Electronic Supplementary Information

Mechanism studies of addition reactions between the pyrimidine type radicals and their 3'/5' neighboring deoxyguanosines

Shoushan Wang\textsuperscript{a, b}, Min Zhang\textsuperscript{b}, Peng Liu\textsuperscript{b}, Shilei Xie\textsuperscript{b}, Faliang Cheng\textsuperscript{b\textdagger}, Lishi Wang\textsuperscript{a\textdagger}

\textsuperscript{a} School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510641, People's Republic of China.

\textsuperscript{b} Guangdong Engineering and Technology Research Center for Advanced Nanomaterials, School of Environment and Civil Engineering, Dongguan University of Technology, Dongguan 523808, People's Republic of China.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure_s1.png}
\caption{Prototype structures of the six related closed-shell DNA intrastrand cross-links.}
\end{figure}
Figure S2 Spin density distributions of stationary points along the reaction path of the \( {U_{CH2}} \) radical addition to the \( C_8 \) site of its 5’ neighboring deoxyguanosine.

Figure S3 Spin density distributions of stationary points along the reaction path of the \( {T_{GOH}} \) radical addition to the \( C_8 \) site of its 5’ neighboring deoxyguanosine.

Figure S4 Spin density distributions of stationary points along the reaction path of the \( {C_{GOH}} \) radical addition to the \( C_8 \) site of its 5’ neighboring deoxyguanosine.
Figure S5 Spin density distributions of stationary points along the reaction path of the ‘U_{CH2} radical addition to the C₈ site of its 3’ neighboring deoxyguanosine.

Figure S6 Spin density distributions of stationary points along the reaction path of the ‘T_{OH} radical addition to the C₈ site of its 3’ neighboring deoxyguanosine.
Figure S7 Spin density distributions of stationary points along the reaction path of the \(^{\cdot}C_{6OH}\) radical addition to the C8 site of its 3' neighboring deoxyguanosine.
Figure S8 Reaction free energies calculated for the OH$^+$ radical reacting with the canonical 5'-GT-3', 5'-GC-3', 5'-TG-3', and 5'-CG-3' sequences forming the 5'-G(UCH2)-3', 5'-G(TIOH)-3', 5'-G(CIOH)-3', 5'-G(UCH2)G-3', 5'-G(TIOH)G-3', 5'-G(CIOH)G-3', and 5'-G(CIOH)G-3' sequences, respectively.
Figure S9 Reaction free energies calculated for formation of the closed-shell 5'-G(8-5m)T-3', 5'-G(8-5)T_{OH}-3', 5'-G(8-5)C-3', 5'-T(5m-8)G-3', 5'-T(5-8)G-3', and 5'-C(5-8)G-3' intrastrand cross-links starting from the radical adducts, 5'-G_{8H}(8-5m)T-3', 5'-G_{8H}(8-5)T_{OH}-3', 5'-G_{8H}(8-5)C-3', and 5'-C_{8H}(5-8)G-3', respectively.