

• 快报 •

DIRECT OBSERVATION OF RADICAL ION PAIR FROM INTERACTION OF DNA WITH TRIPLET ANTHRAQUINONE-2-SULFONATE

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Our previous work dealing with transient laser spectroscopy and kinetics of DNA have offered time resolved evidence for electron transfer modification of DNA at guanine moiety by triplet acetone (Ac^*)^[1]. However observation of radical ion pair resulting from electron transfer oxidation of DNA by planar aromatic photonuclease is hampered by the failure of direct observation of radical cation of DNA^[2,3].

We recently reported that the interaction of triplet anthraquinone-2-sulfonate (AQS) with DNA nucleotide was investigated using KrF laser flash photolysis. The transient absorption spectra and kinetics obtained from electron transfer oxidation of nucleosides by $^3\text{AQS}^*$ demonstrated that the radical ion pair, radical cations of nucleoside and radical anion of AQS was detected simultaneously^[4]. In this communication we report, for the first time, the transient laser spectroscopy and kinetics of radical ion pair from electron transfer oxidation of DNA and its nucleotide by “strong” planar photosensitizer, AQS. Laser flash photolysis of DNA in the presence of AQS with KrF laser pulse generates radical ion pair, radical cation of DNA and radical anion of AQS, simultaneously. The transient absorption of radical cation characterized with λ_{max} at 310 nm and another weak λ_{max} at 390 nm is very similar to that produced from electron transfer oxidation of dGMP by $^3\text{Ac}^*$ and in good accord with that from electron transfer oxidation of DNA by $^3\text{Ac}^*$ ^[1]. While the transient is to absorption with λ_{max} at 510 nm is assigned to radical anion of AQS^[4]. In addition, comparative study of transient laser spectroscopy of DNA nucleotide have offered more unambiguous evidence for assignment of DNA radical cation. First, transient laser spectroscopy from electron transfer oxidation of dGMP by AQS reveals its character with λ_{max} at 310 and 390 nm respectively, identical to that from interaction of DNA with $^3\text{AQS}^*$; Secondly, transient absorption from interaction of dAMP with $^3\text{AQS}^*$ displays an absorption maximum at 360 nm, which is different from that of radical cation of dGMP; Finally, transient absorption spectra from electron transfer oxidation of TMP or dCMP displays weak, characterless spectra.

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Furthermore, the formation rates of radical cations of nucleotide and radical anion of AQS are nearly equal to rate of decay of $^3\text{AQS}^*$. However, the decay of radical anion of AQS is speedy than that of radical cations of nucleotide.

Moreover, difference in electron transfer oxidation reactivities between pyrimidine and purine nucleotide is in good accord with that in free energy change in “normal” free energy region, which demonstrates synergetically that dGMP is most easily oxidizable among DNA nucleotide.

KEYWORDS DNA, Nucleotide, Anthraquinone-2-sulfonate triplet state, Radical ion pair, Transient laser spectroscopy, Electron transfer oxidation

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DNA 与 2- 磺酸蒽醌三重态相互作用生成阴、阳离子 自由基对的直接检测

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摘要 平面型光核酸酶激发态通过电子转移光氧化定域损伤 DNA 的研究已成为当前的一个热门课题。但是由于直接检测 DNA 阳离子自由基遇到困难, 所以未能获得光氧化的主要瞬态产物, 阴、阳离子对的瞬态吸收光谱。中国科学院辐射化学开放实验室在 1997 年成功地获取了丙酮三重态电子转移光氧化 DNA 和首次确证 DNA 阳离子自由基的基础上, 现用激光光解研究了 2 - 磺酸钠蒽醌三重态对 DNA 四种核苷酸电子转移光氧化生成的阴、阳离子对。在与光氧化核苷酸生成的阴、阳离子对对比后, 准确地鉴别了 DNA 阳离子自由基与 2 - 磺酸钠蒽醌阴离子自由基的瞬态吸收光谱。进而分别研究了它们的生成与衰减动力学。

关键词 DNA, 脱氧核苷酸, 2 - 磺酸蒽醌三重态, 阴、阳离子自由基对, 瞬态激光光谱, 电子转移光氧化