Analysis of Organic Light-Emitting Diodes (OLEDs) Using an Atmospheric Pressure MALDI Source Coupled to an Orbitrap-Based Mass Spectrometer

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Overview

→ AP LDI coupled to an Orbitrap-based mass spectrometer is a useful tool to study organic substances and their degradation products in OLEDs without sample preparation or addition of matrix

→ **New and aged OLEDs show significantly different intensities of specific ions deriving from the organic compounds or degradation products**

→ **Mass Spectral Imaging (MSI) of OLEDs provides information about localization of ions underneath and/or beside the electrodes.** MSI may allow detecting differential transitions in electrode locations with electrical defects

→ Mass spectral behavior of degradation products of the electron blocker NPB requires further investigation
($M^{+\cdot}$ (aged OLEDs) vs. „$[M-H]^+$“(new OLEDs)

Introduction

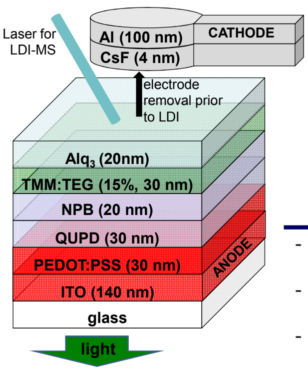
- OLEDs provide a new display technology with brighter colors, wider viewing angles, and higher power efficiency compared to Liquid Crystal Display (LCD) technologies. Futhermore, fabrication of thin, flexible, large-area, transparent OLEDs provides new possibilities of application as alternative light source.

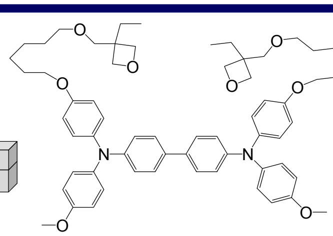
- One of the remaining drawbacks of OLEDs is their limited lifetime which may be due to degradation of the organic materials or impurities in the devices[1-4].

- For OLEDs prepared by vacuum deposition, solubility in common electrospray solvents is problematic which makes analysis by ESI-MS challenging or incomplete. Specific positions on the OLED with e.g. electrical defects may be of special interest.

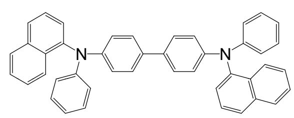
→ **Therefore, we propose to analyze OLEDs by Atmospheric Pressure Laser Desorption/Ionization (AP LDI) – Orbitrap mass spectrometry**

Methods

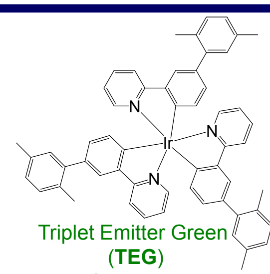




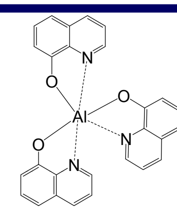
Hole transport layer
QUPD-Monomer
$C_{62}H_{76}N_2O_8$
M_{mo}: 976.5602



Electron blocking layer
NPB
$C_{44}H_{32}N_2$
M_{mo}: 588.2566



Triplet Emitter Green
(TEG)
$C_{57}H_{48}IrN_3$
M_{191Ir}:965.3454
M_{193Ir}:967.3477

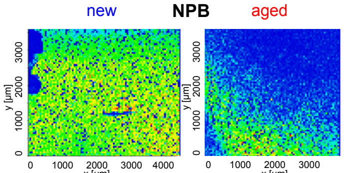


Electron transport / hole blocking layer
Alq$_3$
$C_{32}H_{25}AlN_2O_3$
M_{mo}: 459.1164

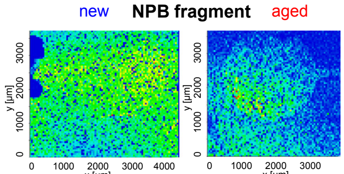
- OLED preparation: by vaccum deposition; except for the QUPD layer: electrosprayed onto the substrate and cross-linked
- „Aging“ of OLEDs (1-3 of each substrate): 2 voltage ramps 0-20 V; 0.25V/s; OLEDs had effiicencies of 30-35 Cd/A at a voltage of 2.5-3 V
- Ion sources
  - AP MALDI source from MassTech Inc. (Columbia, MD, USA) for comparison of new and aged OLEDs
  - AP SMALDI10™ ion source from TransMIT (Giessen, Germany) for imaging of the electrode areas
- Mass spectrometer: Thermo Scientific™ Q Exactive™ MS, Thermo Fisher Scientific (Bremen) GmbH, Germany
- Analysis: No sample preparation, no matrix → Laser Desorption Ionization (LDI) after removal of the cathode using adhesive tape (no adhesive tape residues were found on the samples)
- Analysis software for comparing groups: Thermo Scientific™ Sieve 2.1™ (beta-version, Thermo Fisher Scientific), MSI: Thermo Scientific™ ImageQuest™ Software

Results: AP LDI MS Imaging

XIC *m/z* 588.256

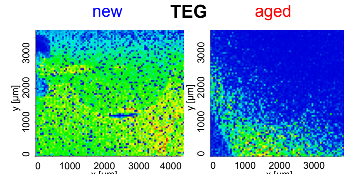


XIC *m/z* 371.167



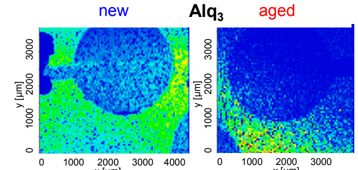
NPB does not localize underneath the electrode in the new device.
Intensity decreases in electrode area in the aged OLED.
Intensity of the fragment (*m/z* 371.167) increases in the aged OLED.

XIC *m/z* 965.345

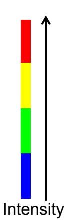


TEG does not localize in the new device and decreases in the electrode area in the aged OLED

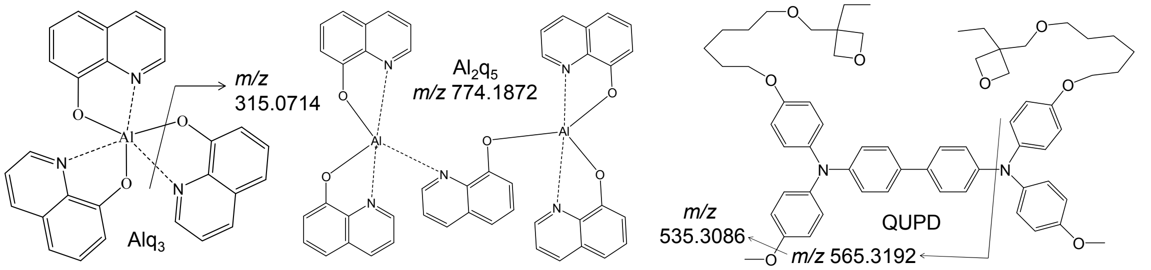
XIC *m/z* 459.116

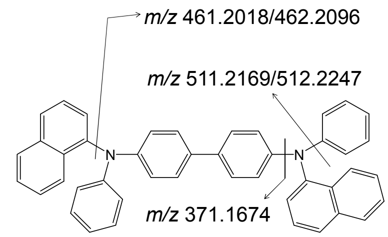


Alq$_3$ amount underneath the electrode is lower than beside



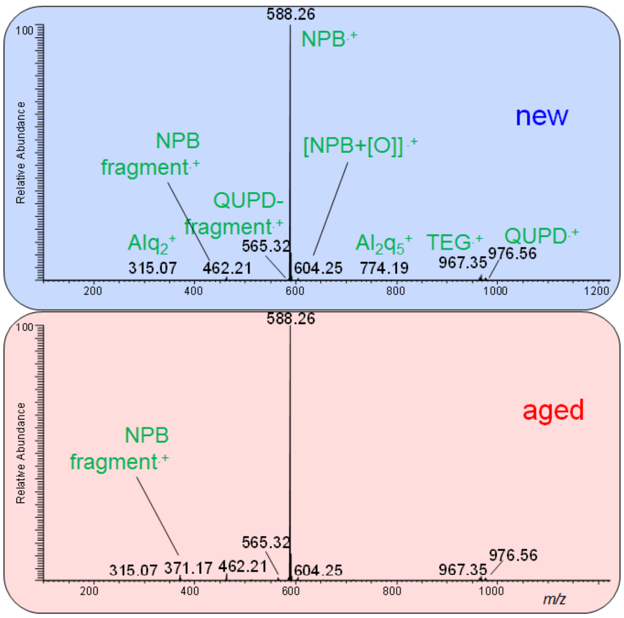
Results: Identification of degradation products





Ionized Compounds and degradation products found in new and aged OLEDs

Results: Comparison of new and aged OLEDs



Mass spectra of new and aged OLEDs. Most substances are detected as radical cations according to their hole transporting properties[6].

NPB dominates the spectrum and also shows most degradation products. NPB fragment ions with uncommon MS behavior are shown in the spectra on the right hand side.
Alq_3 is detected as radical cation as well as after loss of one quinoline substituent as Alq_2^+ and as Al_2q_5.
TEG is detected as radical cation.
QUPD monomer left after cross-linking and two degradation products thereof are detected.

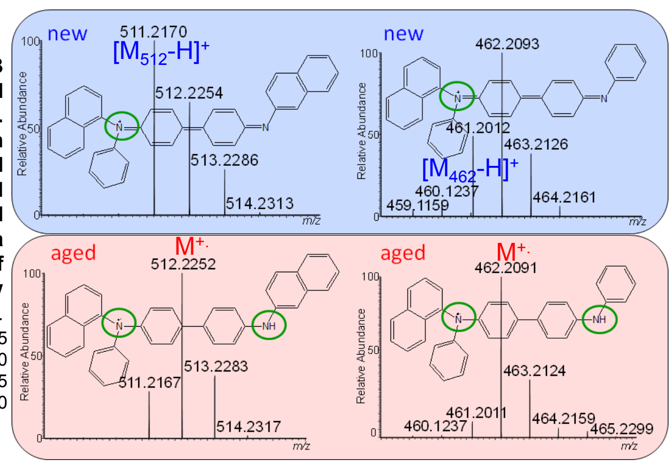
NPB	Ratio aged/new	SD	p value
588.2559	0.5	0.09	0.00004
371.1669	8.5	3.00	0.004
Alq_3			
459.1158	0.7	0.4	n.s.
315.0707	0.3	0.1	0.0002
TEG			
967.3449	0.3	0.08	0.00002
QUPD			
976.5595	0.3	0.3	0.006
565.3187	2.4	0.3	0.002

Significant changes of substances between new and aged devices (using Sieve software). All OLED substances decrease in intensity while specific degradation products increase.

NPB fragment with *m/z* 371 increases ~9-fold during aging.
High variation of Alq_3 may be due to electrode removal.
TEG decreases but no evidence of degradation products is found.
For QUPD, monomers may be left in different amounts after cross-linking which may explain the high variation.
blue=decrease; red=increase in aged devices

Mass spectra of NPB fragments in new and aged samples. These degradation products are detected mainly as radical cations in the aged samples and have a higher percentage of [M-H]+ in new samples.

461: C34H25N2, RDBe 23.5
462: C34H26N2, RDBe 23.0
511: C38H27N2, RDBe 26.5
512: C38H28N2, RDBe 26.0



Conclusions:

- An AP MALDI source coupled to a high resolution/high accuracy mass spectrometer is a useful tool for analysis of OLEDs and other organic electronic devices (e.g. organic solar cells) without the need to dissolve the analytes.
- Sieve software 2.1 (beta version) provided a valuable evaluation tool for statistical comparison of groups of new and aged OLEDs and yielded significant changes for OLED substances and their degradation products.
- LDI MS Imaging shows localization of different masses and may allow a correlation of differences in the mass spectra to positions of electrical defects.
- Further studies may allow more detailed proposal of degradation pathways which will contribute to optimization OLEDs.

Acknowledgements:

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References:

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