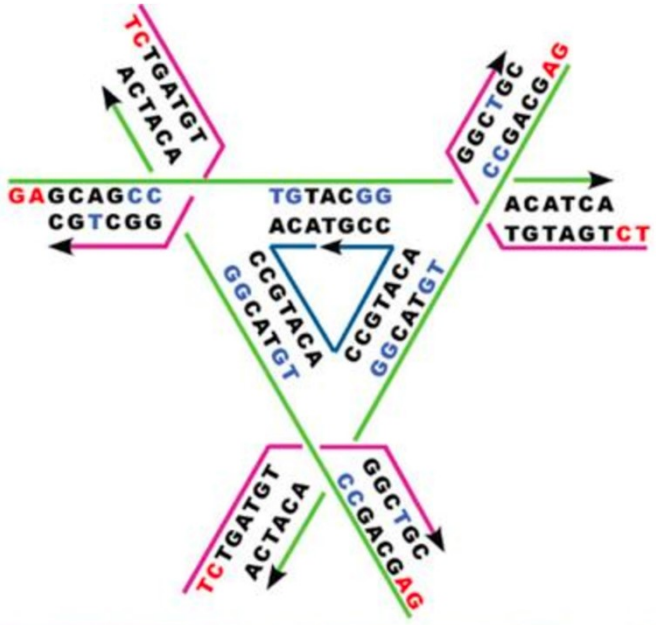
Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Supporting Information

Contents:

Figure S1: Secondary structure and sequence of Zheng et al. tile which assembles into Small-tile Crystals (SC)



Sequence of SC (5'→3'):
GAGCAGCCTGTACGGACATCA
TCTGATGTGGCTGC
ACACCGTACACCGTACACCGT

Figure S2: Secondary structure and sequence of our asymmetric, expanded tile which assembles into Expanded Crystals (EC)

Target Tile Assembly **NUPACK Hybridization Target**

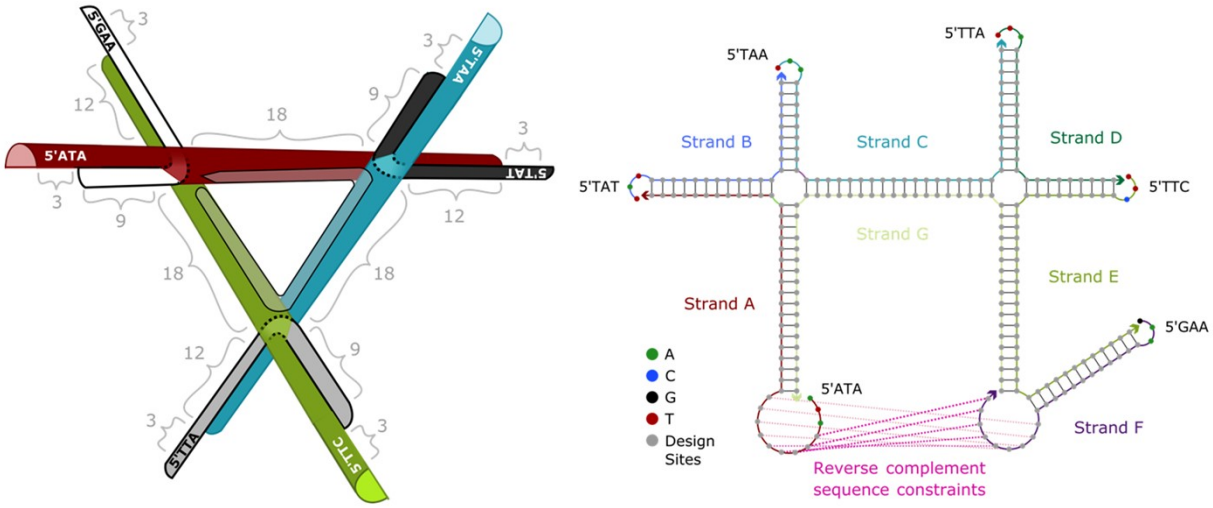


Figure S2. Target secondary structure for NUPACK design calculation of a seven-strand tile assembly intermediate. The overhang sequences (ATA, TAA, TTC) and their reverse complements were fixed to maximize tile crystallization fidelity.

Sequence of EC (5'→3'):
A: ATAATGGCCGGACGGTTCCGTGCATGTGGCCGATCAGAACCG
B: TATCGGTTCTGATCGCCTTGGTGC
C: TAAGCACCAAGGGCTACAATCCTCGCGTCGGCTCCACGAGGC
D: TTAGCCTCGTGGAGCGCTCTGTTG
E: TTCCAACAGAGCCCGACCTCAGGGTTCTGCGGTCAGACGAAC
F: GAAGTTCGTCTGACCTCCGGCCAT
G: GCAGAACCCTGAGGTCGGCGACGCGAGGATTGTAGCGCCACATGCACGGAACCG

Figure S3:

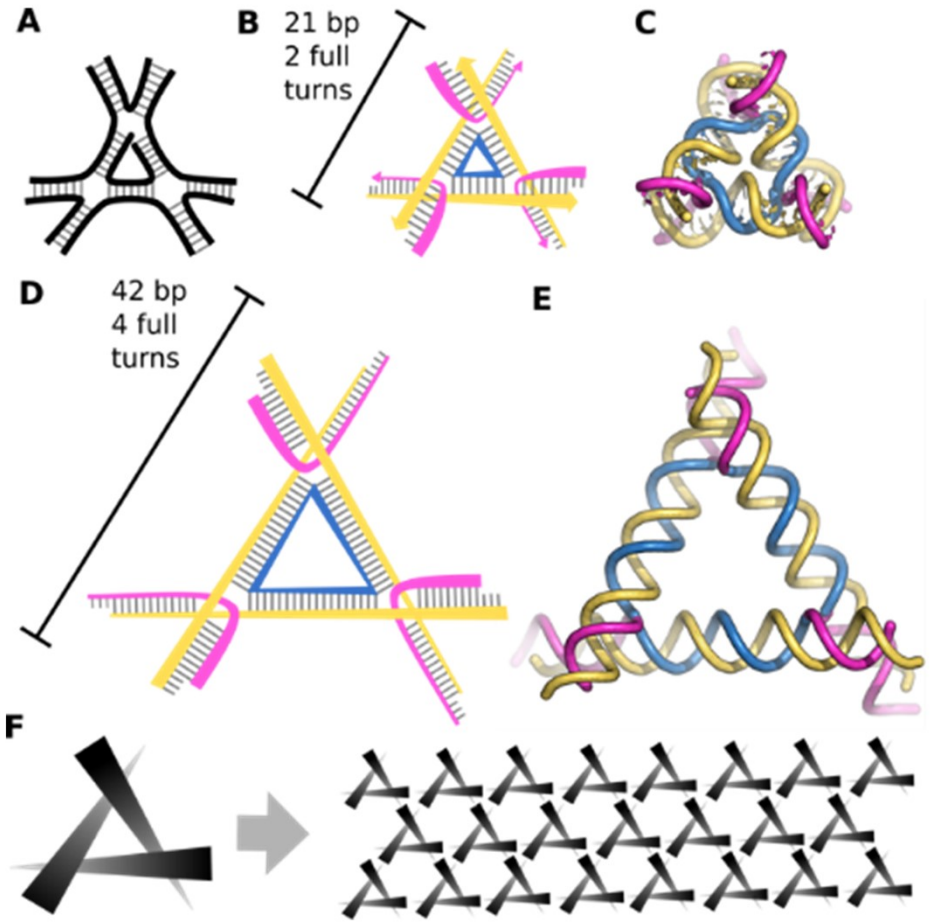


Figure S3. Original 3-fold symmetric tensegrity triangle tile (A) 2D cartoon, (B) 3D cartoon illustrating three distinct strand sequences (yellow, blue, pink), (C) the 3D crystal structure of the tile from PDB entry 3gbi. In comparison, (D) the new tile is predicted to have 4 turns of dsDNA per beam, (F) Sticky overhangs at the ends of the protruding arms encode asymmetric assembly in 3 dimensions.

Figure S4:

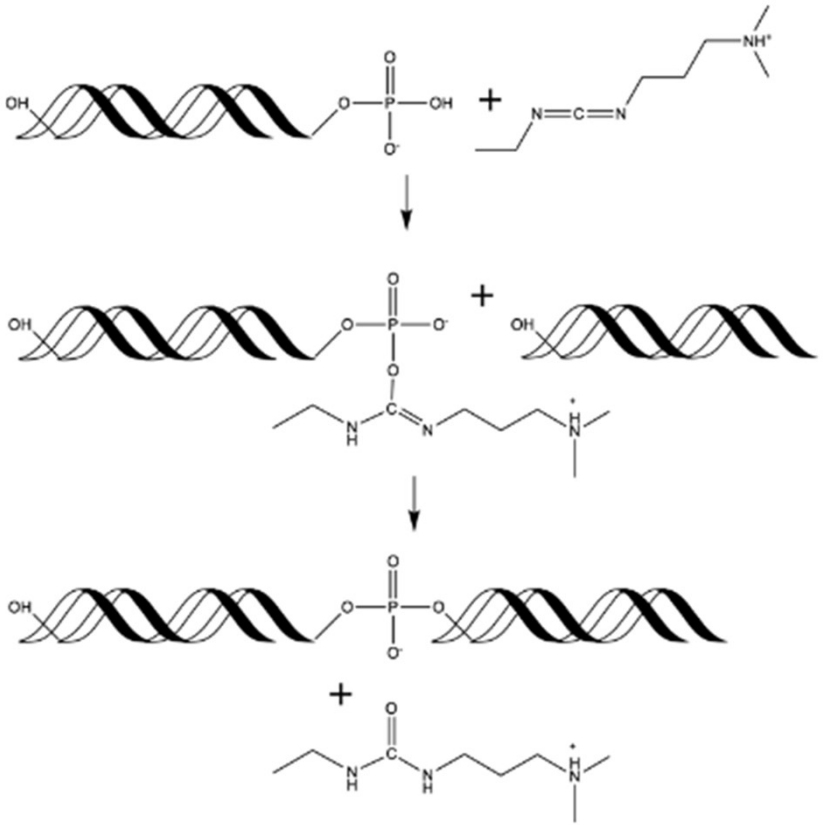


Figure S4. EDC chemical ligation mechanism

Figure S5:

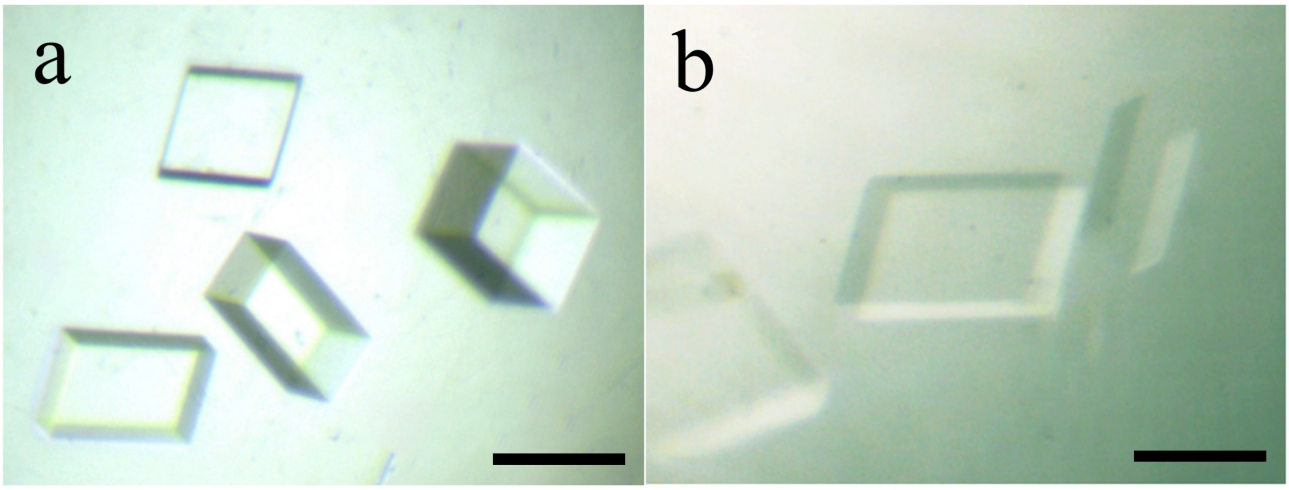


Figure S5. Light microscope images of **(a)** small-tile crystals (SC) of DNA strands without terminal phosphate groups. **(b)** Expanded-tile crystal (EC) of DNA strands without terminal phosphate groups. The scale is 100 μm.

Figure S6:

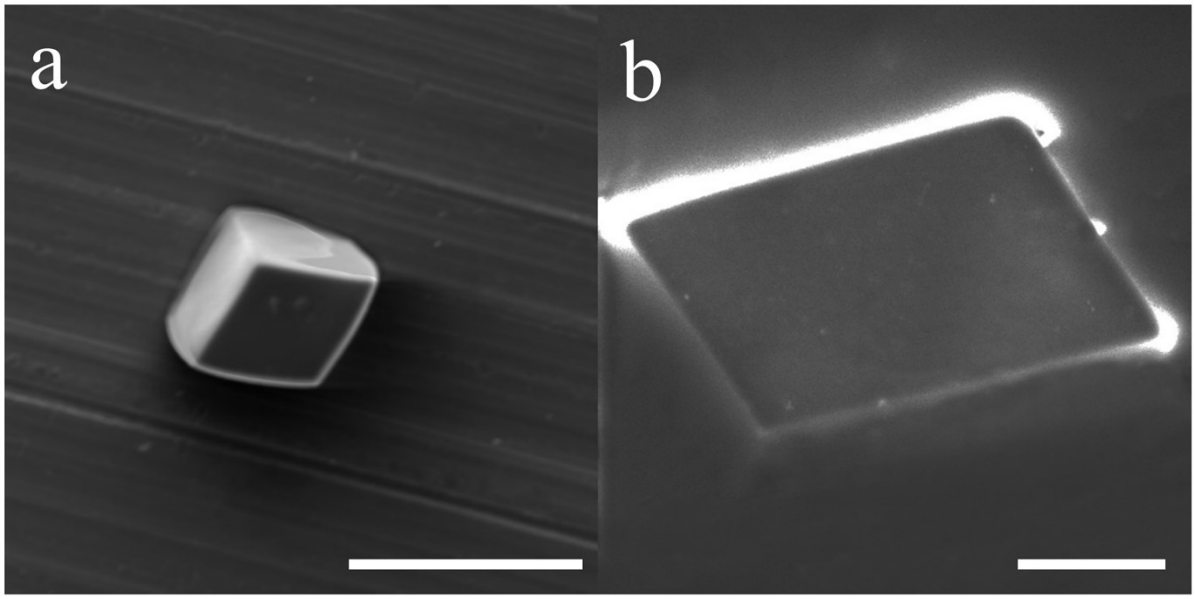
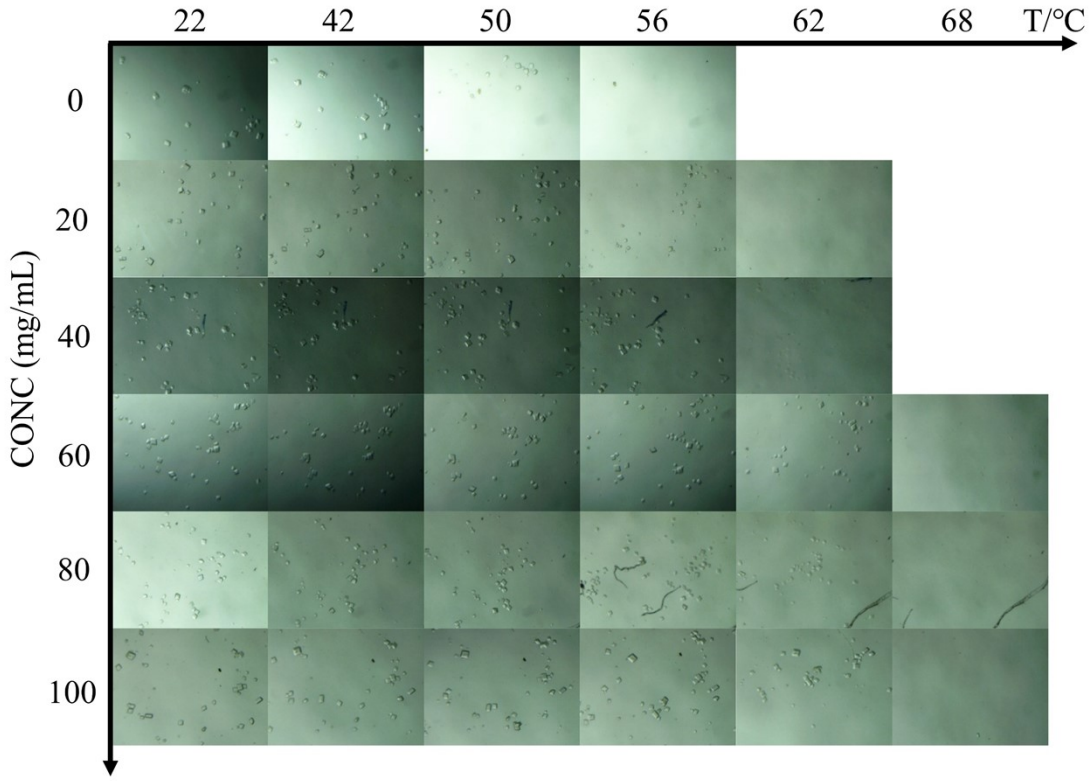
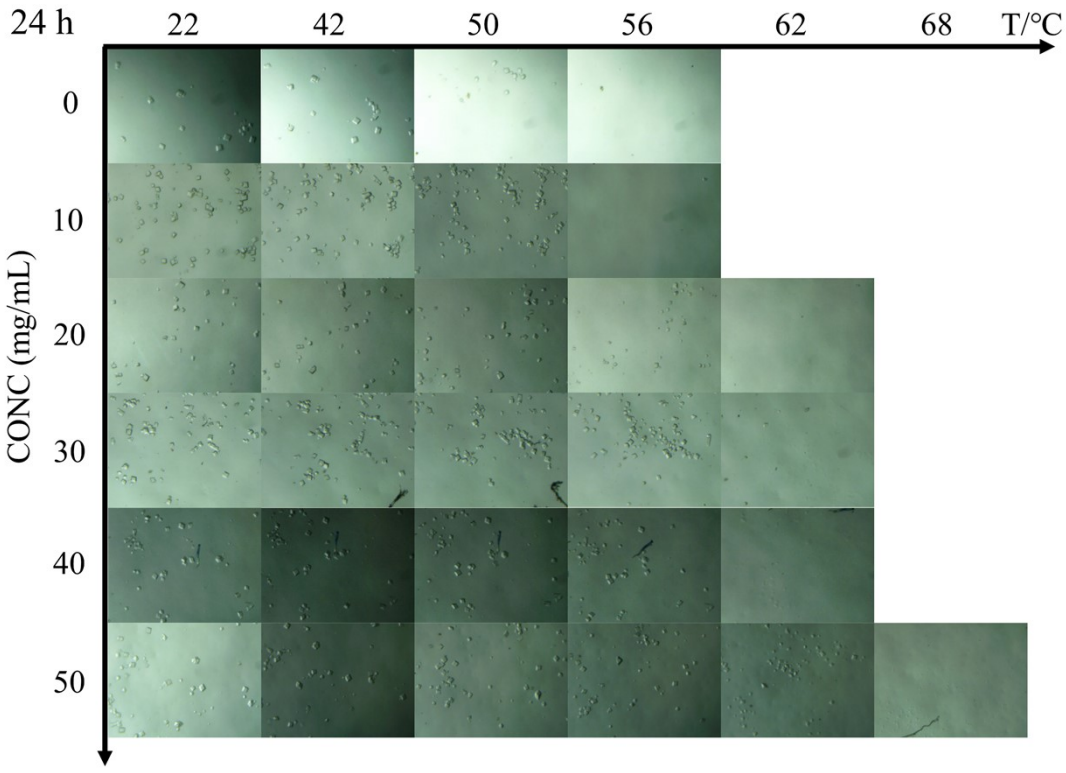


Figure S6. SEM images of (a) CLSC, (b) CLEC. The scale bar is 100 μm.

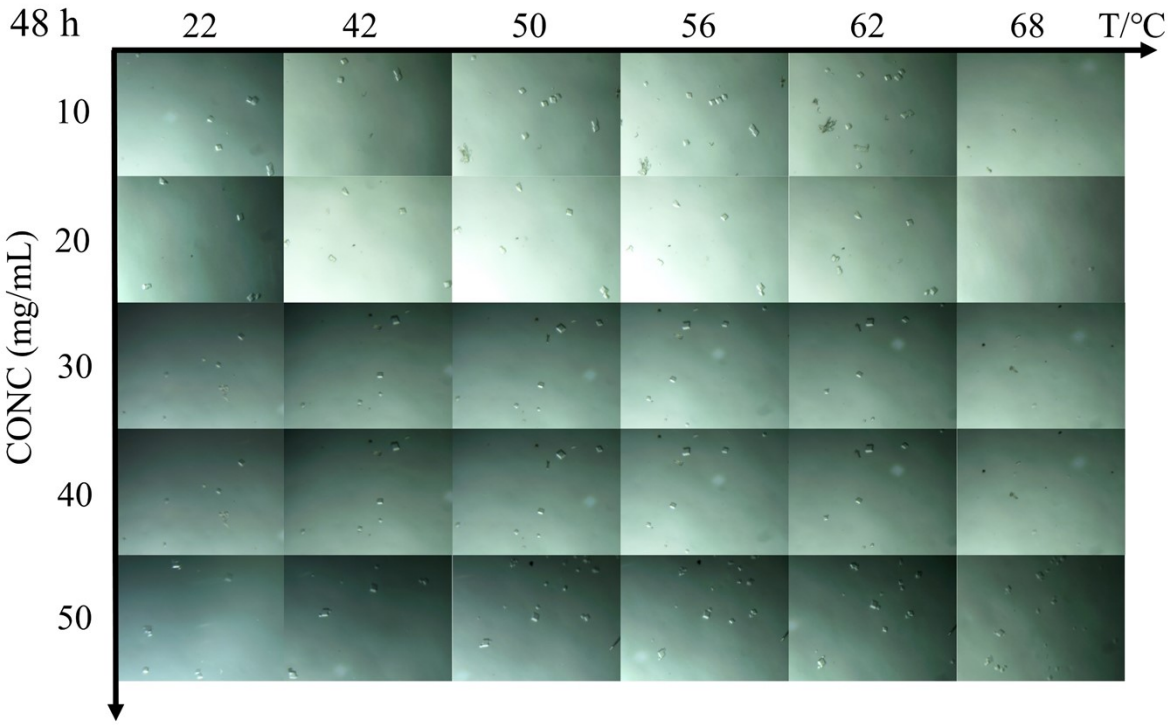
Figure S7:



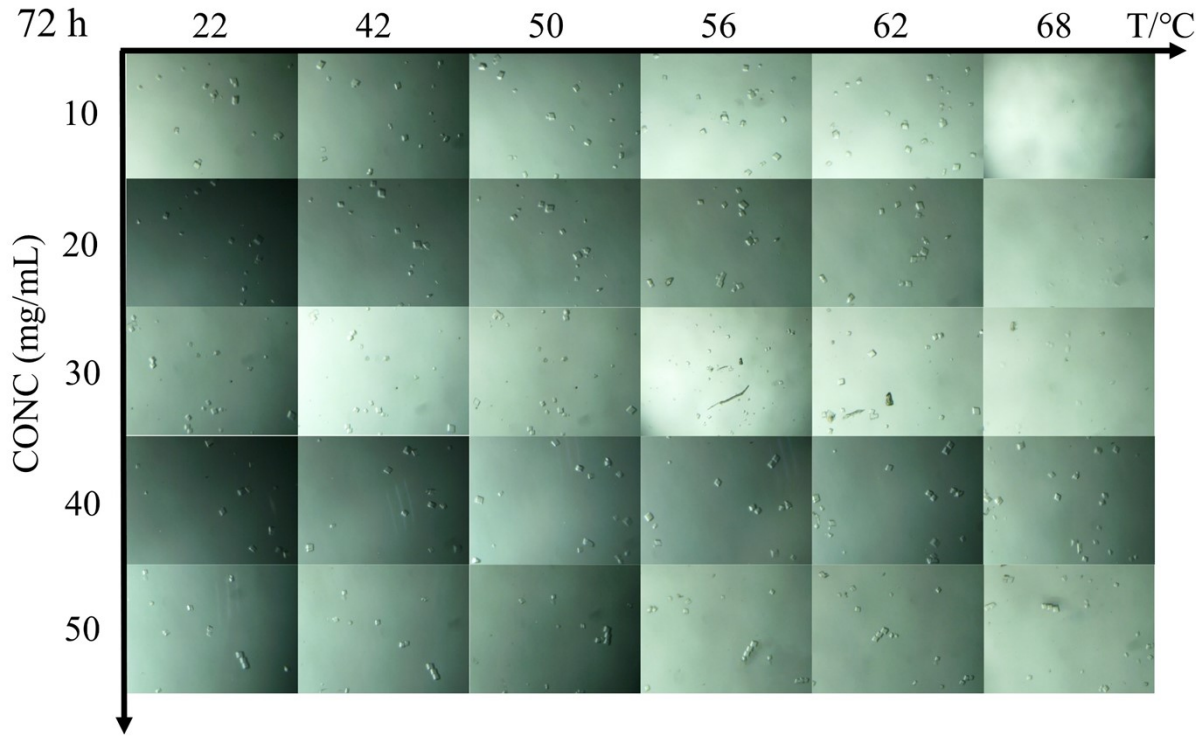
Effect of EDC concentration on the thermal stability of SC-5P.



After EDC chemical ligation for 24 hours, the effect of different EDC concentration on thermal stability of SC-5P.



After EDC chemical ligation for 48 hours, the effect of different EDC concentration on thermal stability stability of SC-5P.



After EDC chemical ligation for 72 hours, the effect of different EDC concentration on thermal stability of SC-5P.

Table S7

These Tables contains outcomes from a close visual inspection of the crystal microscope images shown aboveduring heating. Outcomes: **U**: The crystal was basically unchanged, **PD**: The crystal was Partly dissolved, **TD**: The crystal was Total dissolved.

Crystal dissolving observations as a function of EDC concentration (for fixed EDC incubation time of 24 hours)

CONC (mg/ml)	22 ℃	42 ℃	50 ℃	56 ℃	62 ℃	68 ℃
0	U	U	PD	TD		
20	U	U	U	PD	TD	
40	U	U	U	U	PD	TD
60	U	U	U	U	PD	PD
80	U	U	U	U	PD	TD
100	U	U	U	U	PD	TD
1000	TD					

Cross-linking for 24 hours, effect of crosslinking concentration on thermal stability.

Crystal dissolving observations as a function of EDC concentration and EDC incubation time

CONC (mg/ml)	24 h	48 h	72 h
0	56℃ TD	56℃ TD	56℃ TD
10	56℃ TD	68℃ TD	68℃ TD
20	62℃ TD	68℃ TD	68℃ PD
30	68℃ TD	68℃ PD	68℃ PD
40	68℃ TD	68℃ PD	68℃ U
50	68℃ PD	68℃ PD	68℃ U

Effect of crosslinking time on thermal stability of crystals with different concentrations of crosslinking agents. Data points that match the upper Table are underlined.

Figure S8:

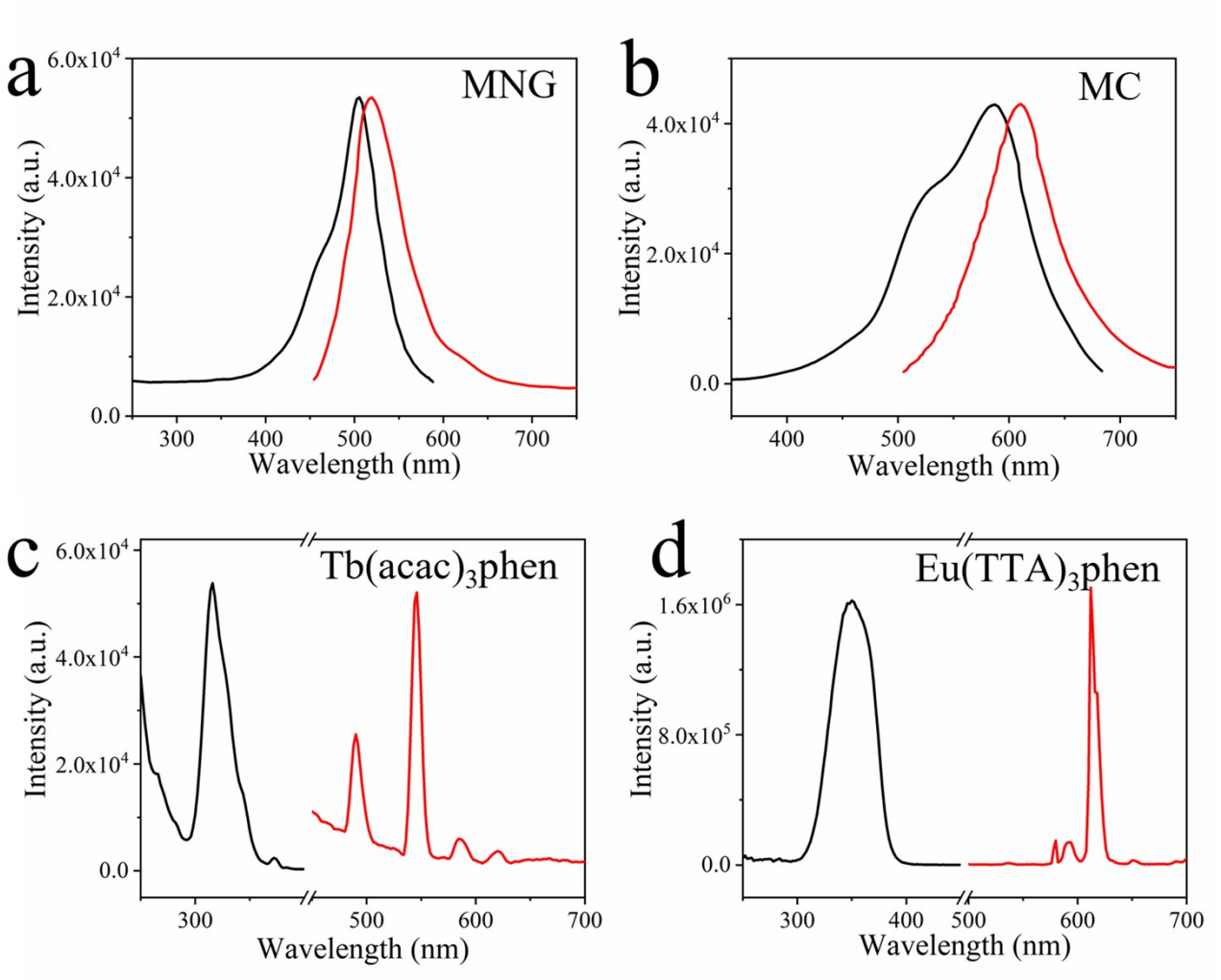


Figure S8. Excitation and emission spectra of fluorescent proteins and luminescent rare earth complexes.

Figure S9: Size Comparison Between SC Solvent Channels and Mng

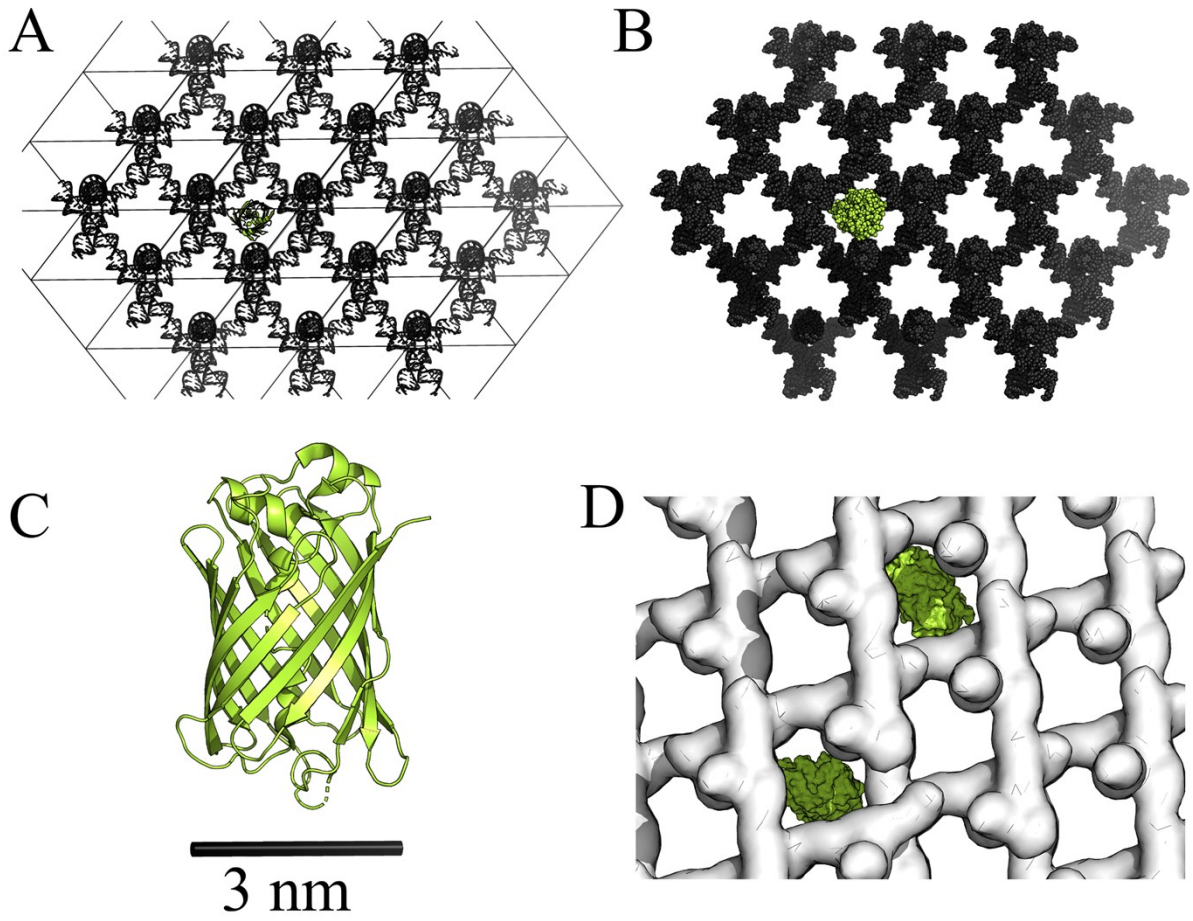


Figure S9 (A) The DNA crystal lattice for SC (PDB entry 3gbi) is shown in black), where the entire crystal has been rotated to showcase the largest solvent channels. For comparison, the backbone cartoon for mNG (PDB entry 5ltr) is shown, rotated to show the minimum cross-section radius. **(B)** The same view but using a space-filling representation shows steric clashes. **(C)** The shape of fluorescent proteins like mNG (and mC) is a barrel with the smaller dimension being about 3 nm. **(D)** Another representation showing a surface representation for mNG (green) and the DNA scaffold (white) suggests that mNG entrapment might be physically possible, but diffusion would be very challenging.

Figure S10:

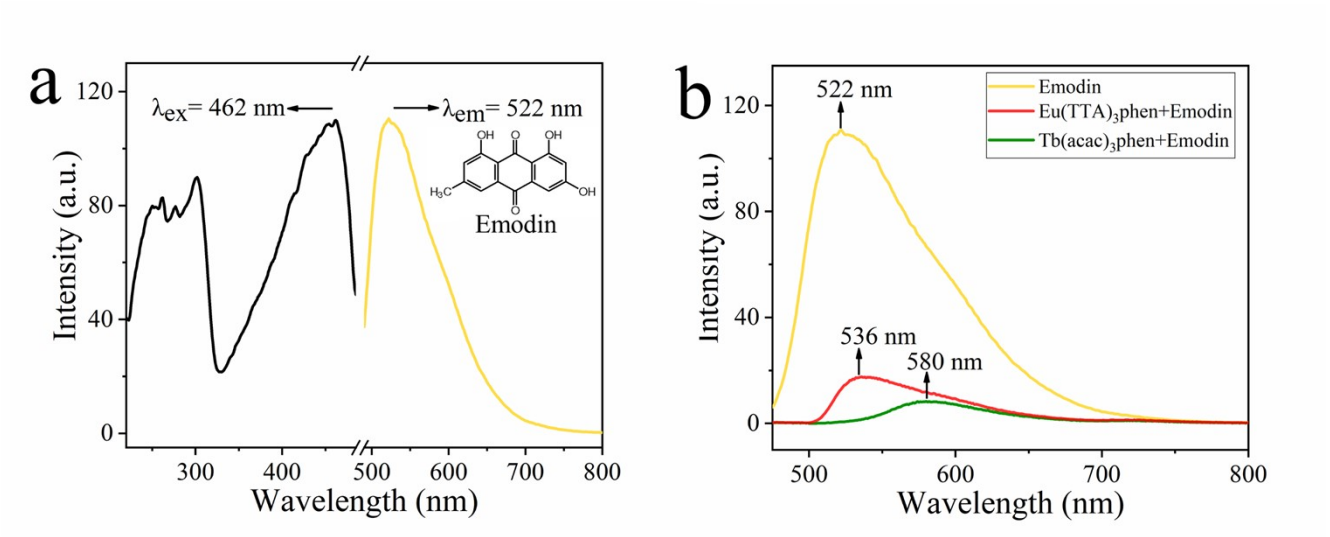


Figure S10. (a) Excitation and emission spectra of emodin (10 mM). **(b)** Emission spectra of emodin, europium complex (10 mM) with emodin, terbium complex (100 mM) with emodin at 462 nm excitation light.

Figure S11:

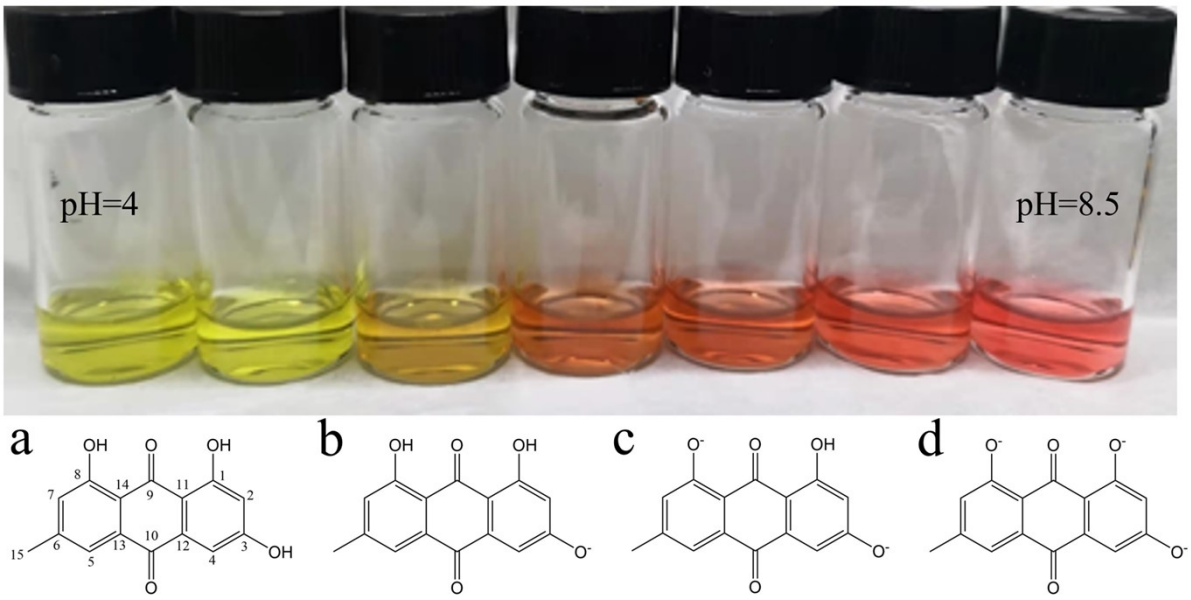


Figure S11. Emodin changes color under different pH due to deprotonation process, and the anionic/deprotonated form is red. **(a)** Molecular structure and atomic number of emodin in neutral form, and the stepwise dissociation of three protons: first in position 3 **(b)** 3-oxido-6-methyl-1,8-dihydroxy-9,10-anthraquinone, second in position 8 **(c)** 3,8-oxido-6-methyl-1-hydroxy-9,10-anthraquinone and third in position 1 **(d)** 1,3,8-oxido-6-methyl-9,10-anthraquinone.

Figure S12:

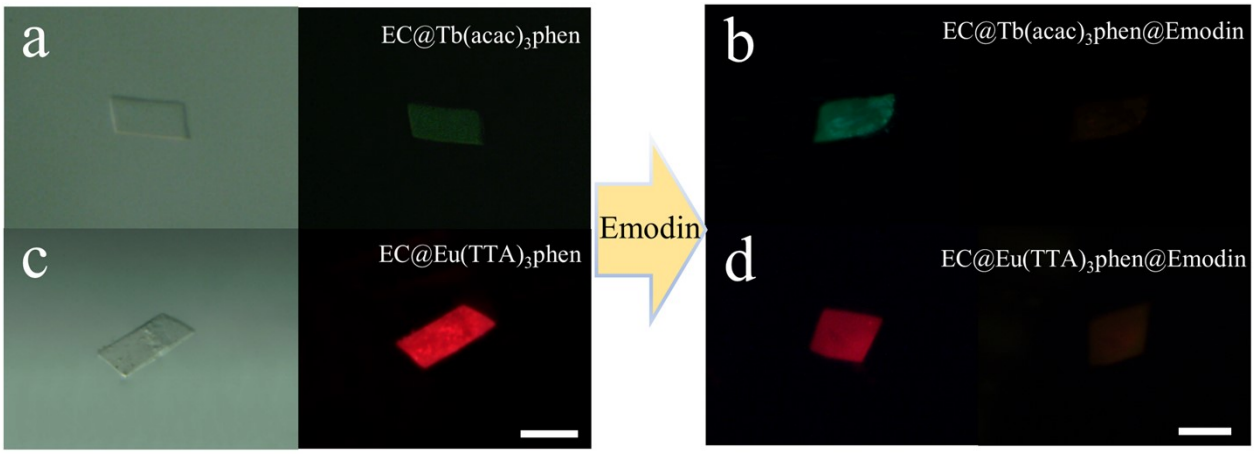


Figure S12. Light and fluorescence microscopy (365 nm excitation light) of rare earth loading of CLEC. **(a)** Incubating a CLEC in $Tb(acac)_3phen$ after 2 min. **(c)** Incubating a CLEC in $Eu(TTA)_3phen$ after 2 min. **(b, d)** the crystals after transfer into a 10 mM solution of emodin at 1 min, and 3 min. The scale bar is 100 μm.

Figure S13:

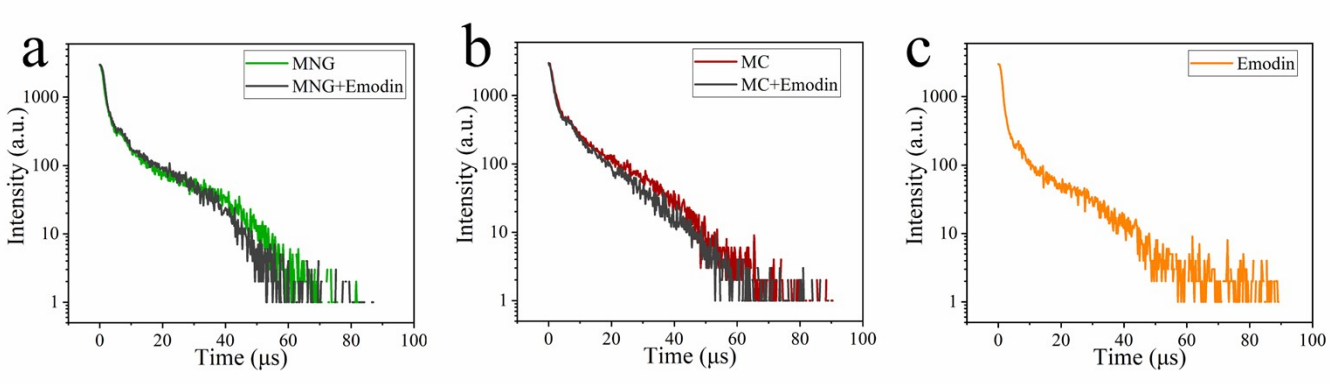


Figure S13. The fluorescence lifetime for **(a)** mNeonGreen in water, with and without 1 mM emodin. The excitation wavelength was 506 nm, and **(b)** mCherry in water, with and without 1 mM emodin. The excitation wavelength was 588 nm. **(c)** The fluorescence lifetime for emodin was also measured.

Figure S14:

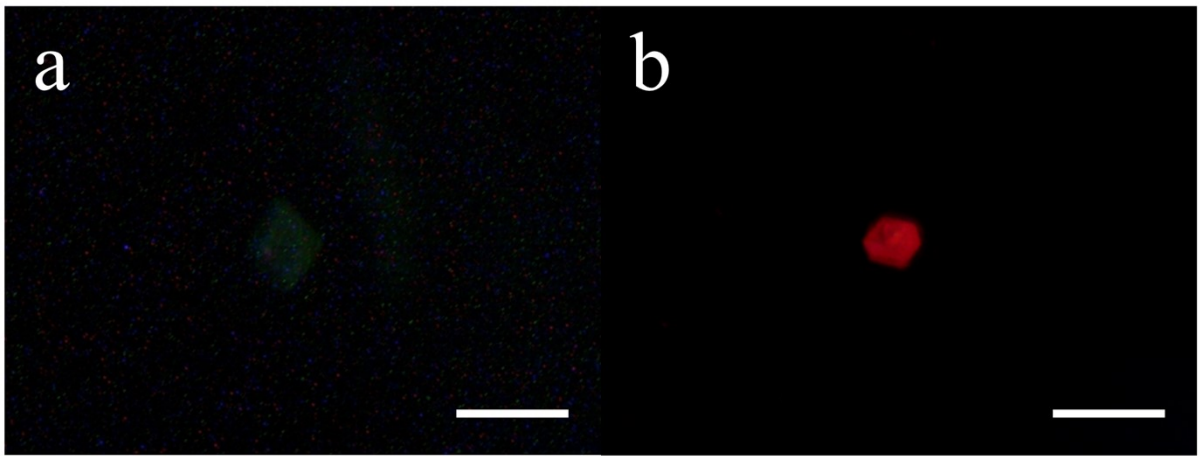


Figure S14. Fluorescence microscopy (365 nm excitation light) of rare earth loading of CLSC. **(a)** Incubating a CLSC in $Tb(acac)_3phen$ after 2 min. **(b)** Incubating a CLSC in $Eu(TTA)_3phen$ after 2 min. The scale bar is 100 μm.

Table 1

DNA Crystal Growth Protocols

Crystal type	Solution conditions	Temperature cooling
SC and SC-5P	Three kinds of DNA strands 0.06 M sodium dimethyl arsonate 0.11 M $MgCl_2$ 0.10 M NaCl 0.05 M HEPES (pH=6)	Cooling from 60℃ slowly to 22℃. Incubation at 22℃ for 24 hours until crystal growth is complete.
EC and EC-5P	Seven kinds of DNA strands 0.30 M sodium dimethyl arsonate 0.55 M $MgCl_2$ 0.50 M NaCl 0.25 M HEPES (pH=6)	Cooling from 90℃ slowly to 22℃. Incubation at 22℃ for 72 hours until crystal growth is complete.