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Supporting Information for Intramolecular and Intermolecular Hole Delocalization Rules the Reducer Character of Isolated Nucleobases and Homogeneous Single-Stranded DNA

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Table 1: Calculated one-electron oxidation potentials using the CAM-B3LYP functional with the 6-311G(d) basis set by means of static direct scheme. The first value in Nucleoside, Nucleotide and Methylated NUcleotide refers to the RNA-like fragment while the second represent the value of this property within the DNA-like moieity. All the potentials are given in V.

N	Nucleobase	Nucleoside	Nucleotide	Methylated Nucleotide
A	1.54	1.56/1.54	1.45/1.46	1.58/1.52
C	1.95	1.79/1.83	1.73/1.72	1.88/1.84
G	1.19	1.20/1.19	1.10/1.11	1.18/1.17
T	1.88	-/1.81	-/1.71	-/1.73
U	2.25	2.14/-	2.01/-	2.10/-

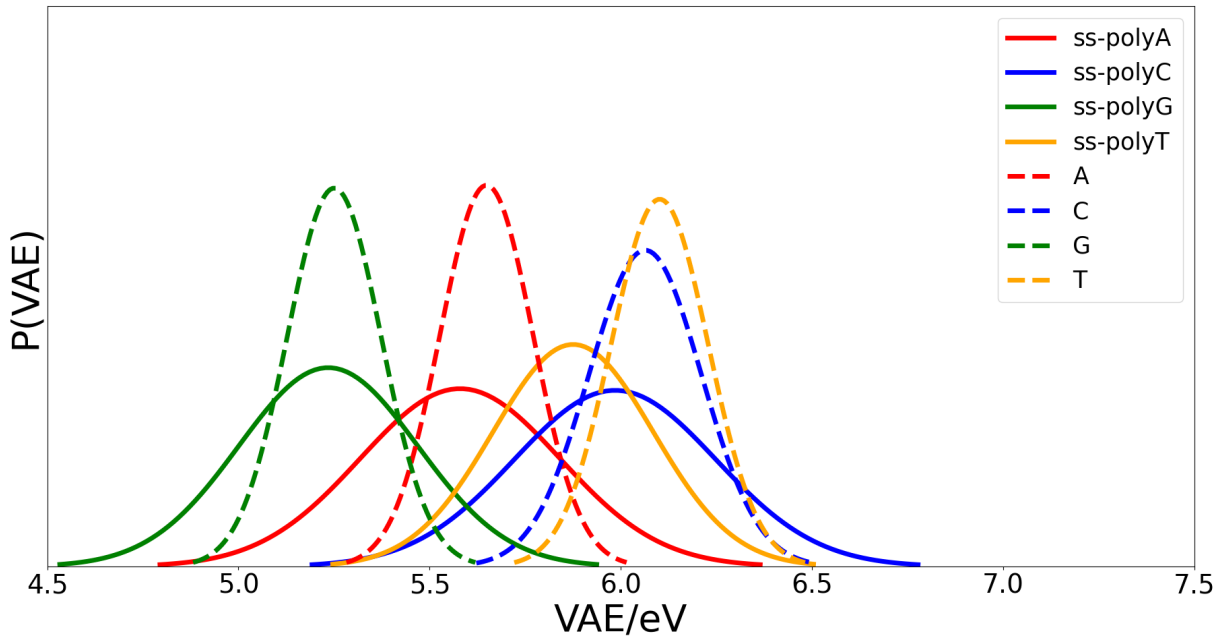

Figure 1: Probability distributions of the VAEs for the free nucleobases (dashed lines) and the ss-polyX systems (solid lines) in aqueous phase. For each system, the calculation of the VAE was reported from an ensemble of 200 geometries previously selected from classical MD simulations and and subsequently relaxed running further hybrid QM/MM MD simulations. The ensemble of results for each system has been fitted to a Gaussian function in order to represent not only the expectation value but also the standard deviation of the VAE. The area of the Gaussian functions have been normalized to unit. Colour code: A in red, C in blue, G in green, T in orange.

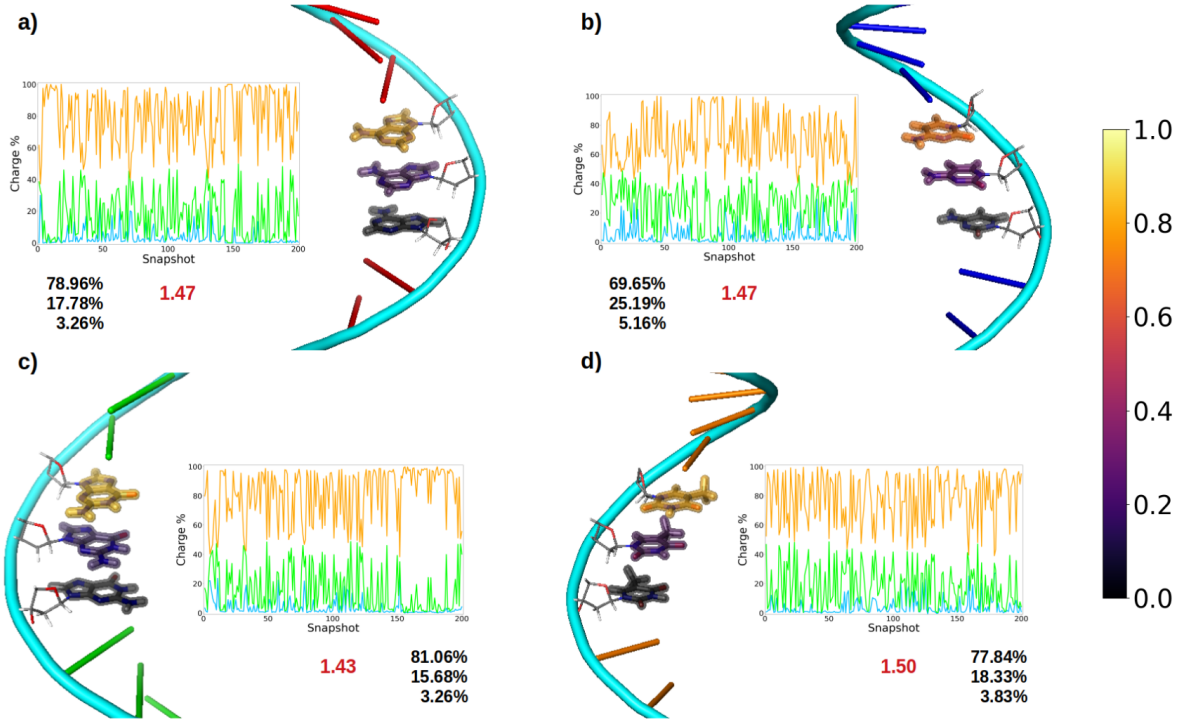

Figure 2: Schematic representation of the charge delocalization after vertical attachment along the nucleobases of a) ss-polyA, b) ss-polyC, c) ss-polyG and d) ss-polyT. For a specific system each nucleobase involved in the QM1 region is coloured in terms of the amount of the positive charge that holds. The legend is displayed as a colour bar in the right. For each system the temporal evolution of the stored charge in the nucleobases of the QM1 layer is also printed. Orange corresponds to the nucleobase that carries the largest positive charge, followed by the second (green) and the third (blue) one. Finally, the delocalization number n and the percentage of the charge among each nucleobase are written below the plot.