Exploring Triphenylene Ethynylene Structures as MALDI Matrices

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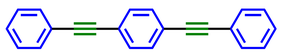
Background

Triphenylene Ethynylene (TPEE)

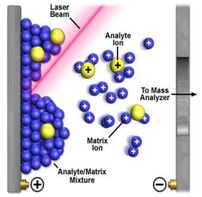
Triphenylene Ethynylene-
three phenyl rings linked by ethyne



Ring substitutions change the TPEE.

MALDI

Matrix-**A**ssisted **L**aser **D**esorption **I**onization

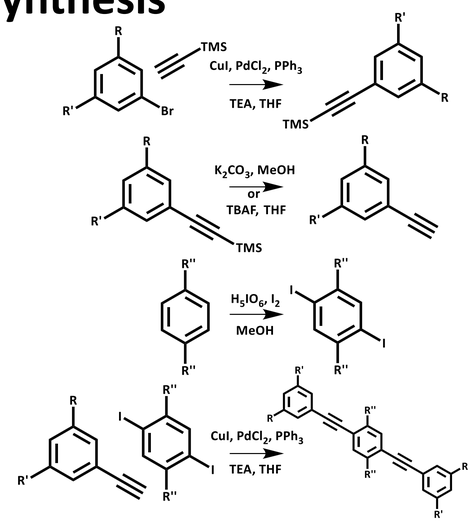


MALDI is a mass spectrometry method used to determine the mass and composition of a molecule. The molecule is dissolved in a host matrix deposited on a charged plate and irradiated with a UV laser. The molecule is given a positive or negative charge depending on the chemistry of the matrix. The mass-to-charge ratio of the molecular ion is determined by the instrument.

Objective

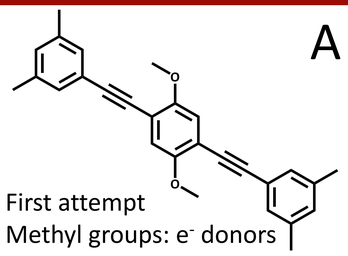
We are looking to synthesize MALDI matrices whose photochemistry allows clean donation and withdrawal of electrons.

Synthesis



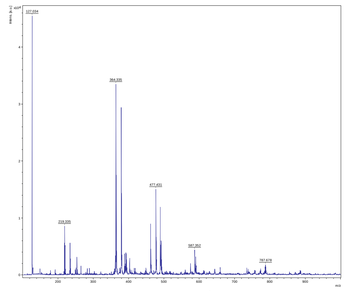
Electron-Donating Matrices

A



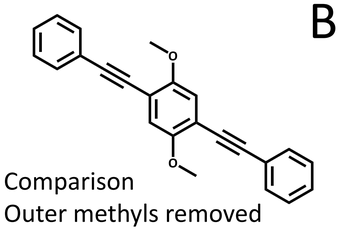
First attempt
Methyl groups: e^- donors

Problem:
Extensive fragmentation



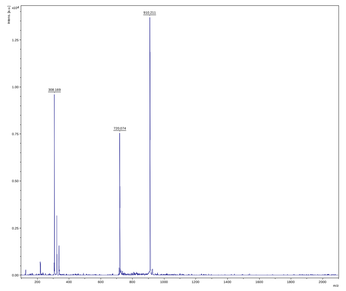
No substrate, matrix concentration 0.5 g/L laser strength 20%, 500 pulses, anion mode

B



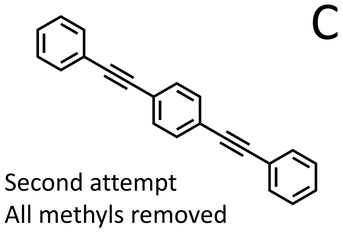
Comparison
Outer methyls removed

Low fragmentation
High matrix peak



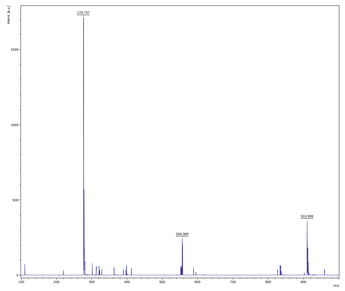
Substrate: PCBM (MW 911), substrate concentration 0.5 g/L, matrix concentration 0.5 g/L laser strength 20%, 500 pulses, anion mode

C



Second attempt
All methyls removed

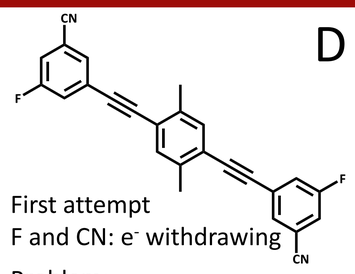
Problem:
Matrix is electron acceptor



Substrate: PCBM (MW 911), substrate concentration 5 g/L, matrix concentration 5 g/L, laser strength 20%, 500 pulses, anion mode

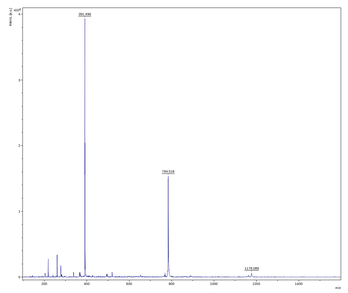
Electron Withdrawing Matrices

D



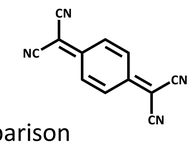
First attempt
F and CN: e^- withdrawing

Problem:
Polymerization



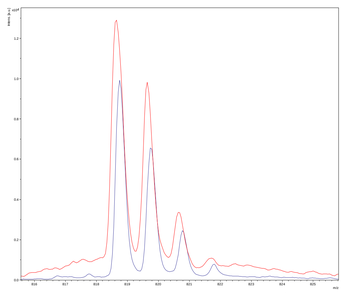
No substrate, matrix concentration 0.5 g/L, laser strength 25%, 500 pulses, cation mode

TCNQ



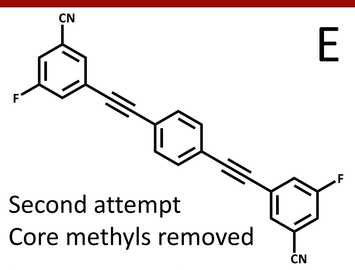
Comparison
Common matrix (TCNQ)

High concentrations
favor TCNQ over matrix E



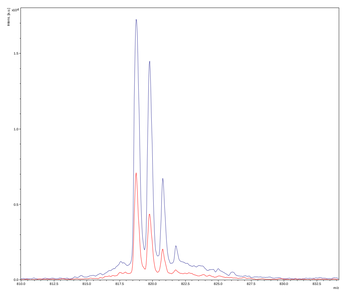
Substrate: TPEE (MW 818), substrate concentration 0.5 g/L, TCNQ concentration 2.5 g/L, TPEE matrix concentration 5 g/L, laser strength 25%, 100 pulses, cation mode

E



Second attempt
Core methyls removed

Low concentrations
favor matrix E over TCNQ



Substrate: TPEE (MW 818), substrate concentration 0.5 g/L, TCNQ concentration 0.25 g/L, TPEE matrix concentration 0.5 g/L, laser strength 25%, 100 pulses, cation mode

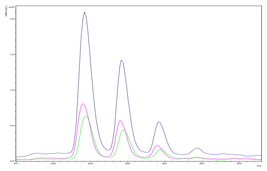
Conclusions

- Matrix A has too much fragmentation
- Matric C yields a high matrix peak
- Matrix B shows promise due to low fragmentation and strong analyte signal

- Matrix D polymers yield high interference
- Matrix E shows strong performance

Matrix E has several advantages:

- High signal strength at low concentrations
  - -less matrix required
  - -signal at very low substrate concentrations
- Simple synthesis
  - -two step synthesis with *in situ* deprotection
- Low rate of sublimation- good for automation
  - -shows strong signal after 7+ hours



Substrate: TPEE (MW 818), substrate concentration 0.5 g/L, matrix concentration 0.5 g/L, laser strength 25%, 5x25 pulses, anion mode, 0 minutes (blue), 20 minutes (green), 420 minutes (magenta)

Future Work

- Further engineer the electron-donating matrices to reduce fragmentation and the size of the matrix peak

- Benchmark our electron-withdrawing TPEE
  - -compare with other common matrices, especially under vacuum
  - -test using other electron-rich analytes
  - -refine the synthesis to give higher yield
  - -develop stronger electron-withdrawing TPEE matrices

Acknowledgements

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-Dr. Matthew B. Zimmt

MALDI image borrowed from National High Magnetic Field Laboratory.