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Analysis of OLEDs by Laser Desorption Ionization Using a Novel Imaging Mass Microscope

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Introduction

Organic Light Emitting Diodes (OLEDs) are a key component of smartphone and television displays. Compared to LCD screens, OLED screens can deliver much higher contrast, deeper blacks, brighter colors, and higher resolution image display. Because they use organic components however, OLEDs can have lower lifetime than other technologies. In this work, we analyzed OLEDs by laser desorption ionization in imaging mode. The integrated microscope allows easy comparison of optical and MS data.

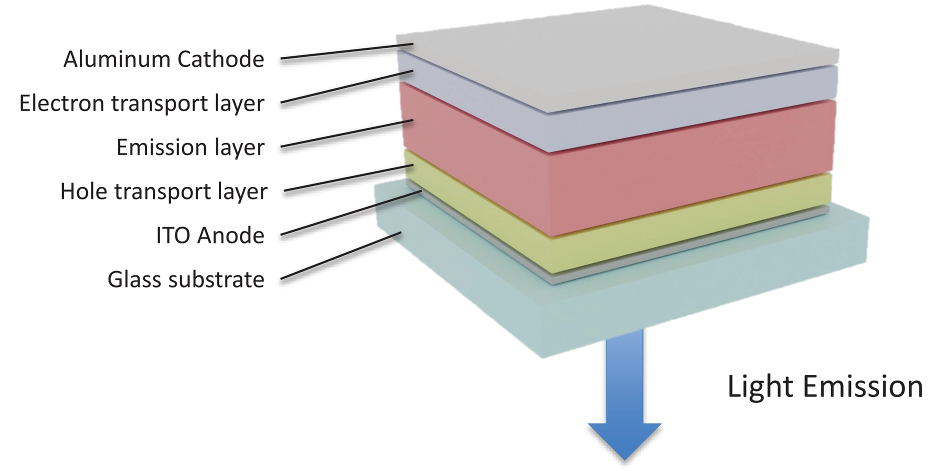

Figure 1. Simplified bottom-emitting OLED structure. Organic and inorganic layers are deposited onto the glass substrate. Analysis by Imaging MS is done from the top side. Optical images can be taken from both sides.

Methods

OLED displays were purchased from commercial vendors and the glass-sandwhiched packages were split open. Samples were affixed to a metal plate with conductive tape and analyzed by a newly-developed, high resolution imaging mass microscope. The instrument combines an optical microscope attached to a quadrupole time-of-flight mass spectrometer for chemical analysis. The sample was irradiated at 5 x 5 micron spatial resolution using a UV laser to induce laser desorption ionization at atmospheric pressure.

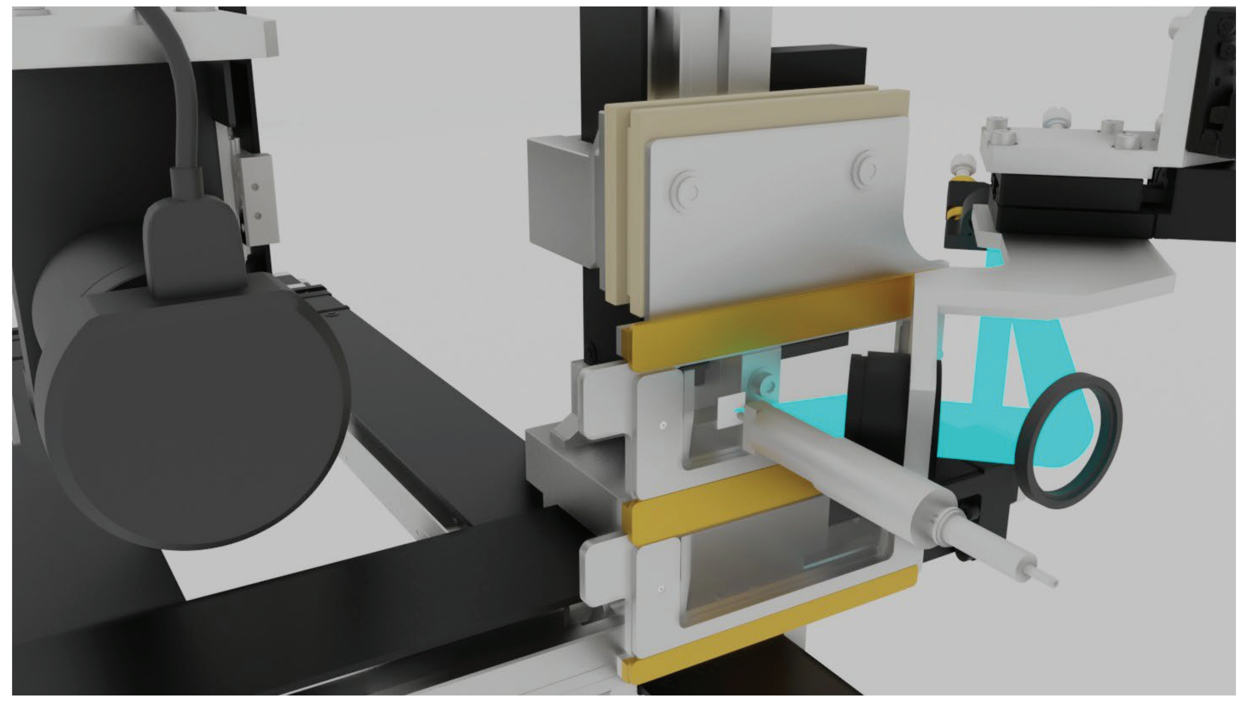

Figure 2. Analysis of OLEDs using the imaging MS microscope. The laser irradiates the sample attached to a precision stage, and ions are pulled into the MS by a heated capillary.

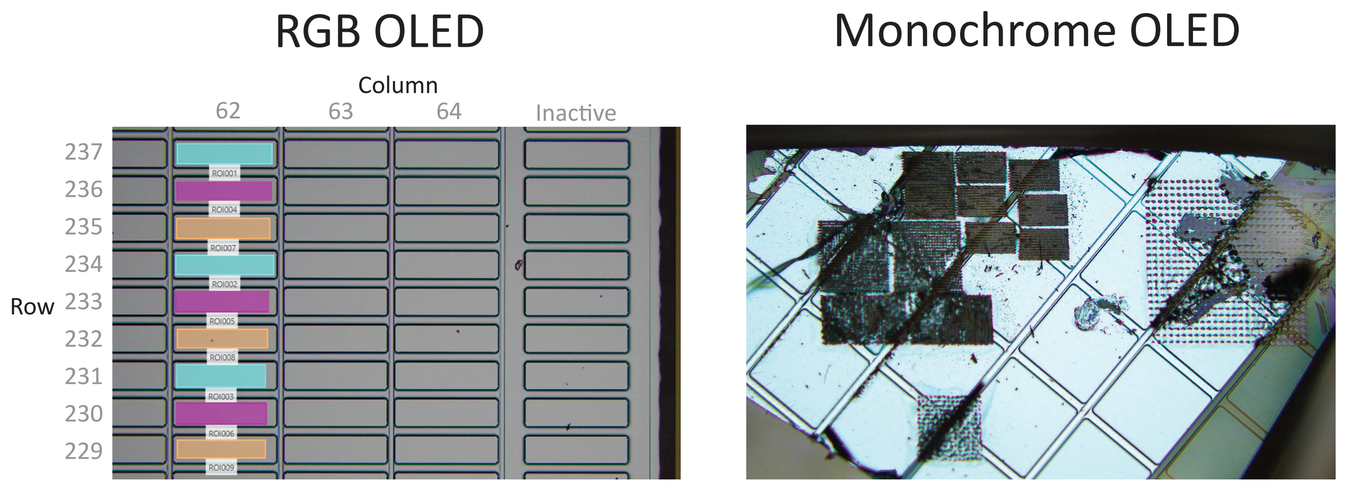

Figure 3. (Left) Microscope image of an RGB OLED taken before analysis, and showing regions of interest selected later for statistical analysis. Every third row is the same type of pixel, either Red, Green, or Blue. OLED Pixels are 200 microns wide. (Right) Microscope image of monochrome OLED taken after analysis, showing shot marks. OLED Pixels are about 200 microns square.

Pitch X and Y	5.0[um]
Polarity	Positive
Scan range	m/z 100 to 1000
Sample Voltage	5.00[kV]
Detector Voltage	2.30[kV]
DL Temperature	250[C]
Laser Irradiation Number	80[shots]
Laser Repetition Frequency	2000[Hz]
Laser Diameter Setting	0 (about 5 micron)
Laser Intensity Setting	40%

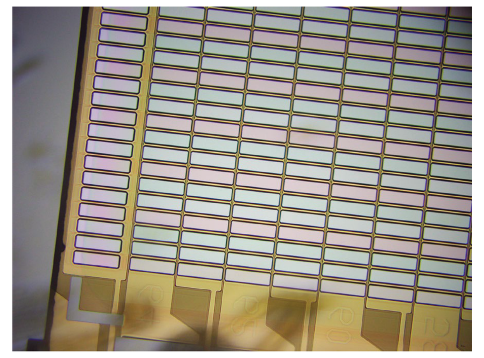

Figure 4. (Left) Analysis conditions for MS imaging for the RGB OLED. No matrix was used—the organics absorb UV energy in a Laser Desorption Ionization mechanism. (Right) Bottom-side microscope image of RGB OLED.

After acquisition, data was processed using ImageReveal processing software. For the RGB OLED, every third row has the same composition, so regions of interest were selected corresponding to this pattern for statistical analysis. Analysis of Variance (ANOVA) was performed to determine which features were detected in only the red, green, or blue pixels.

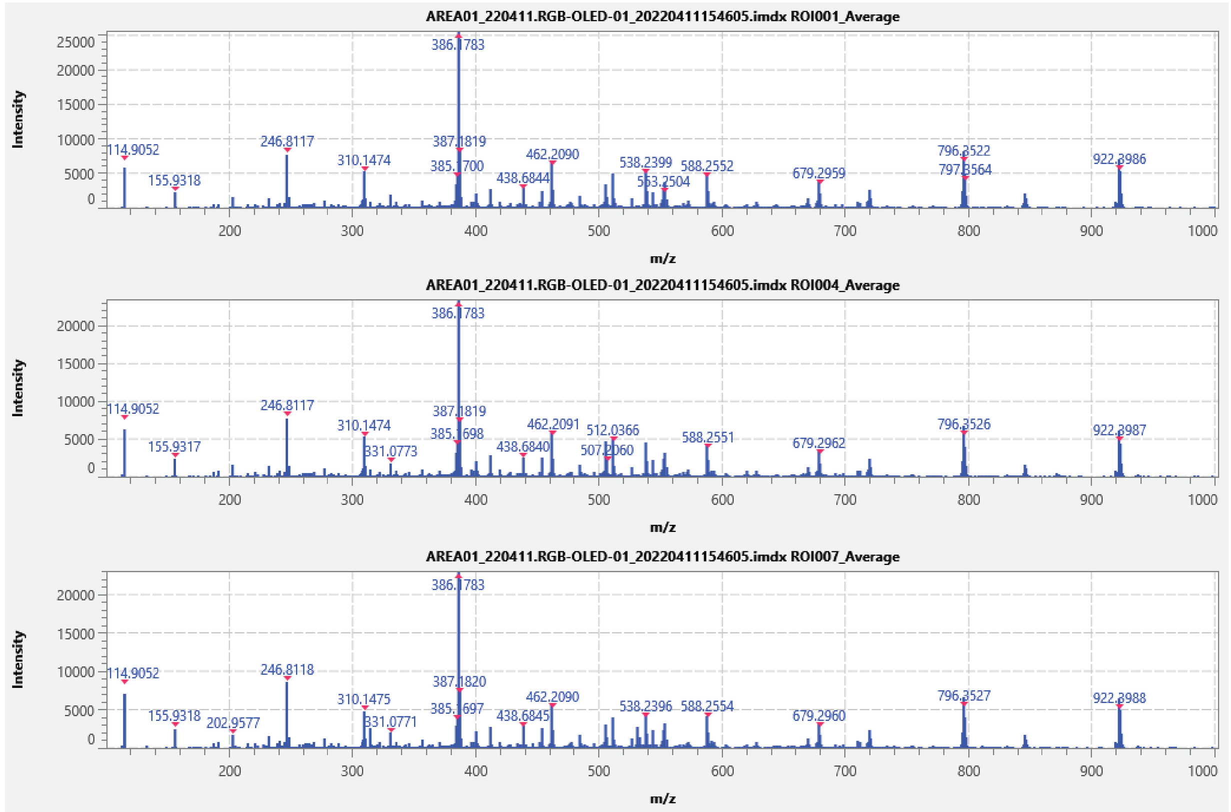

Figure 5. Laser desorption ionization mass spectra in positive mode from regions of interest 1, 4, and 7, representing blue, green, and red pixel types respectively.

Results

Statistical analysis revealed several components that were located only in one or another pixel type. Figure 6 shows the components strongly associated with the red and green pixel rows. No statistically significant signal from the blue pixel rows was found in the statistical analysis.

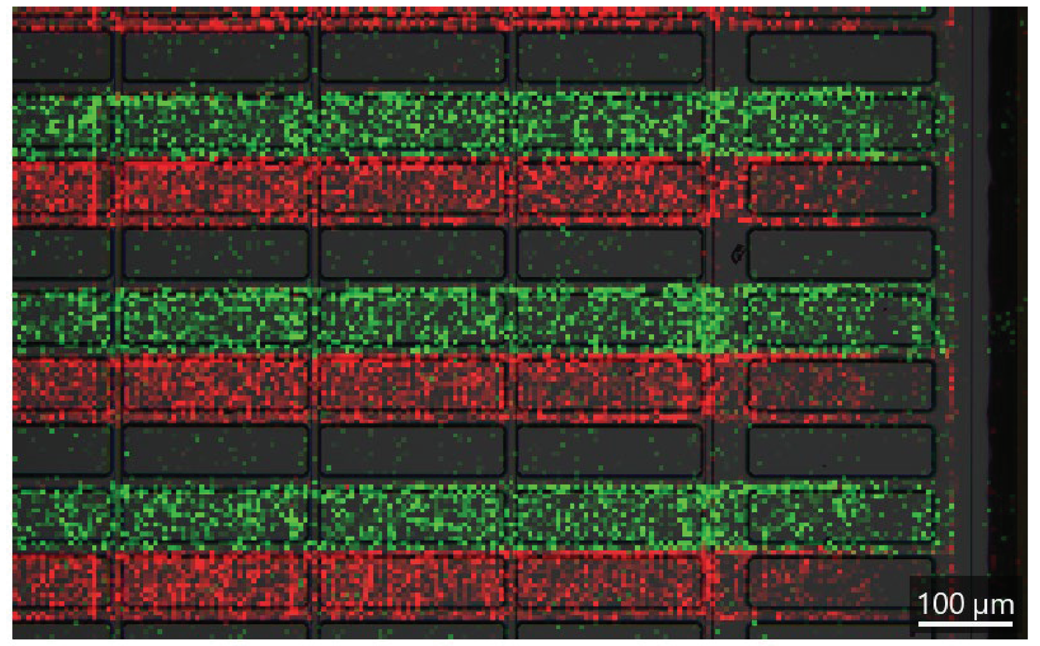

Figure 6. MS Image of the two most significant peaks discovered in statistical analysis of the RGB OLED. In red, *m/z* 532.2594 and in green, *m/z* 872.6594 which correspond to red and green pixel rows respectively. The image is overlaid with the microscope image.

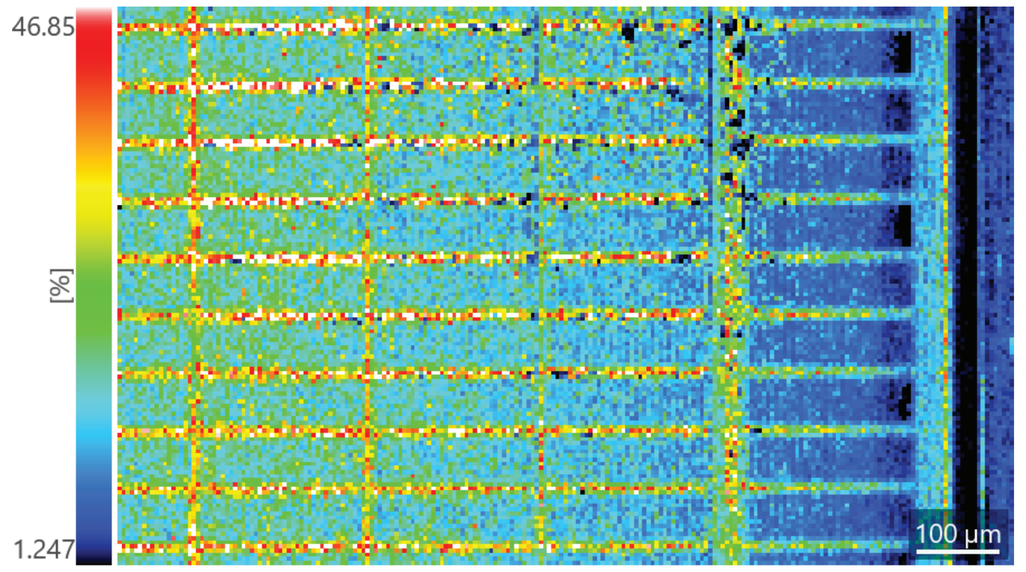

Figure 7. TIC image from RGB OLED

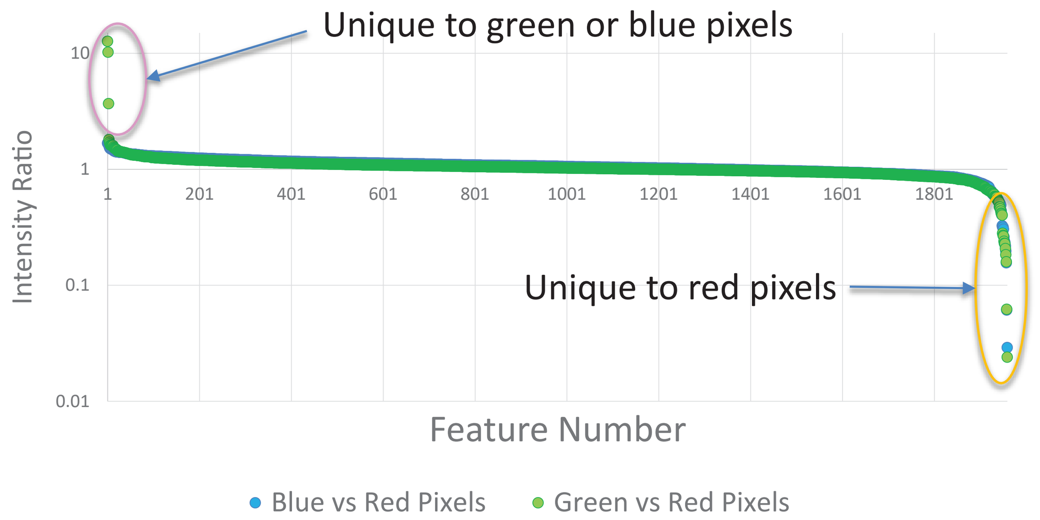

Figure 8. Ratio of *m/z* features detected in blue or green pixels relative to red pixels. Features which have greater or less than 2x difference with p value less than 0.05 were evaluated to determine if they were unique to one of the color rows.

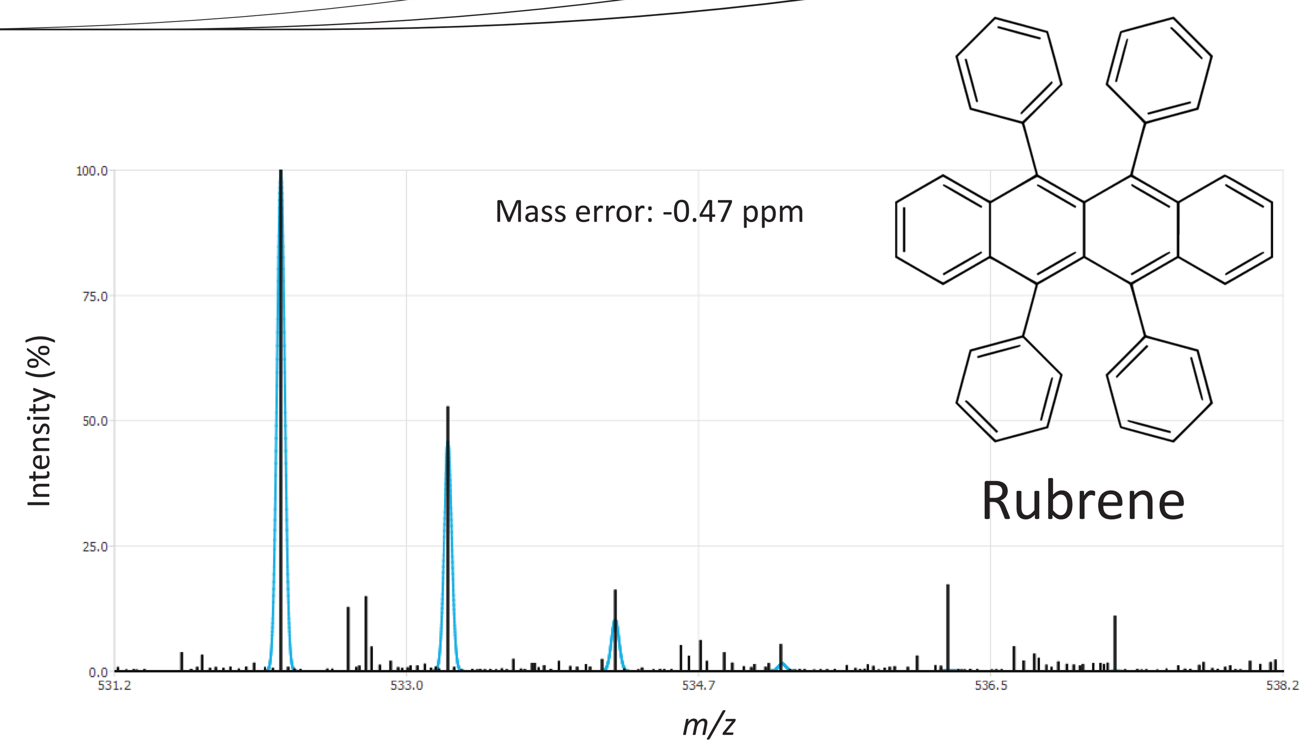

Figure 9. Observed mass spectrum of the red-pixel-unique feature *m/z* 532.2594 (in black) overlaid with predicted mass spectrum of the radical cation of $C_{42}H_{28}$ (in blue). This feature is tentatively identified as rubrene.

The feature *m/z* 532.2594 was found to be unique to red pixels and formula prediction showed a likely composition of $C_{42}H_{28}$ if the ion was formed as a radical cation [M+]. The mass error of the assignment was -0.47 ppm. The isotope pattern excludes most transition metal elements such as iridium or platinum that are frequently used in OLEDs.

A search of public compound databases revealed rubrene among the possible substances matching the predicted formula. Rubrene is a well-known organic semiconductor used in red OLEDs and similar applications. The isotope pattern is an excellent match for $C_{42}H_{28}$ and we tentatively identify it as rubrene.

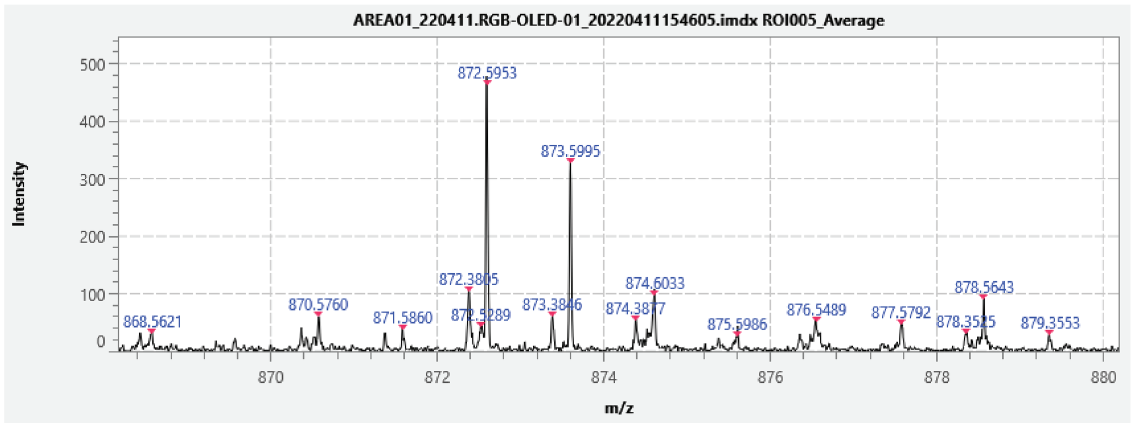

Figure 10. Observed mass spectrum of the green-pixel-unique feature *m/z* 872.6594.

Conclusions

- Monochrome and RGB OLEDs were analyzed by high spatial resolution imaging MS.
- An integrated microscope allows easy comparison of optical and MS images.
- High resolution mass spectra were acquired and analyzed by ANOVA to determine which features are present in each pixel area
- We determined that rubrene was likely used as the emission layer dopant in the red pixels of the RGB display with high mass accuracy, despite being sandwiched inside many layers of other organic and inorganic materials.