Supporting Information

Revisiting the Hole Size in Double Helical DNA with Localized Orbital Scaling Corrections

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S1. Redox potential change and the charge delocalization

The hole delocalization in ploy(G) DNA was examined by Voityuk using the computed charge distribution.[1] In this section, we show that the redox potential change is equivalent to the hole charge distribution. For a complex consisting of n base pairs, the redox potential change is defined as the redox potential energy difference between complexes with n and $n-1$ base pairs.

We consider a 2-site model consisting of two fragments 1 and 2. In diabatic states φ_1 and φ_2 (assumed to be orthonormalized), the positive charge (hole) is localized on sites 1 and 2, respectively. The state energies ϵ_1 and ϵ_2 correspond to oxidation potentials ($F = 1eV \cdot V^{-1}$) of these sites, and the electronic coupling V measures the electronic interaction between these two states. The adiabatic states ψ_1 and ψ_2 are obtained by diagonalizing the 2-state hamiltonian with associated state energy ε_1 and ε_2 (see S1). The energy of the ground state (ψ_1) represents the oxidation potential of the whole two-site system.

$$\begin{pmatrix} \epsilon_1 & V \\ V & \epsilon_2 \end{pmatrix} \xrightarrow{\text{Diag.}} \begin{pmatrix} \varepsilon_1 & 0 \\ 0 & \varepsilon_2 \end{pmatrix} \tag{S1}$$

According to Voityuk,[1] the charge delocalization can be characterized by the charge difference $\Delta q = q_2 - q_1$. A charge localization is indicated by $|\Delta q| = 1$, and $\Delta q = 0$ indicates that the charge is uniformly delocalized. The difference of charge is determined by the electronic coupling V and the oxidation potential difference $\Delta\epsilon = \epsilon_2 - \epsilon_1$,

$$\Delta q = \frac{\Delta\epsilon}{\sqrt{\Delta\epsilon^2 + 4V^2}}. \tag{S2}$$

Here the oxidation potential difference includes contributions from the differences in ionization energies, internal reorganization energies and interactions with solvent environments. For simplicity, we rescale ϵ_1 and ϵ_2 to zero and $\Delta\epsilon$ ($\Delta\epsilon \geq 0$). Therefore, the adiabatic state energy ε_1, also as the oxidation potential of the whole system E_{oxi}, can be written as

$$E_{oxi} = \frac{1}{2}(\Delta\epsilon - \sqrt{\Delta\epsilon^2 + 4V^2}) \tag{S3}$$

It can be shown by mathematical manipulations (Taylor expansion) that, for a given electronic coupling V, both $|\Delta q|$ and E_{oxi} decrease as $\Delta\epsilon$ decreases, indicating that the redox potential change is equivalent to the hole charge distribution. Thus, for a dimer complex, a lower redox potential of the complex corresponds to a more delocalized charge distribution. For n-site systems ($n > 2$), these arguments are valid, albeit there is no simple general mathematical expression (except some special cases).

References

(1) Voityuk, A. A. Are radical cation states delocalized over GG and GGG hole traps in DNA? *J. Phys. Chem. B* **2005**, *109*, 10793–10796.