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Application News

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MALDI-TOF Mass Spectrometry

Confirmation of Synthesis of Organic Functional Materials Using Benchtop MALDI-TOF MS

The Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometer (MALDI-TOF MS) has the advantage of simply and quickly obtaining molecular weight information on diverse types of samples from low molecular to macromolecular materials. MALDI-TOF MS instruments are widely used in confirmation of the molecular weights of synthetics and natural substances in the field of R&D and quality control.

In comparison with LC-MS and other types of mass spectrometers, MALDI-TOF MS enables use of diverse solvents, is quick and simple in optimizing acquisition parameters, and detects mainly the peaks of singly charged ions (one component = one peak), even with samples having large molecular weights. Due to these advantages, it is possible to confirm synthesis of organic functional materials such as organic dyes, organic light-emitting diode (OLED) materials, and organic photovoltaic cells simply and quickly.

Here, we introduce examples of measurement of various types of organic functional materials using a benchtop MALDI-TOF MS.

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Sample Pretreatment

The sample materials used here were commercially-available organic functional materials purchased from Tokyo Chemical Industry Co., Ltd. or Sigma-Aldrich Co. LLC. These samples were dissolved in THF (tetrahydrofuran) so as to obtain a concentration of approximately 1 mg/mL. The sample solutions were spotted on a stainless steel plate for MALDI measurement together with a matrix (DCTB (trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile), 10 mg/mL THF solution) and dried. Measurements were then carried out using a Shimadzu MALDI-8020 benchtop MALDI-TOF MS (Fig. 1).

Examples of Measurement of Organic Functional Materials

As examples of measurements of organic functional materials, Fig. 2 shows the mass spectra of polymeric semiconductor building blocks and an OLED material. The singly charged radical cations of the respective samples were measured with good S/N ratios, and the patterns of the measured isotopic distributions also showed good agreement with the theoretical isotopic distributions. These results demonstrate that confirmation of synthetic products is possible not only from the measured mass of the molecular ion but also from the isotopic distribution pattern when using MALDI-TOF MS.

Fig. 1 MALDI-8020 Benchtop MALDI-TOF MS

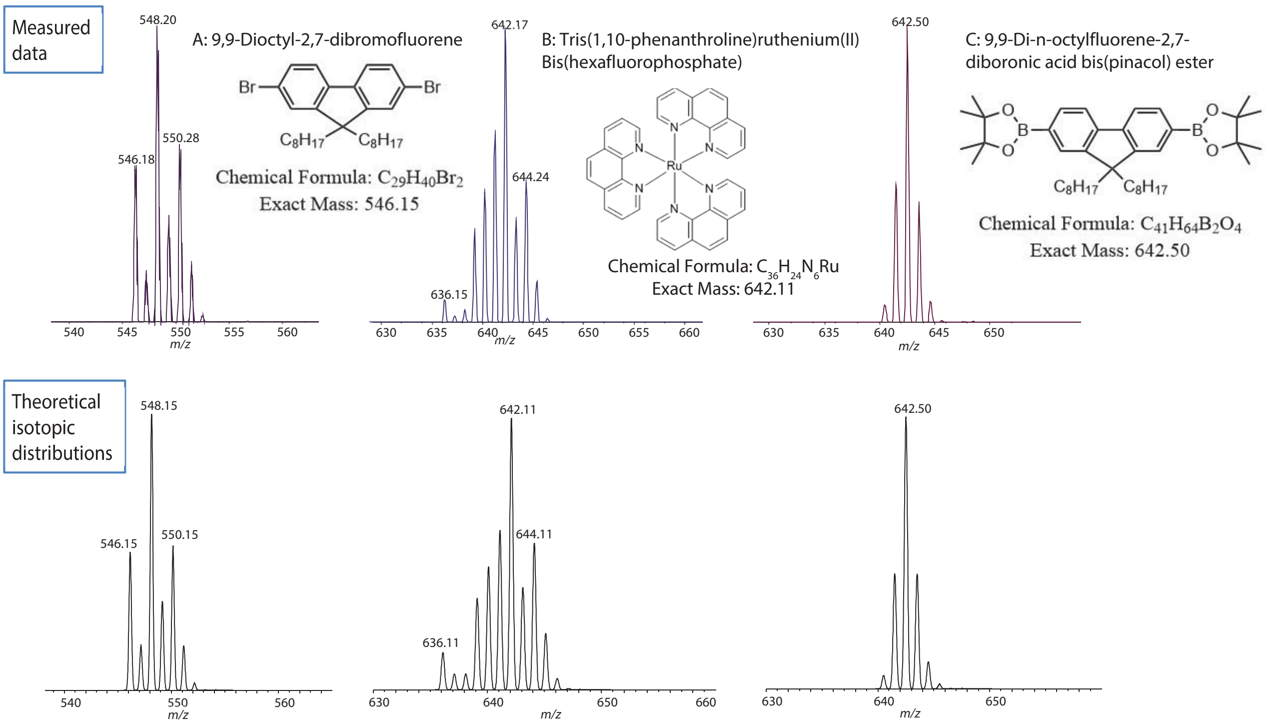


Fig. 2 Mass Spectra of Polymeric Semiconductor Building Blocks (A, C) and OLED Material (B)
Top: Measured data, Bottom: Theoretical isotopic distributions
***Structural Formulae from Website of Tokyo Chemical Industry Co., Ltd.**

Examples of Measurement of Organic Functional Materials with Molecular Weights Exceeding 1,000 Da

It is possible to obtain similar data for organic compounds having molecular weights of less than 1,000 Da, as shown in Fig. 2, by using DART® (Direct Analysis in Real Time), which is a direct ionization method. However, the difficulty of ionizing molecules having molecular weights exceeding 1,000 Da is a problem with DART-MS. Since organic functional materials include substances with molecular weights exceeding 1,000 Da, the range that can be covered by DART is limited.

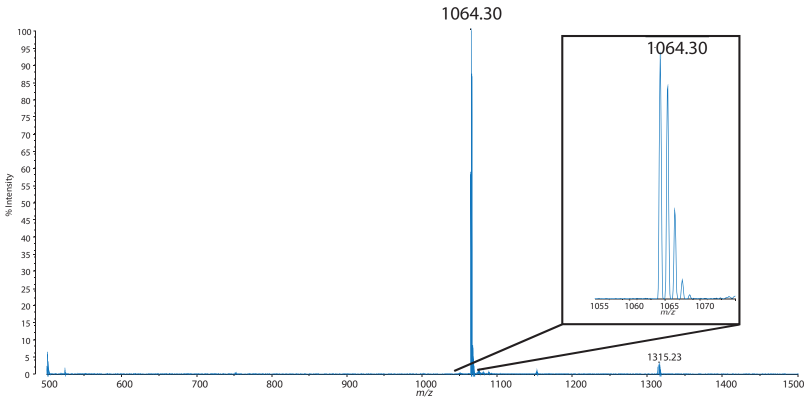
Because MALDI-TOF MS enables measurement of a greatly wider mass range than is possible with DART, molecules with molecular weights greater than 1,000 Da can also be ionized easily. Therefore, molecules having molecular weights exceeding 1,000 Da among fullerenes and metallic complexes used as materials for organic photovoltaic cells were measured by MALDI-TOF MS as test materials (Fig. 3). For both of these examples, singly charged radical cations were measured with good S/N ratios and, from the enlarged figure, it can be observed that good separation of the respective isotopic peaks was also obtained.

Conclusion

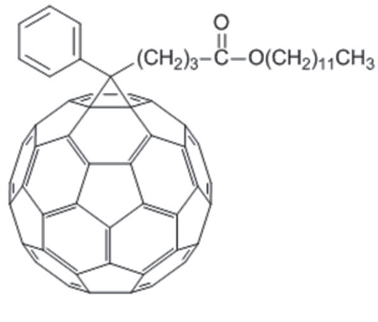
This experiment showed that the MALDI-8020 benchtop MALDI-TOF MS is capable of measuring organic functional materials such as OLED and organic photovoltaic cells with molecular weights exceeding 1,000 Da. Not limited to these materials, MALDI-TOF MS is also effective for confirmation of synthesis of various types of organic functional materials and their synthetic intermediates because it is possible to measure substances that are difficult to measure with other types of mass spectrometers (e.g. organic compounds with low solubility or comparatively large molecular weights and complex structures).

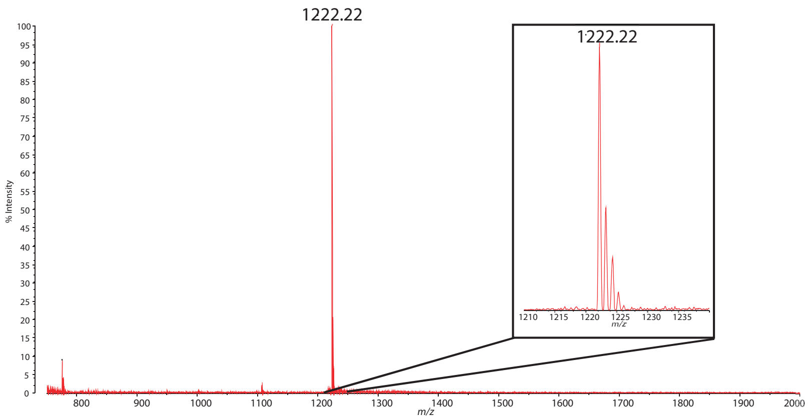
Recent MALDI-TOF MS instruments have become increasingly complex and large in scale simultaneously with the development of higher performance specifications. As a result, those systems may be over-specification for measurement needs using the linear mode, which account for a large part of MALDI applications, and their size and purchase/maintenance costs are also substantial hurdles to system introduction.

In contrast, the MALDI-8020, which offers ample performance for confirmation of synthetic products in spite of its compact size, is a product that satisfies the measurement needs of organic functional materials. Future development is expected.



[6,6]-Phenyl-C_{61}-butyric Acid Dodecyl Ester





Tris[4-*tert*-butyl-2-(1*H*-pyrazol-1-yl)pyridine] cobalt(III) Bis(trifluoromethanesulfonyl)imide

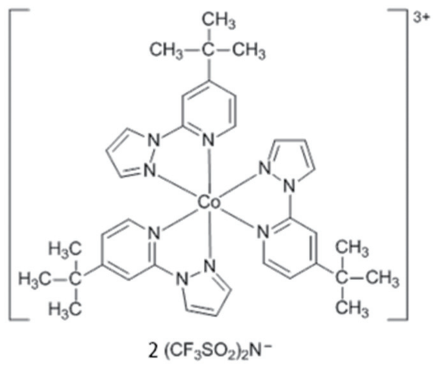


Fig. 3 Mass Spectra of Organic Functional Materials with Molecular Weights Exceeding 1,000 Da
Top: Organic Thin-Film Photovoltaic (OPV) Cell Material, Bottom: Dye-Sensitized Solar Cell (DSSC) Material
***Structural Formulae from Website of Tokyo Chemical Industry Co., Ltd.**

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