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Programming the Assembly of Unnatural Materials with Nucleic Acids.

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Nature directs the assembly of enormously complex and highly functional materials through an encoded class of biomolecules, nucleic acids. The establishment of a similarly programmable code for the construction of synthetic, unnatural materials would allow researchers to impart functionality by precisely positioning all material components. Although it is exceedingly difficult to control the complex interactions between atomic and molecular species in such a manner, interactions between nanoscale components can be directed through the ligands attached to their surface. Our group has shown that nucleic acids can be used as highly programmable surface ligands to control the spacing and symmetry of nanoparticle building blocks in structurally sophisticated and functional materials. These nucleic acids function as programmable "bonds" between nanoparticle "atoms," analogous to a nanoscale genetic code for assembling materials. The sequence and length tunability of nucleic acid bonds has allowed us to define a powerful set of design rules for the construction of nanoparticle superlattices with more than 30 unique lattice symmetries, tunable defect structures and interparticle spacings, and several well-defined crystal habits. Further, the nature of the nucleic acid bond enables an additional level of structural control: temporal regulation of dynamic material response to external biomolecular and chemical stimuli. This control allows for the reversible transformation between thermodynamic states with different crystal symmetries, particle stoichiometries, thermal stabilities, and interparticle spacings on demand. Notably, our unique genetic approach affords functional nanoparticle architectures that, among many other applications, can be used to systematically explore and manipulate optoelectronic material properties, such as tunable interparticle plasmonic interactions, microstructure-directed energy emission, and coupled plasmonic and photonic modes.