Electronic Supplementary Information

Vibrational Characteristics of DNA Nanostructures Obtained Through a Mass-weighted Chemical Elastic Network Model

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The Electronic Supplementary Information includes experimental section, simulation section, and supplementary figures and tables (Fig. S1, Fig. S2, Fig. S3, Table S1, and Table S2).

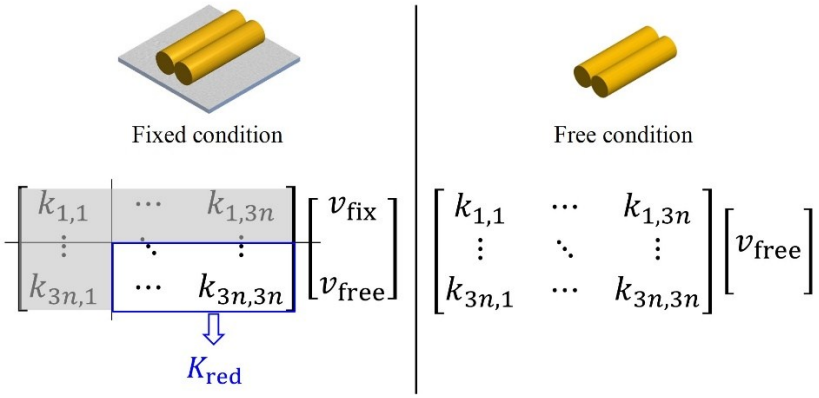
1. Experimental Section.

1. 1 *Fabrication of double-crossover (DX) DNA lattices in solution.* Synthetic oligonucleotides purified via high-performance liquid chromatography (HPLC) were purchased from BIONEER (Daejeon, Korea), and complexes containing an equimolar mixture (100 nM) of 8 different DX strands were formed by mixing with 1× TAE/Mg^{2+} buffer solution (40 mM Tris base, 20 mM Acetic acid, 1 mM EDTA (pH 8.0), and 12.5 mM magnesium acetate). For annealing, the DX DNA strands were inserted into a sample-tube with a total sample volume of 250 μL and were then placed in a Styrofoam box with 2L of boiled water to cool slowly from 95 °C to 25 °C over a period of at least 24 hours in order to facilitate hybridization.

1. 2. *AFM imaging*. For AFM imaging, 5 μL of the annealed DX DNA sample was deposited onto the cleaved mica substrate and incubated for a few minutes. Subsequently, 30 μL of 1× TAE/Mg^{2+} buffer solution was added onto the mica substrate, and another 20 μL of 1× TAE/Mg^{2+} buffer was dispensed on a silicon nitride AFM tip (Veeco Inc., USA). The AFM images were obtained by using a Multimode Nanoscope (Veeco Inc., USA) in the liquid tapping mode.

2. Simulation Section.

How to apply fixed boundary condition in normal mode analysis. In this paper, the fixed boundary condition was applied in order to precisely reflect the experimental setup such as DNA duplex fixed on a substrate. Also, we performed simulations at free boundary condition to measure the boundary effect on the simulation results. In the mathematical framework of normal mode analysis, the first six zero eigenvalues are excluded because they correspond to rigid body motions (i.e., three translational motions and three rotational motions) of the given system at free boundary condition. Unlikely, the fixed boundary condition can be assigned as follows: Suppose that we have a system composed of n atoms and then m surface atoms are fixed on a substrate. Generally, a $3n \times 3n$ global stiffness matrix K is constructed and a $3n \times 1$ eigenvector v is divided into two parts v_{free} and v_{fix}. For m fixed atoms, eigenvector components can be initially set to be zero such that $v_{fix} = 0$. Then, one can solve the typical eigenvalue problem having a $3(n\text{-}m) \times 3(n\text{-}m)$ reduced matrix, K_{red}, for v_{free} as shown in below.



3. Supplementary Figures and Tables.

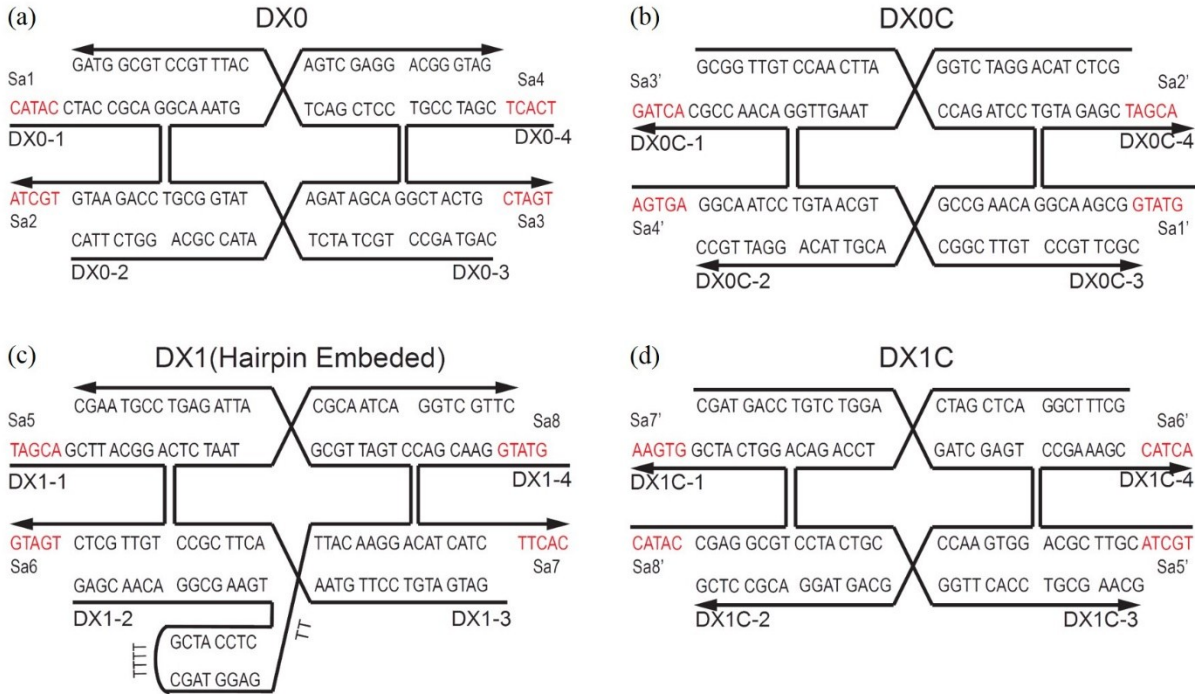


Fig. S1 A schematic sequence diagram of the double-crossover (DX) tiles. Each tile consists of four strands DX0-1, DX0-2, DX0-3, and DX0-4 for DX0 and DX1-1, DX1-2, DX1-3, and DX1-4 for DX1. The complementary sticky end pairs are shown as Sa and Sa' in the sequence drawings (red). DX0C (DX1C) is a connector between DX0 (DX1) tiles. Consequently, DX0 (DX1) lattices can be formed by combining DX0 and DX0C (DX1 and DX1C) tiles.

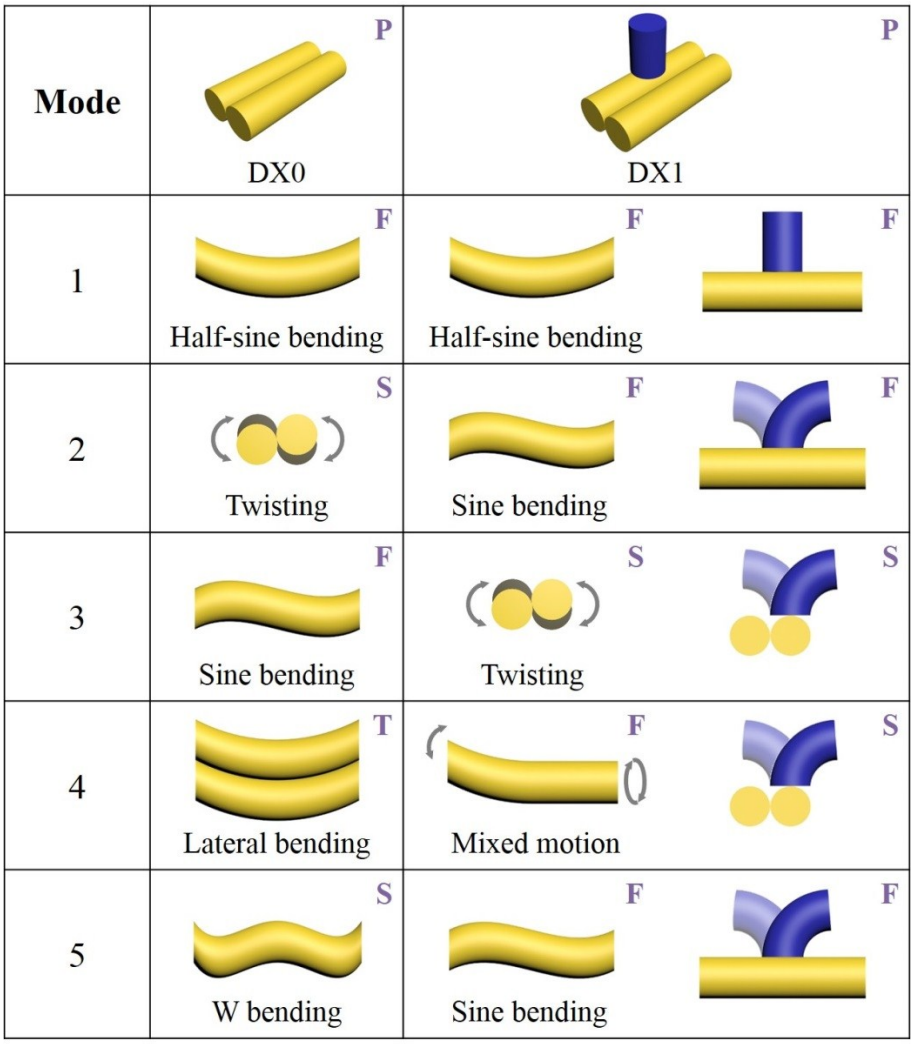


Fig. S2 Vibrational mode shapes of DX0 and DX1. A mass-weighted chemical based normal mode analysis has been performed to obtain both vibrational mode shapes and their frequencies. Major vibration modes of DX0 and DX1 are depicted in above. DX tile and hairpin are colored by gold and blue, respectively. The viewpoints of DX0 and DX1 are described as F (front view), T (Top view), S (Side view), and P (perspective view). From the first lowest mode to the fifth lowest mode, DX0 and DX1 bodies show bending and twisting motions as like vibration motion of general DNA rod motion. However, because of hairpin, DX1 body uniquely shows a mixed motion of bending and twisting at the forth lowest mode.

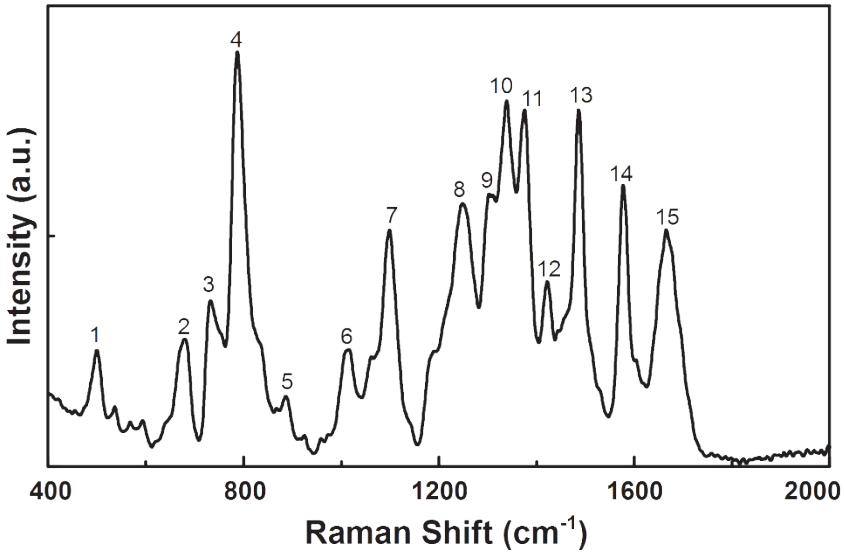
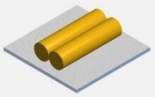
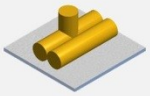
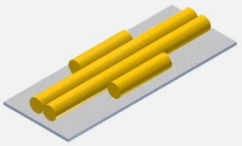


Fig. S3 Raman spectrum of DNA molecules obtained from pristine DNA obtained from salmon. The 15 significant Raman peaks, positioned at 497, 678, 732, 786, 890, 1012, 1095, 1248, 1306, 1336, 1375, 1420, 1486, 1576, and 1666 cm^{-1}, represent the characteristic Raman bands for DNA molecules.

Table S1 Raman band assignments for the DNA molecules shown in Fig. S3. The significant contributions of DNA nucleotides are divided into three regions: 400 – 750 cm^{-1} for nucleobases, 750 – 1200 cm^{-1} for sugar phosphate backbone groups, and 1200 – 2000 cm^{-1} for nucleobases (A. Kulkarni, B. Kim, S. R. Dugasani, P. Joshirao, J. A. Kim, C. Vyas, V. Manchanda, T. Kim, and S. H. Park, *Sci. Rep.* **3**, 2062 (2013); B. Gnapareddy, S. R. Dugasani, T. Ha, B. Paulson, T. Hwang, T. Kim, J. H. Kim, K. Oh, and S. H. Park, *Sci. Rep.* **5**, 12722 (2015)).

No.	Raman Shift (cm^{-1})	DNA Vibrational modes
1	497	Phosphoionic scissor
2	678	Ring breathing vibrations of G and T
3	732	Ring breathing vibrations of A
4	786	Vibrations of C, T, and symmetric stretching of PO_2^-
5	890	Deoxyribose ring vibrations
6	1012	C−O stretching vibrations of deoxyribose
7	1095	Phosphodiester stretching vibrations
8	1248	Vibrations of C and A
9	1306	Ring vibrations of A and C
10	1336	Ring modes of G and A
11	1375	Ring modes of T and A
12	1420	Deoxyribose sugar moieties
13	1486	N7 vibrations of G and ring modes of A
14	1576	In-plane ring vibrations of A and G
15	1666	C=O stretching vibration modes of T and C

Table S2 Vibrational characteristics of 5 different cases using two types of DX tiles (DX0 and DX1) and two boundary conditions (free and fixed). In this paper, we provided 5 different simulation results (i.e., DX0-fixed, DX0-free, DX1-fixed, DX1-free, and DX0 lattice-fixed) in order to investigate morphological variation sensitivity and boundary condition effect. For all cases, vibrational characteristics present from collective motion to local molecular vibrations as frequency increases, and we were able to classify the set of frequencies into 4 different ranges such as collective part, phosphate backbone part, base part, and specific region part as shown in Table S2.

Case / Frequency range [cm^{-1}]	DX0		DX1		DX0 lattice
	Fixed	Free	Fixed	Free	Fixed
					
Collective motion	9.51 ~ 21.61	0.99 ~ 17.16	5.78 ~ 20.22	1.04 ~ 17.22	17.31 ~ 41.30
Phosphate backbone	22.08 ~ 150.90	17.41 ~ 136.78	20.25 ~ 146.73	17.50 ~ 142.20	41.60 ~ 171.73
Base	150.97 ~ 265.01	136.92 ~ 276.65	146.81 ~ 264.56	142.40 ~ 259.56	171.78 ~ 287.49
Specific region	265.18 ~ 1166.90	276.90 ~ 1167.26	264.62 ~ 1176.85	259.80 ~ 1176.85	287.60 ~ 2954.08