基盤科学セミナーのお知らせ

下記のようにアイスランド大学のO. Ingólfsson教授による基盤科学教室セミナーを開催します。
興味のある教員・学部生・大学院生は奮って御参加下さい。
日時：　平成21年4月22日（水）16:00 – 18:00
場所：　総合研究教育棟3階　共同会議室

Influence of sodium on the fragmentation and reaction paths of Charged　Oligonucletides in the gas phase

A matrix assisted laser desorption/ionization time of flight mass spectrometry study

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Here we present a study on the stability of negatively and positively charged oligonucleotides in the metastable time frame when these are formed through deprotonation or protonation in matrix assisted laser desorption/ionization (MALDI). We study systematically the influence of the degree of sodiation i.e., when the acetic protons are one by one exchanged against sodium, and we show that the sodium adduct formation is not of less significance in the gaseous phase than it is in aqueous solutions.

The model systems used in this study are all combinations of the synthetic hexameric nucleotides 5´-d(TTXYTT)-3´, where X and Y are dC, dG or dA. The sodium free and the sodium adducts with 1-5 protons exchanged for sodium were studied for all six combinations in the negative and with up to 7 protons exchanged positive mode. In the case of the negatively charged oligonucleotides the sodiation gradually quenches all dissociatin channels that lead to back bone cleavage in the favor of simple base loss showing clearly the role of proton transfer in the fragmentation mechanism. In the case of the positively charged oligonucleotides a similar effect is observed, however, superimposed we observed a drastic and abrupt *switching* between completely different dissociation channel as the degree of sodium increases.

However, the most remarkable observation in the case of the protonated oligonucleotides is that the exchange of 2 protons against sodium ions opens up a new dissociation channel that is completely independent of the nature of the central bases and their sequence. This channel leads to the loss of the two central bases with one sugar and one diphosphoester unit from the center of the backbone. The two terminal TT units recombine in the process presumably over a cyclic phosphate intermediate leading to the formation of either a 5´-d(TTTT)-5´ or the corresponding 3´-d(TTTT)-3´ sequence. The first sequence would result from a recombination of the 3´end with the second phosphodiester group the second sequence from a recombination of the 5´ end with the fourth phosphodiester group. In both cases these these T4 units are terminated by a phosphodiester linked furanol unit at one end and a simple hydroxyl group at the other end. This channel, which gradually increases in intensity with increasing sodiation, is then again abruptly closed when six protons are exchanged against sodium ions. This show clearly that the dissociation paths of the protonated oligomers depend even more strongly on the degree of sodiation than those of the deprotonated and that the number of sodium atoms determines with high selectivity which dissociation channels are active.

セミナー修了後、金沢八景駅付近の居酒屋にて懇親会を開く予定です。

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