UV-activated multilayer nanomatrix provides one-step tunable carbohydrate structural characterization in MALDI-MS†

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dAbstract
The structure-specific fragmentation of gas-phase ions in tandem mass spectrometry among other techniques provides an efficient analytical method for confirming unknown analytes or for elucidating chemical structures. Using concentration-dependent UV-absorbing matrix-functionalized magnetic nanoparticles and matrix-assisted laser desorption-ionization mass spectrometry (MALDI MS), we developed a single-step pseudo-MS/MS approach for tunable ionization and fragmentation to facilitate structure determination. Without chemical derivatization, we have demonstrated that this approach successfully distinguished isomeric sets of di-, tri- and tetrasaccharides. Low concentration of nanomatrix provided an enhanced signal for accurate mass determination of the intact molecular ions of analytes present in the sample. In contrast, high concentration of nanomatrix induced extensive and unique fragmentation, including high-energy facile bond breakage (A- and X-type cross-ring cleavages), which facilitated the linkage and sequence characterization of oligosaccharides without conventional tandem mass spectrometric instrumentation. The practicality of this approach for complex sample analysis was evaluated by an oligosaccharide mixture, wherein molecular ions are unambiguously observed and signature product ions are distinguishable enough for molecular identification and isomer differentiation by this simple tunable approach. By probing the roles of the multilayer nanomatrix components: matrix (energy absorption), silane-coating (energy pooling and dissipation) and core Fe3O4 (fragmentation), a plausible energy transfer mechanism was proposed based on a computational study and photoelectron experiments. The differentiation of tri- and tetra-oligosaccharide shown in this study not only demonstrated the first step toward glycan characterization by nanoparticle-assisted MALDI-MS, but also shed some insight on the nanoparticle-mediated energy transfer dynamics behind our approach.