

Supporting Information

Isomer-selected photoelectron spectroscopy of isolated DNA oligonucleotides: phosphate and nucleobase deprotonation at high negative charge states

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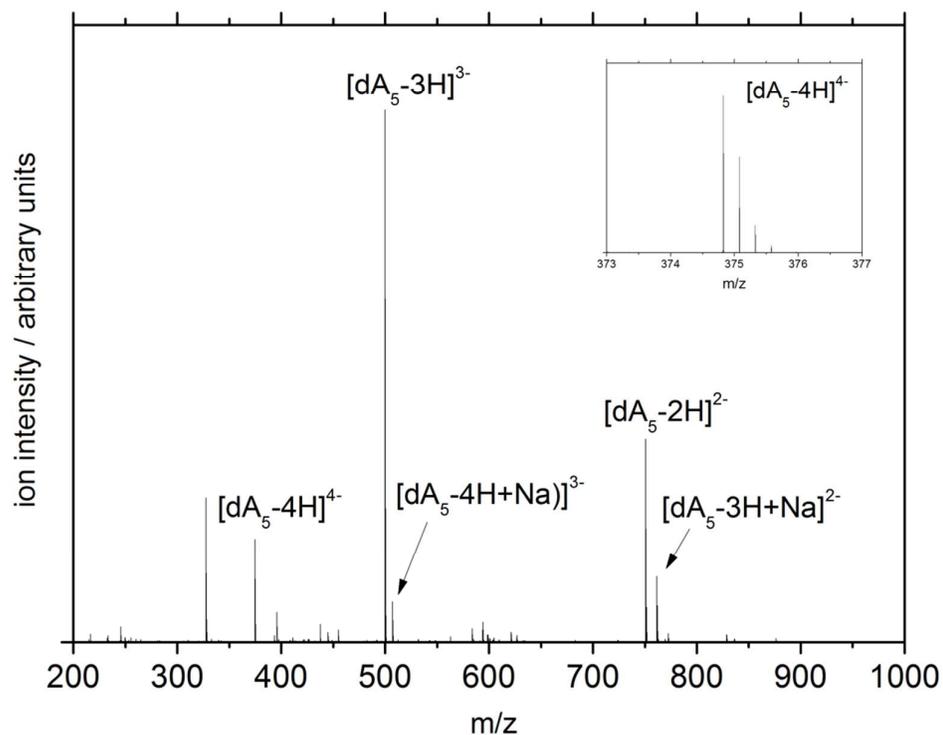


Figure S1. High resolution mass spectrum of the dA₅ sample solution also for IMS-PES measurements. The mass spectrum shown was recorded with an LTQ XL ETD Orbitrap (Thermo Scientific) using electrospray conditions optimized for dA₅⁴⁻ signal. No measurable amounts of sodiated species were observed at the 4⁻ charge state.

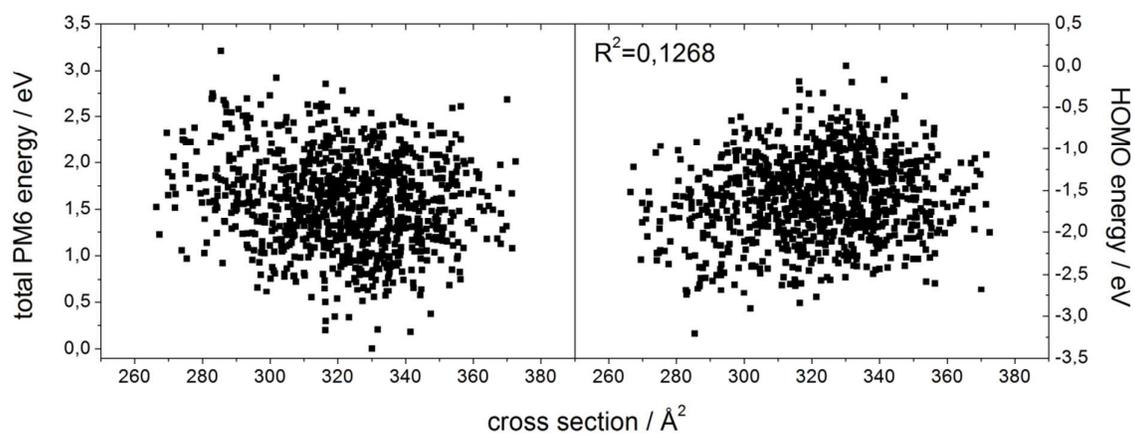


Figure S2. Representation of the results of PM6 calculations for all 1000 class A trial structures of dA_5^{4-} (for procedures used see section 3). Plotted are total and HOMO energies versus the collision cross sections generated from the PM6 geometries using the angle averaged projection model. Whereas the HOMO energy plot indicates a weak correlation with collision cross section, there is no obvious correlation to total energy.

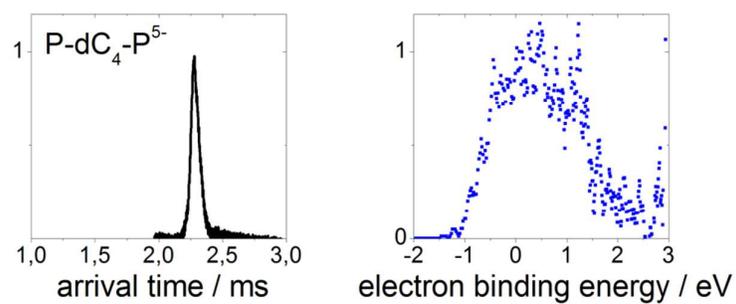


Figure S3. ATD (left) and corresponding PES spectrum (right) obtained for the P-dC₄-P derivative in its quintuply charged/deprotonated state. The corresponding ADE of ~ -1.1 eV is consistent with a “Coulomb shifted” (P-dC₄-P)⁴⁻ spectrum - subject to an additional negative charge (and thus also consistent with a structure having at least one deprotonated base).

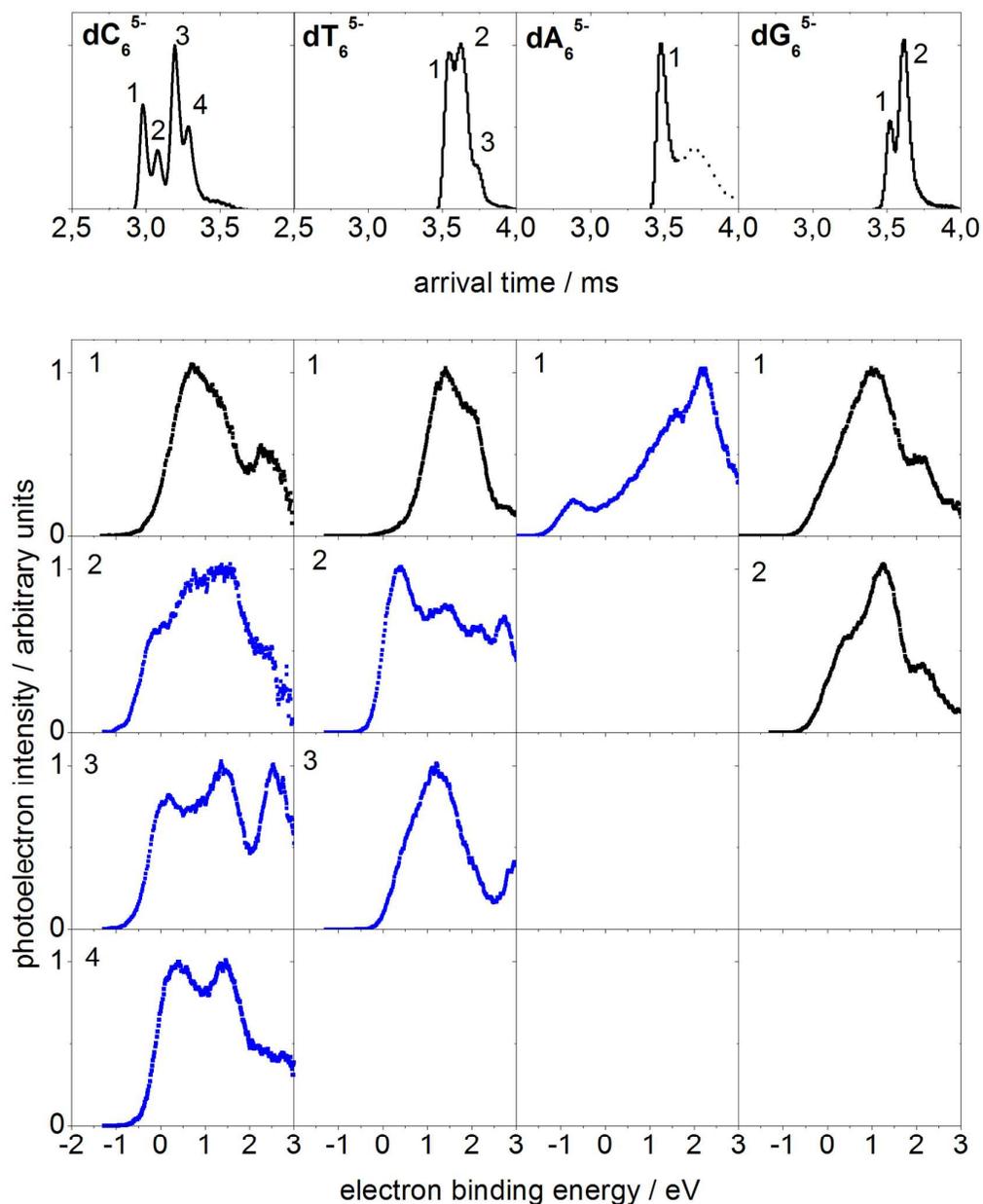


Figure S4. ATDs (top) and corresponding PES spectra (below; in vertical sequence of elution time) recorded at 266 nm for the quintuply charged hexanucleotides, dN_6^{5-} . Blue curves highlight isomers which we assign to structures having at least one deprotonated base – see text. The shoulder on the ATD of dA_6^{5-} is an artefact (due to the settings of the second ion funnel required to transmit this low EA species).

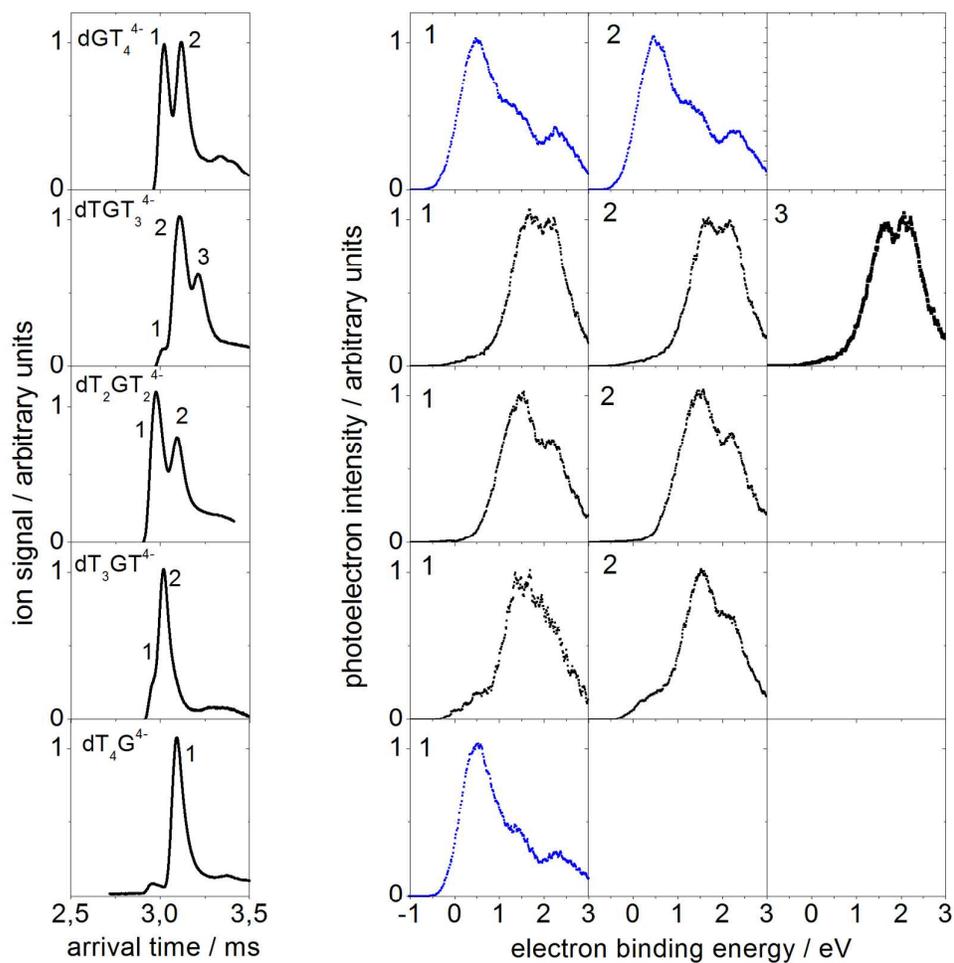


Figure S5. Arrival time distributions (ATD) and photoelectron spectra of quadruply charged pentanucleotides containing thymine and guanine. Blue curves indicate isomers which can be assigned as having a deprotonated base