Figure S1. $^1$H NMR spectrum of D$_2^{2+}$ recorded in DMSO at 400 MHz
Figure S2. $^1$H NMR spectrum of D3$^{2+}$ recorded in DMSO at 400 MHz
Figure S3. Distribution diagram of the Cu(II) complexes formed by D3$^{2+}$ in water. [D3$^{2+}$] = [Cu(II)] = $1\times10^{-3}$.

Figure S4. UV-Vis spectra for the HD2$^{3+}$ titration by copper(II). $C_{D2} = 1\times10^{-5}$ M, $I = 0.10$ M, pH = 7.0, T = 25$^\circ$C, $C_{Cu} = 0$ M (a), $1.1\times10^{-4}$ M (b).
**Figure S5.** UV-vis absorption spectra of D3$^{2+}$ (a) and D2$^{2+}$ (b) recorded in water at different pH values and 25°C.
Figure S6. UV-Vis spectrum of D₃²⁺ in ethanol (A). Fluorescence emission spectra of D₃²⁺ in ethanol, water and ethanol/water mixtures (B). Percentages (v:v) are referred to water in ethanol. [D₃²⁺] = 1×10⁻⁵M, T = 25°C.
Figure S7. Analysis of fluorescence titration data for the DNA/CuD2\(^{4+}\) system to equation (6). 
\[I = 0.10 \text{ M, pH} = 7.0, T = 25^\circ\text{C}.\]
Figure S8. Spectrofluorometric titration of the DNA/HD$^{3+}$ system (A), relevant binding isotherm at $\lambda_{em} = 600$nm (B) and analysis of the fluorescence titration data to equation (5) (C). $C_D = 8.8 \times 10^{-6}$ M, $C_P$ from 0 (a) to $6.5 \times 10^{-5}$ M (b), $\lambda_{ex} = 450$nm, I = 0.10 M, pH = 7.0, T = 25°C.
Figure S9. Spectrofluorometric titration of the DNA/CuD3$^{4+}$ system (A), relevant binding isotherm at $\lambda_{\text{em}} = 600\text{nm}$ (B) and analysis of the fluorescence titration data to equation (5) (C). $C_D = 8.8 \times 10^{-6}$ M, $C_P$ from 0 (a) to $4.6 \times 10^{-5}$ M (b), $\lambda_{\text{ex}} = 450\text{nm}$, $I = 0.10$ M, pH = 7.0, T = 25°C.
**Figure S10.** Binding isotherms from spectrophotometric titrations of the DNA/HD2$^{3+}$ (A) and DNA/HD3$^{3+}$ (B) systems under low added salt conditions; $C_D = 1.1 \times 10^{-5}$ M, $I = 0.003$ M, $pH = 7.0$, $\lambda = 360$ nm, $T = 25^\circ$C. Circled points in (A) are related to precipitation phenomena.
Figure S11. Spectrophotometric titrations of the DNA/H$_2$D$^{1+}$ system; I = 0.10 M, pH = 7.0, T = 25°C. (A) Visible range: $C_D = 1.2 \times 10^{-5}$ M, $C_P$ from 0 (a) to $1.0 \times 10^{-4}$ M (b). (B) UV range: $C_D = 5.0 \times 10^{-6}$ M, $C_P$ from 0 M (a) to $7.4 \times 10^{-5}$ M (b), differential titration (DNA added in both sample and reference cells). (C) Binding isotherm at 288nm from titration (B); the inset is an enlargement of the first part of the plot.
Figure S12. Fluorescence spectra for the DNA/H$_2$D$^{4+}$ system recorded during titration (a) and relevant binding isotherm at 607 nm (b). C$_D$ = 1.2×10$^{-5}$ M, I = 0.10 M, pH = 7.0, T = 25°C, $\lambda_{ex}$ = 450 nm, C$_P$ = 0 M (a), 2.1×10$^{-4}$ M (b).

Figure S13. Spectrofluorometric titration of the DNA/CuD$^{4+}$ system; I = 0.10 M, pH = 7.0, $\lambda_{ex}$ = 450 nm, T = 25°C. (A) Collected spectra C$_D$ = 1.3×10$^{-5}$ M, C$_P$ from 0 (a) to 1.4×10$^{-4}$ M (b). (B) Binding isotherm at $\lambda_{em}$ = 607 nm.
**Figure S14.** Electrophoresis experiments on the DNA/HD2$^{3+}$, DNA/CuD2$^{4+}$, DNA/HD3$^{2+}$ and DNA/CuD3$^{4+}$ systems, alone or in the presence of H$_2$O$_2$ (1.8×10$^{-3}$M). $C_{DNA} = 2.5$×10$^{-4}$M, Tris-acetate-EDTA buffer (pH = 7.4), 1% agarose gel with 1×10$^{-6}$M Ethidium staining, 65V, 50mA.

**Figure S15.** Stopped-flow curves for the DNA/HD2$^{3+}$ system (A) and for the DNA/HD3$^{2+}$ system (B) at I= 0.10 M, pH = 7.0, $\lambda$ = 360nm, T = 25°C; the line is least-square bi-exponential data fitting. (A) $C_D = 9.4\times10^{-6}$ M, $C_P = 9.5\times10^{-5}$ M; (B) $C_D = 1.0\times10^{-5}$ M, $C_P = 2.0\times10^{-4}$ M.
**Figure S16.** Calculated conformation for the ATATATATAT/Δ-HD$_3^{3+}$ adduct.

**Figure S17.** Calculated conformation for the ATCGCGCGAT/Δ-HD$_3^{3+}$ adduct.
**Figure S18.** Calculated conformation for the CGATCGATCG/Δ-HD$^{3+}$ adduct.

**Figure S19.** Calculated conformation for the CGCGATATCG/Λ-HD$^{3+}$ adduct.
**Figure S20.** Calculated conformation for the GCGCGCGCGC/Δ-HD$_3^{3+}$ adduct.

**Figure S21.** Calculated conformation for the ATATATATAT/Δ-HD$_2^{3+}$ adduct.
Figure S22. Calculated conformation for the ATATATATAT/Δ-H₂D²⁺ adduct.

Figure S23. Calculated conformation for the ATCGCGCGAT/Λ-H₂D²⁺ adduct.
Figure S24. Calculated conformation for the CGATCGATCG/Λ-H$_2$D$_2$$^+$ adduct.

Figure S25. Calculated conformation for the CGATCGATCG/Λ-HD$_2$$^+$ adduct.
Figure S26. Calculated conformation for the CGCGATATCG/Δ-H2D2⁴⁺ adduct.

Figure S27. Calculated conformation for the GCGCGCGCGC/Λ-H2D2⁴⁺ adduct.