CHIRAL AND STRUCTURE SELECTIVE MALDI USING MOLD MATRIX

Jiawei Xu, Tatsuya Fujino

(1) Department of Applied Chemistry, Graduate School of Science and Engineering, Toyo University, 2100 Kujirai, Kawagoe, 350-8585, Japan. (2) Bio-Nano Electronics Research Centre, Toyo University,

Matrix Assisted Laser Desorption Ionization (MALDI) is one kind of soft ionization methods for mass spectrometry analysis. Analyte can be ionized and detected at its molecular weight without fragmentation in MALDI. However, for the molecules with the same molecular weight, traditional mass spectrometry methods are not available, especially for the optical isomers whose enantiomers have such similar structures.

On the other hand, it has been understood that matrix molecules play an important role in the desorption and ionization process in MALDI and specially designed matrix can achieve dramatic ionization effect. Here, we used temperature responsive polymer and developed a new kind of "Mold Matrix" which is able to recognize molecular structures and selectively ionize the target molecules. In this presentation, we will introduce the application of this "Mold Matrix" on selective ionization of enantiomer of amino acid and trisaccharide.

In this study, Poly(vinyl Methyl Ether) (PVME), one kind of temperature responsive polymers, was dissolved in a mixture solvent (ethanol: H2O = 4:1) and the concentration was adjusted to 10% (w/v). 2,4,6-trihydroxyaceto- phenone (THAP) and L-Alanine (L-Ala) were mixed with the ratio of 1:0.125 (w/w), and then dissolved in the PVME solution described above to make the concentration of THAP to 4 mg/mL. This solution was transferred to a dialysis tube and the temperature was increased to 50℃ in order to change the PVME to globular state. Then dialysis was performed for three times in order to get rid of L-Ala and complete the mold matrix. This matrix solution was kept at 50℃ for further experiments. L-Ala and D-Ala were dissolved in a mixture solvent (acetonitrile: H2O = 7:3) separately and the concentration was adjusted to 1 mg/mL. The samples were mixed with the mold matrix solution on the sample plate which was kept at 50℃. After the solvent evaporated, the sample was introduced into a MALDI mass spectrometer for measurements.

In Fig 1 (a), no peak can be observed, which indicates that during the dialysis, all Ala molecules were removed from the mold matrix. Then, when measuring D-Ala with this mold matrix, at m/z = 112.1, which is the molecular weight of [Ala+Na]+, the peak can barely be observed (S/N < 3) (Fig 1 (b)). On the other hand, when measuring L-Ala, the peak of [Ala+Na]+ with strong intensity was observed, which suggests that the mold matrix developed showed strong selectivity to enantiomers of chiral molecules. It is obvious that the mold matrix developed in this study can ionize specific enantiomer of chiral molecules and is useful for further research

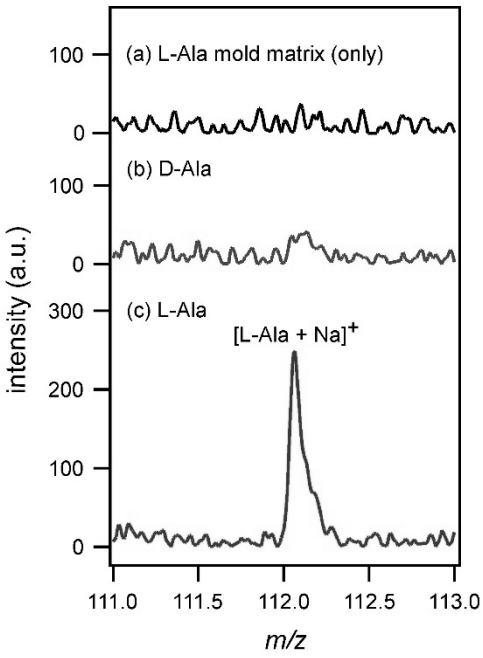

Figure 1. Measurments of (a) mold matrix only, (b) D-Ala and (c) L-Ala

Reference:

[1] Y. Fujii, J. Xu, T. Fujino. Sci. Rep.,8: 13138 (2018)