSION

In this work, we have assembled nanoparticles into superlattices using molecular additives capable of competitive binding, and elucidated the fundamental principles that govern this underdeveloped strategy for controlling colloidal crystallization kinetics. These additives lower multivalency which facilitates the exchange of bridging complexes and enables particle reorganization to occur over a wider temperature range. In this manner, high quality superlattices of a range of particle size and polymer lengths were formed entirely at room temperature. Faceted single crystals were also accessed by incrementally lowering the concentration of binding agent from that which initially prevents any bridging complexes to be formed between particles. Competitive binding agents widen the range of conditions under which nanoparticles can equilibrate to its thermodynamically stable configuration. This strategy has the potential to enable the use of more diverse types of building block bridging chemistries and binding strength regimes to assemble nanoparticles. With a greater understanding of the design parameters that govern building block reorganization kinetics and superlattice formation, we anticipate that future work will better enable application of these colloidal crystals to technologies that require rapid processing or well-controlled crystallite sizes. Additionally, further investigations of these mechanisms of

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crystal growth may also permit this approach to be extended to control over crystallite shape or faceting, as has been demonstrated for atomic and molecular crystals.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnanoscienceau.4c00062.

Instrumentation methods and experimental protocols as well as additional characterization to support the conclusions detailed in the manuscript (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

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