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Capture of cationic ligands bound diffusely to base pairs during the DNA refolding

Shu-ichi Nakano, Toshimasa Kirihata, and Naoki Sugimoto

Frontier Institute for Biomolecular Engineering Research (FIBER), and Department of Chemistry, Faculty of Science and Engineering, Konan University, 8-9-1 Okamoto, Higashinada-ku, Kobe 658-8501, Japan.

Supporting Information

Table S1. The values of the binding cooperativity parameter *n* for the cationic ligand binding to the DNAs[a]

Ligand[b]	**d14cg**	**d16cg**	**d18cg**	**d20cg**	**d22cg**	**d24cg**
Na^+ (+1)	1.6 ±0.1	1.3 ±0.1	1.3 ±0.1	nd	nd	nd
NH_3^+ (+1)	1.5 ±0.1	1.3 ±0.08	1.2 ±0.1	nd	nd	nd
Lys (+1)	1.5 ±0.1	1.4 ±0.1	1.4 ±0.2	nd	nd	nd
Mg^{2+} (+2)	1.0 ±0.1	0.92 ±0.07	0.94 ±0.05	0.84 ±0.09	0.70 ±0.05	0.55 ±0.03
Putrescine (+2)	1.0 ±0.1	0.94 ±0.13	0.70 ±0.07	0.73 ±0.08	0.80 ±0.06	0.62 ±0.06
Lys_2 (+2)	1.1 ±0.1	0.89 ±0.07	0.83 ±0.06	0.73 ±0.08	0.67 ±0.07	0.54 ±0.06
$Co(NH_6)^{3+}$ (+3)	0.97 ±0.05	0.81 ±0.04	0.89 ±0.07	0.75 ±0.07	0.78 ±0.02	0.78 ±0.02
Spermidine (+3)	1.0 ±0.1	1.0 ±0.7	0.87 ±0.07	0.82 ±0.07	0.75 ±0.09	0.79 ±0.05
Lys_3 (+3)	0.94 ±0.1	0.86 ±0.10	0.93 ±0.11	0.82 ±0.06	0.79 ±0.06	0.65 ±0.05
Spermine (+4)	nd	nd	0.95 ±0.05	0.95 ±0.07	0.87 ±0.04	0.77 ±0.08
Lys_4 (+4)	nd	nd	0.97 ±0.05	0.89 ±0.14	0.89 ±0.11	0.85 ±0.05

[a] nd indicates that the parameter could not be determined due to a too high or low affinity in order to obtain a reliable value. [b] The value in parentheses indicates the net charge of the ligand.

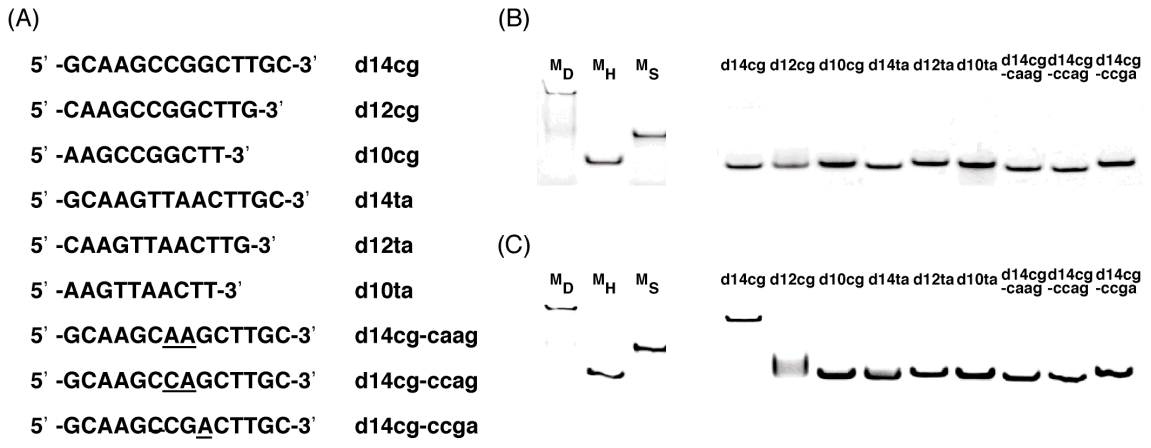

Fig. S1. (A) Oligonucleotide sequences and their abbreviations. All nucleotides were fluorescently labeled with 6-FAM at the 5'-terminal. The underlining indicates the mispaired nucleotides when forming the bimolecular duplex. (B and C) The PAGE images of the DNA oligonucleotides prepared in 10 mM NaCl (B) or 1 M NaCl (C). The marker lanes of M_D, M_H, and M_S indicate the control 14-mer DNA sequences forming a bimolecular duplex (5'-GACTGAGGACCTAC-3'/5'-GTAGGTCCTCAGTC-3'), forming a stable tetraloop hairpin (5'-CGGAGCTTGCTCCG-3'), and being in the unfolded state (5'-GACTGAGGACCTAC-3'), respectively.

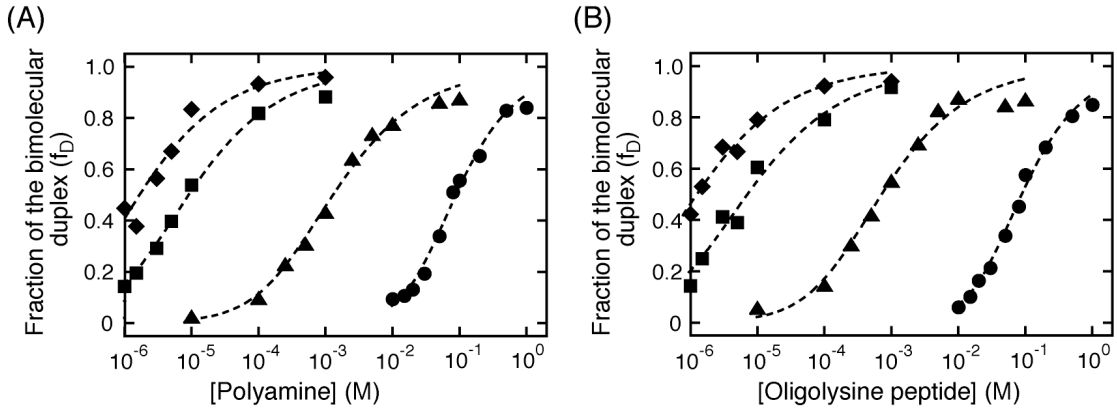

Fig. S2. Dependence of the fraction of the bimolecular duplex (f_D) of **d14cg** on the concentrations of (A) NH_4Cl (circles), putrescine (triangles), spermidine (squares), and spermine (diamonds), or (B) Lys (circles), Lys_2 (triangles), Lys_3 (squares), and Lys_4 (diamonds).

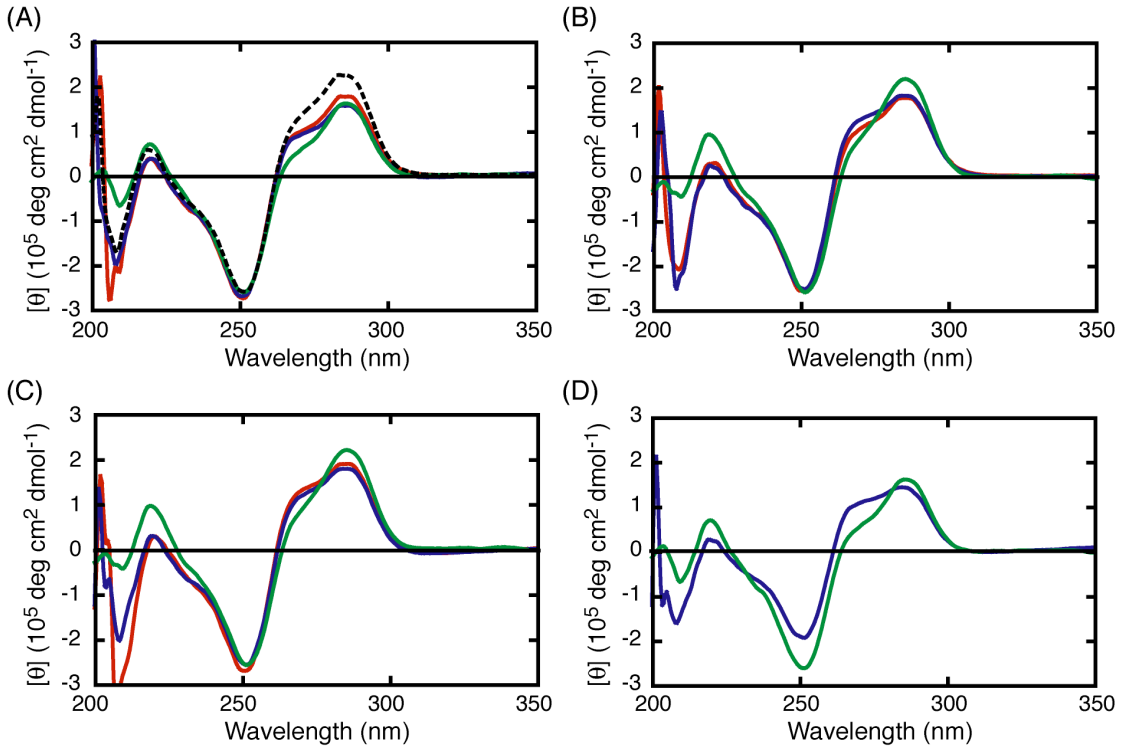

Fig. S3. CD spectra of 50 μM **d14cg** at 37 ˚C forming the bimolecular duplex in the buffer containing (A) monovalent (1 M), (B) divalent (100 mM), (C) trivalent (1 mM), and (D) tetravalent (1 mM) cationic ligands of the series of metal ions (red), polyamines (blue), and oligolysines (green). The melting temperature (T_m) of 50 μM **d14cg** under each condition was 73.0 ˚C for Na^+, 71.1 ˚C for NH_4^+, 66.1 ˚C for Lys, 75.0 ˚C for Mg^{2+}, 60.1 ˚C for putrescine, 61.3 ˚C for Lys_2, 70.0 ˚C for $Co[NH_6]^{3+}$, 71.2 ˚C for spermidine, 65.2 ˚C for Lys_3, 70.1 ˚C for spermine, and 71.2 ˚C for Lys_4. The spectra of the hairpin structure obtained in 10 mM NaCl are also indicated by the dotted line in panel A and its T_m was 68.2 ˚C.

(A)

5' -CGCAAGCCGGCTTGCG-3'	d16cg
5' -ACGCAAGCCGGCTTGCGT-3'	d18cg
5' -AACGCAAGCCGGCTTGCGTT-3'	d20cg
5' -CAACGCAAGCCGGCTTGCGTTG-3'	d22cg
5' -GCAACGCAAGCCGGCTTGCGTTGC-3'	d24cg
5' -CGCAAGTTAACTTGCG-3'	d16ta
5' -ACGCAAGTTAACTTGCGT-3'	d18ta
5' -AACGCAAGTTAACTTGCGTT-3'	d20ta
5' -CAACGCAAGTTAACTTGCGTTG-3'	d22ta
5' -GCAACGCAAGTTAACTTGCGTTGC-3'	d24ta

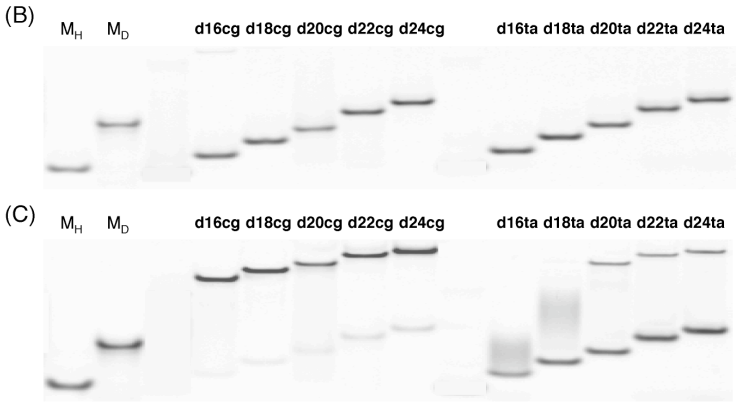

Fig. S4. (A) Oligonucleotide sequences fluorescently labeled with 6-FAM at the 5'-terminal and their abbreviations. (B and C) The PAGE images of the DNA oligonucleotides prepared at 10 mM NaCl (B) or 1 mM spermine (C). The marker nucleotides were identical to those used in Fig. S1.