Supporting Information

**Dynamically Interchangeable Nanoparticle Superlattices
Through the Use of Nucleic Acid-Based Allosteric Effectors**

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Experimental Details

DNA Synthesis and Sequences

All oligonucleotides were synthesized using a MM48 Automated Oligonucleotide Synthesizer and all reagents were purchased from Glen Research. Note that full procedure can be found in reference 17 in the main text.

Table S1. Sequences for synthesized oligonucleotides (written 5' → 3').

One Component System (FCC)	
Thiolated strand 1	AAC AAT TAT ACT CAG CAA [EG ₆] (-SH)
Linker 1	TTG CTG AGT ATA ATT GTT ATT GGA TGT TTT TTC ATC CTT ATT TAG TCA CGA CGA GTC ATTA -TAGCTA
Two Component System (BCC, CsCl, AIB ₂)	
Thiolated strand 1	AAC AAT TAT ACT CAG CAA [EG ₆] (-SH)
Thiolated strand 2	TAT CGT ATT TAC TCT GAT [EG ₆] (-SH)
Linker 2	TTG CTG AGT ATA ATT GTT ATT GGA TGT TTT TTC ATC CTT ATT TAG TCA CGA CGA GTC ATTA -TTCCTT
Linker 3	ATC AGA GTA AAT ACG ATA ACC GAG TCA ATT AAG ACT CCC ATT TAG TCA CGA CGA GTC ATTA -AAGGAA
Linker 4	TTG CTG AGT ATA ATT GTT ATT GGA TGT TTT TTC ATC CTT ATT TAG TCA CGA CGA GTC ATT ACC GAG TCA ATT AAG ACT CCC ATT TAG TCA CGA CGA GTC ATTA -TTCCTT
Effectors	
Comp (Comp1)	AAG GAT GAA AAA ACA TCC AAA AAA CCC
Peel (Peel1)	GGG TTT TTT GGA TGT TTT TTC ATC CTT
Comp2	GGG AGT CTT AAT TGA CTC GGA AAA CCC
Peel2	GGG TTT TCC GAG TCA ATT AAG ACT CCC
Duplexer	
20-base duplexer	AAT GAC TCG TCG TGA CTA AA

* [EG₆] indicates 6 ethylene glycol units linked via a phosphate, incorporated into the oligonucleotides using the same phosphoramidite chemistry used to synthesize oligonucleotides.

Each linker strand was composed of three segments: (1) a recognition sequence that is complementary to the thiolated DNA, (2) a spacer sequence to controllably adjust the desired DNA length, and (3) a sticky-end sequence that facilitates assembly of PAEs by allowing the linkers on particles to hybridize to each other (see refer-

ence 17 in the main text). Linkers with self-complementary sticky-ends (-TAGCTA, 3' end of linker 1 in Table S1) were used to assemble FCC superlattices, while binary component systems (BCC, CsCl, AlB₂) utilized linkers with non-self-complementary sticky-ends (-TTCCTT and -AAGGAA). Two different 20-base stem-loop sequences (colored in red and blue in Table S1) were designed for various linker strands and incorporated in each linker's spacer region. Linker 4 incorporated two different stem-loop sequences (both red and blue) to prevent complementary overlap of stem-loops with each other.

Binary PAE superlattices used two different types of thiolated strands to prevent linker swapping between two particle types. For example, when assembling a BCC superlattice, linker 2 could bind to thiolated strand 1, while linker 3 could only bind to thiolated strand 2. The 20-base duplex forming strand was hybridized to each linker prior to putting linkers on particles to impart strand rigidity.

“Comp” (also referred to as “comp1”) strands were designed to be complementary to stem-loops colored in red (Table S1) while “comp2” strands were complementary to stem-loops colored in blue. Similarly, “peel” (also referred to as “peel1”) strands were complementary to “comp1” and “peel2” were designed to hybridize with “comp2”.

DNA Functionalization and PAE Superlattice Assembly

All gold nanoparticles (AuNPs) were purchased from BB International. Oligonucleotides with terminal alkylthiol moieties were functionalized according to procedures described in the literature (see reference 17 in the main text). The absorbance values for AuNPs and oligonucleotides were measured via Cary 5000 UV/Vis spectrophotometer (Agilent), and the concentrations were calculated using Beer's Law. All extinction coefficients were obtained from the manufacturer's website (Ted Pella for AuNPs and Integrated DNA Technologies for oligonucleotides).

PAEs were vigorously mixed and allowed to precipitate to form amorphous crystalline superlattices. These precipitated aggregates were annealed at a temperature slightly below their melting temperatures (melting temperatures were measured via Cary 5000 UV/Vis spectrophotometer) for 1-3 hours.

Small Angle X-ray Scattering (SAXS) Characterizations

SAXS characterization was performed at the Argonne National Laboratory's Advanced Photon Source (APS), specifically at the DuPont-Northwestern-Dow Collaborative Access Team (DND-CAT) beamline. The beam was set-up with 10 keV collimated x-rays, and the x-rays were collected with a CCD detector to obtain 2-dimensional plot data. Exposure time of 0.1 seconds was used. 1-dimensional scattering data were obtained from radially averaging the 2-dimensional data to plot intensity versus scattering vector q . To obtain the structure factor $S(q)$, the scattering data was divided by the form factor data (form factor scan was collected via SAXS with all PAEs completely dissociated).

Kinetic Study

In order to monitor the rate of the opening and closing, FCC superlattices were assembled at its closed state. The superlattices were then characterized via SAXS every minute after additions of “comp” or “peel” strands, and lattice constants were calculated based on the collected SAXS data. The original lattice with all stem-loops closed had a lattice constant of 54.8 nm. When “comp” strands were added to open the stem-loops, the lattice constant increased to 65.1 nm in less than 10 minutes. After the superlattices fully opened, “peel” strands were immediately added to close the stem-loops, and the superlattices returned to 55.2 nm in less than 10 minutes. This indicates that when the superlattices and allosteric oligonucleotide effectors (“comp” or “peel” strands) were not vigorously mixed, the diffusion of DNA was the rate limiting step in effecting the opening or closing transitions. (Note that with vigorous stirring, the transition occurred in less than 2 minutes.)

Table S2. Interparticle distances of PAE superlattices in the initially closed, the opened, and the closed states for different crystal structures (BCC, CsCl, and AlB₂)

Crystal Structure	State	Interparticle Distance	Expected Interparticle Distance*
BCC	Initial	38.1 nm	37.5 nm
	Opened	45.2 nm	44.6 nm
	Closed	38.7 nm	37.5 nm
CsCl	Initial	30.4 nm	30.9 nm
	Opened	33.9 nm	34.4 nm
	Closed	29.3 nm	30.9 nm
AlB₂	Initial	28.9 nm	28.3 nm
	Opened	31.6 nm	31.8 nm
	Closed	29.0 nm	28.3 nm

* Note that the expected interparticle distances were calculated according to literature (reference #17 in main text).

Supplementary Figures

Figure S1. Inclusion of more than one stem-loop structure in each linker strand was used to effect a greater difference in lattice constants between the opened and closed states. One set of particles (blue) with 109-base linkers was combined with another set of particles (red) with 67-base linker strands. When all stem-loops were closed, the PAEs assembled in a BCC superlattice with a lattice constant of 41.6 nm. When all stem-loops opened after addition of complementary strands, the lattice constant increased to 53.8 nm. The difference in lattice constants between the fully opened and closed states of these BCC superlattices was therefore 12.2 nm.