Probing Ligand Binding to Duplex DNA using $KMnO_4$ Reactions and Electrospray Ionization Tandem Mass spectrometry

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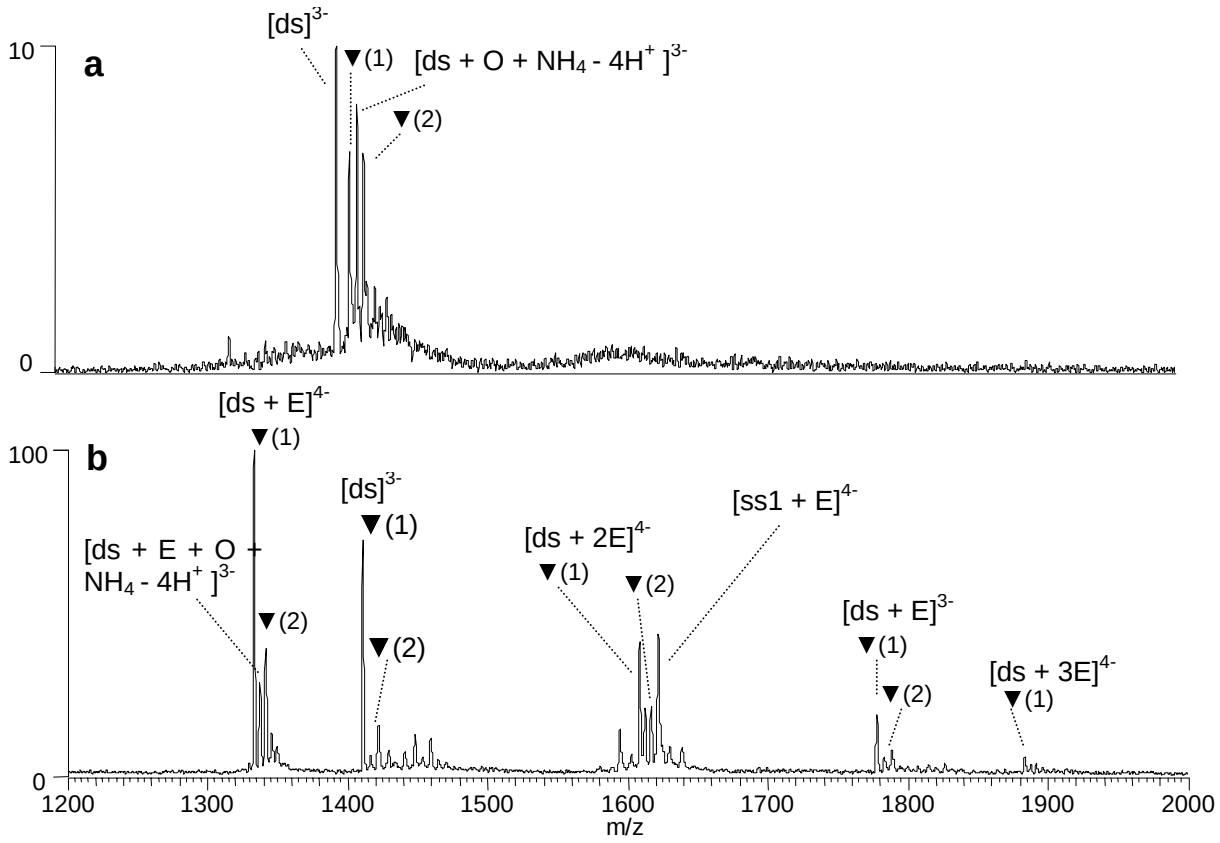

Figure S-1. ESI-mass spectra showing solutions containing the duplex d(GCAGTGA/TCACTGC) (a) after 20 min, reaction with $KMnO_4$, and (b) with echinomycin (E), after 20 min. reaction with $KMnO_4$. Ions containing oxidized thymines are labeled with ▼, with the number in parenthesis indicating the number of oxidation adducts.

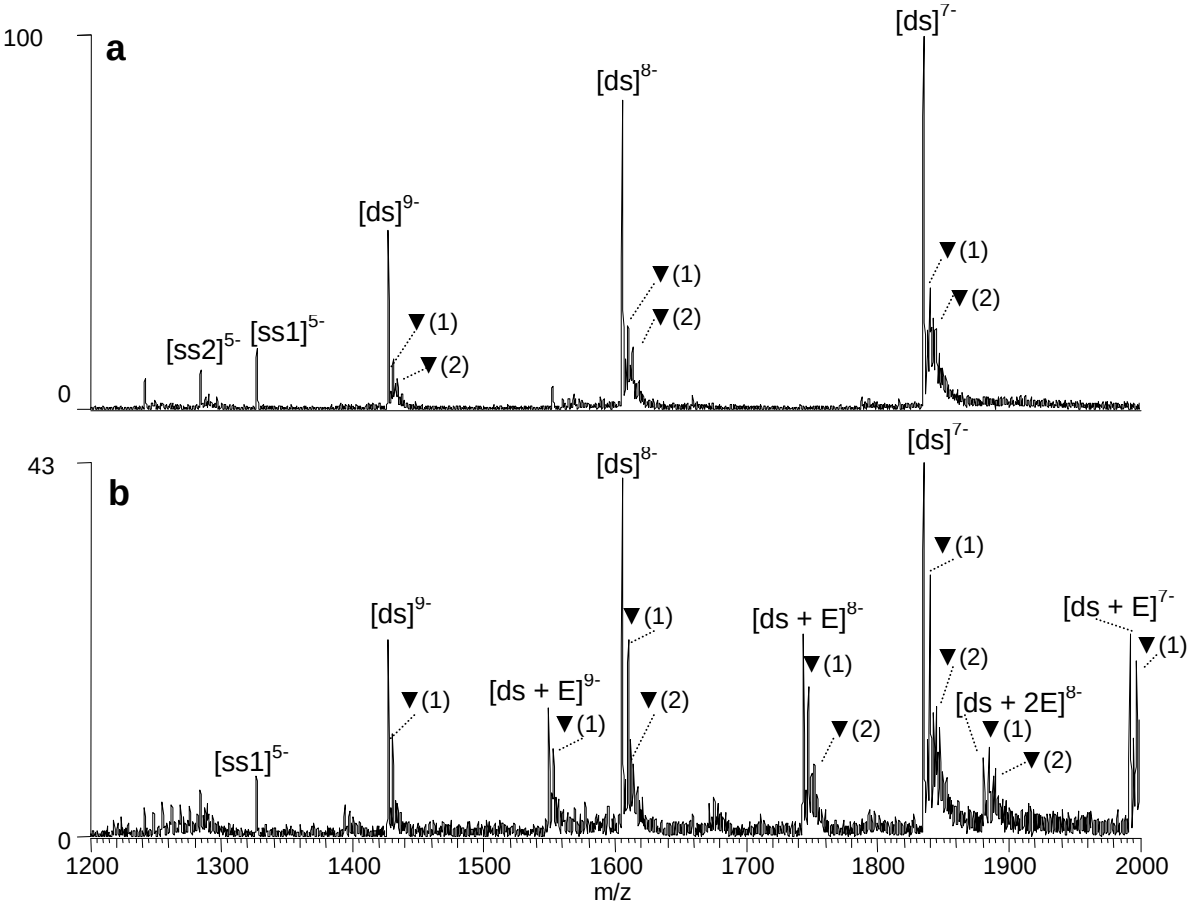

Figure S-2. ESI-mass spectra showing solutions containing the duplex d(GGACAGTGAGGGCAGTGAGGG/CCTGTCACTCCCGTCACTCCC) (a) after 20 min, reaction with $KMnO_4$, and (b) with echinomycin (E), after 20 min. reaction with $KMnO_4$. Ions containing oxidized thymines are labeled with ▼, with the number in parenthesis indicating the number of oxidation adducts.

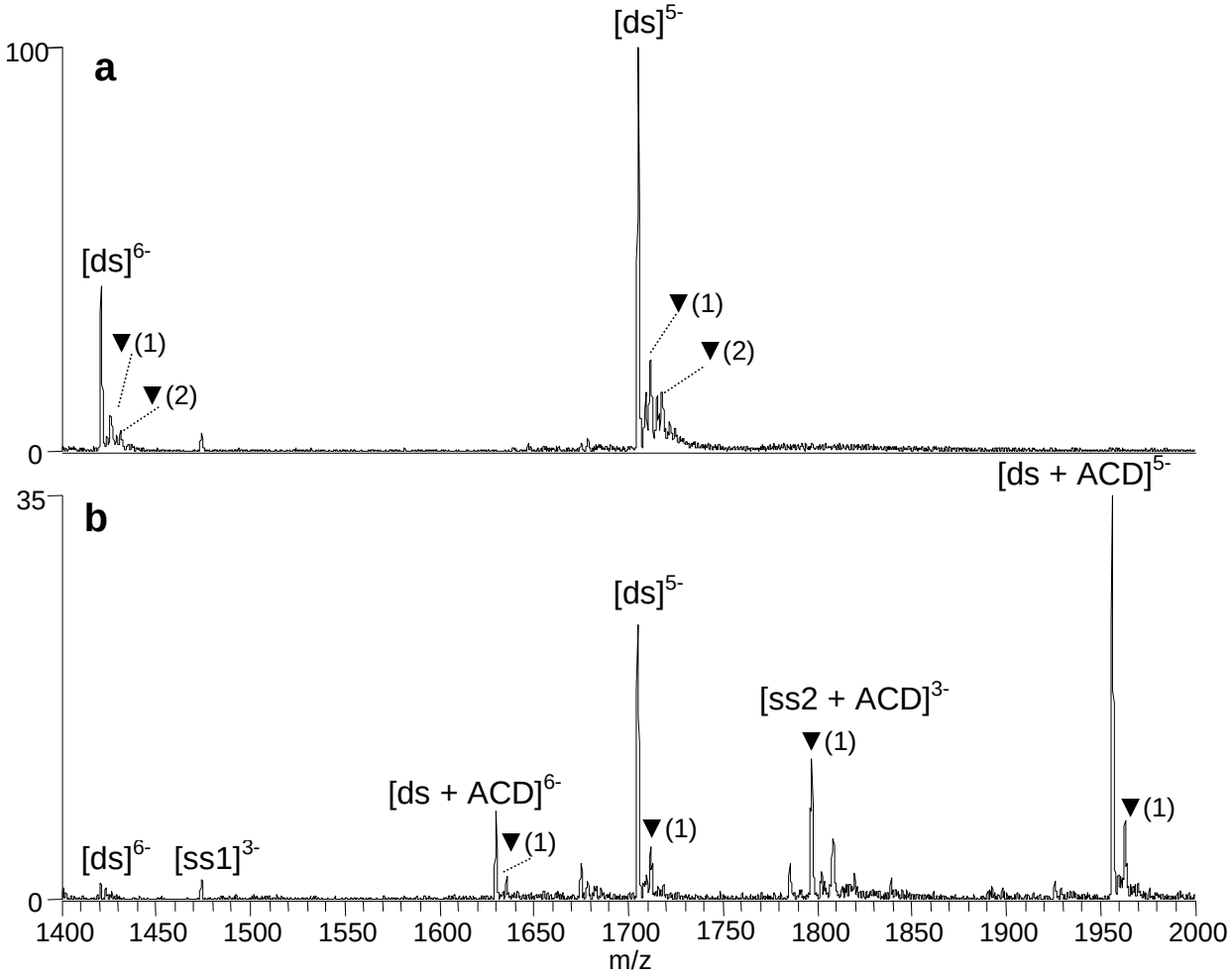

Figure S-3. ESI-mass spectra showing solutions containing the duplex d(GCGGGGATGGGGCG/CGCCCCATCCCCGC) (a) after 20 min, reaction with $KMnO_4$, and (b) with actinomycin-D (ACD), after 20 min. reaction with $KMnO_4$. Ions containing oxidized thymines are labeled with ▼, with the number in parenthesis indicating the number of oxidation adducts. The single strand d(GCGGGGATGGGGCG) is abbreviated as ss1 and d(CGCCCCATCCCCGC) is ss2.

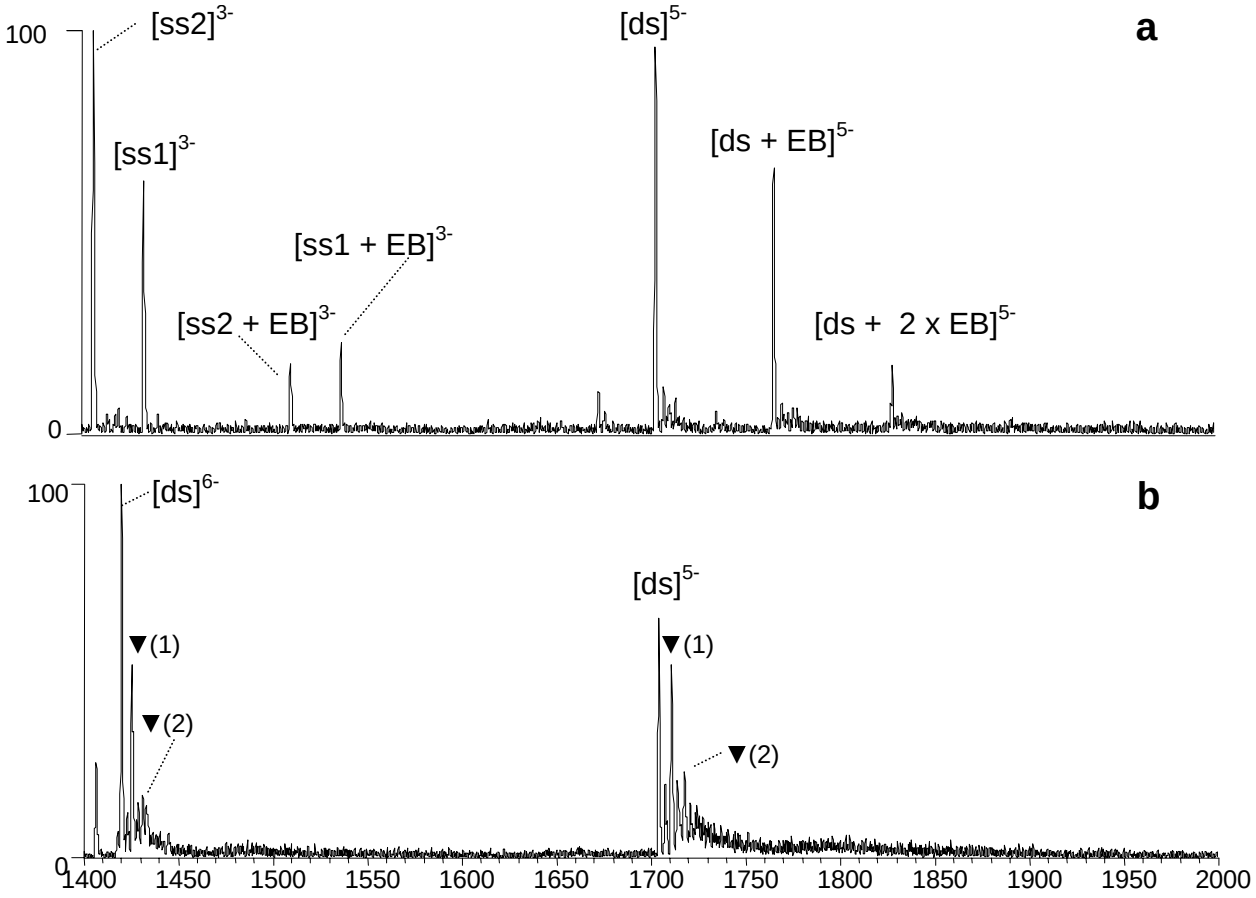

Figure S-4. ESI-mass spectra showing solutions containing the duplex d(GTAGAGTCGACCTG/CAGGTCGACTCTAC) (a) with ethidium bromide (EB) prior to the $KMnO_4$ reaction, and (b) with ethidium bromide after 20 min. reaction with $KMnO_4$. Ions containing oxidized thymines are labeled with ▼, with the number in parenthesis indicating the number of oxidation adducts. The single strand d(GTAGAGTCGACCTG) is abbreviated as ss1 and d(CAGGTCGACTCTAC) is ss2.

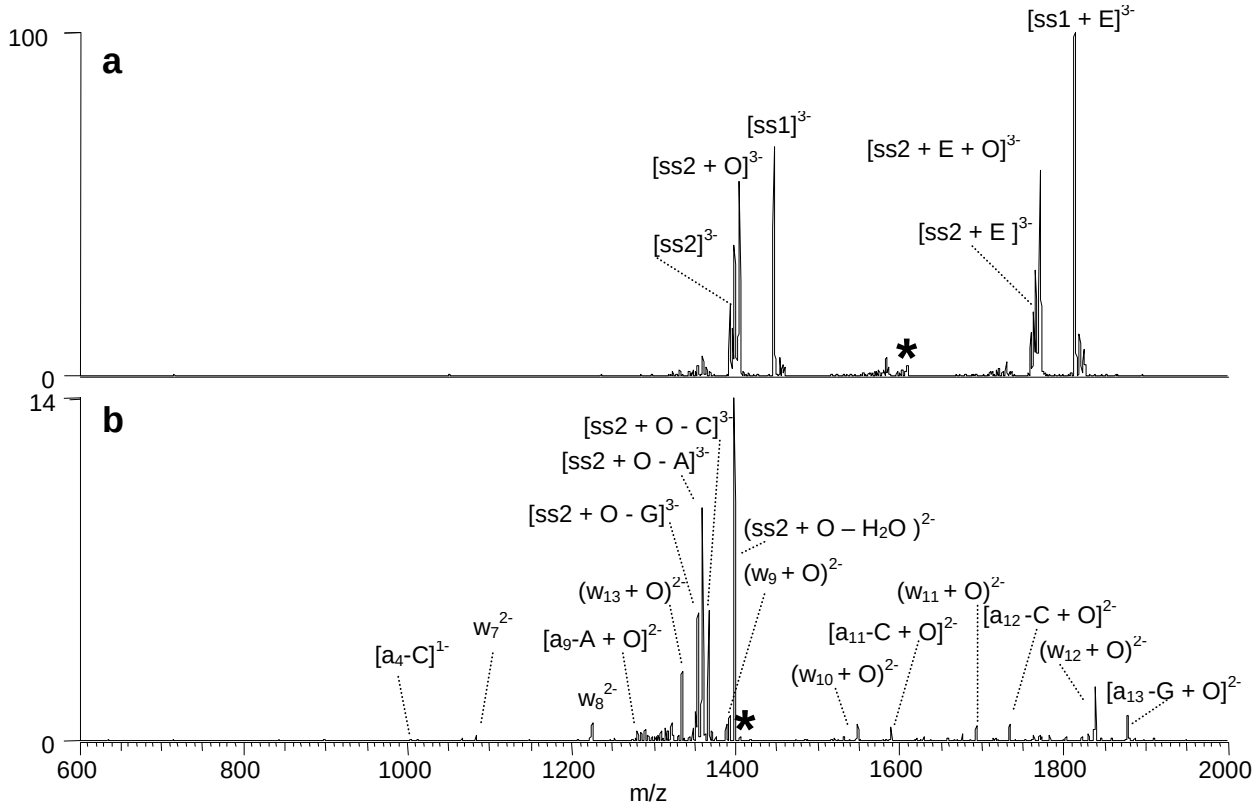

Figure S-5. ESI-MS^3 experiments for $[ds + E + O]^{6-}$ containing d(GCGGATATATGGCG/CGCCATATATCCGC) and echinomycin (E): (a) CAD spectrum of the initial $[ds + E + O]^{6-}$ complex and (b) MS^3 spectrum of the $[ss2 + O]^{3-}$ product ion. "O" is indicative of an oxidation adduct. The sequence structure in Figure 5b summarizes the sequence coverage. The fragments containing an oxidation adduct are labeled with a "▼" symbol. The thymine that was determined to be oxidized is underlined in the sequence shown in Figure 2b.