

Alkali Cation Attachment to Derivatized Fullerenes Studied by Matrix-Assisted Laser Desorption/Ionization

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ABSTRACT

The complexation of alkali metal ions with amphiphilic fullerene derivatives has been investigated by matrix-assisted laser desorption/ionization (MALDI) time-of-flight (TOF) mass spectrometry. The formation of analyte ions occurs via two competing mechanisms including electron transfer from matrix-derived ions and metal ion attachment. The interplay of these processes has been examined by laser fluence dependent sample activation and by variation of the target composition. The attachment of metal ions has been established as the gentler and thus more efficient route towards the formation of intact analyte ions. Investigations into the metal ion complexation have been conducted to reveal the reactivity order of the alkali metals in these reactions and to elucidate the influence of structural differences of the analytes, as well as to unravel effects caused by the anionic counter ion of the metal. The experimental data have been derived by two complementary approaches. Competing reactants were either studied simultaneously, so that the product distribution would provide direct insight into the reactivity pattern, and/or product distributions were obtained in a large variety of separate experiments and normalized for reliable comparison. It has been found that the extent to which complexation is observed follows the charge density order of the alkali metal ions. The structural features of the fullerene-attached ligands were of profound influence on the attachment of the metal ion, inducing enhanced selectivity for the complexation with less reactive metals. The metal ion attachment is reduced with the use of smaller anionic counter ions. Rationalization of these findings is provided within the framework of the mechanisms of ion formation in MALDI. (*J Am Soc Mass Spectrom* 2002, 13, 1448-1458) © 2002 American Society for Mass Spectrometry

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