

## Electrofluorochromism at single molecule level: application of mass-selective matrix isolation spectroscopy

Haupa, K.A.,<sup>1\*</sup> Debnath, S.,<sup>1</sup> Krappel, N.P.,<sup>1</sup> Lebedkin, S.,<sup>2</sup> Strelnikov, D.,<sup>1</sup> Kappes, M.M.,<sup>1,2</sup>

\*presenter

<sup>1</sup> karolina.haupa@gmail.com, Institute of Physical Chemistry II, Karlsruhe Institute of Technology, Fritz-Haber-Weg 2, 76131 Karlsruhe, Germany.

<sup>2</sup> Institute of Nanotechnology, Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany.

The luminescence properties of numerous molecules are stimuli-responsive. Among them, electrofluorochromism (EFC), understood as the dependence of luminescence on the charge state is of particular interest due to its wide range of potential technological applications. Probing EFC at the molecular level remains challenging owing to the limitations of state-of-art methods and correspondingly the fundamentals remain poorly investigated.

In our laboratory at the Karlsruhe Institute of Technology, we have developed the instrumental setup for spectroscopic studies (UV-Vis-NIR absorption and Laser-induced fluorescence – LIF) on mass-selected species deposited into inert gas cryomatrices. Cations are produced in an electron-impact ionization (EI) or electrospray ion source (ESI), transferred via Einzel lenses, mass-selected with a quadrupole mass filter, and soft-landed with an excess of co-deposited Ne gas onto an Al-on-quartz mirror at 5 K. Deposition of only positively charged ions into an insulating matrix result in charge accumulation. Hence, the charge must be partially compensated to prevent further incoming ions from being deflected away. We accomplished this by adding electron scavengers (SF<sub>6</sub> and CH<sub>3</sub>Cl) to the matrix. They capture electrons from the surroundings and produce anions ( $\bar{e} + \text{CH}_3\text{Cl} \rightarrow \text{CH}_3\cdot + \text{Cl}^-$ ). This prevents discharges from conductive mirror substrate to the matrix and minimizes neutralization of trapped cations, as well as compensates for the charge. Thus, it enhances the cation to neutral ratio in the matrix.

We have applied this methodology to study the EFC of a series of fluorescent dyes including free-base phthalocyanine (H<sub>2</sub>Pc), zinc phthalocyanine (ZnPc), vanadyl phthalocyanine (VOPc), magnesium porphyrin (MgP), rhodamine B, pyronin Y, etc. The obtained experimental spectra have been compared with literature data obtained by other methods including scanning tunneling microscopy light emission (STM LE) and ion-beam experiments as well as with theoretical predictions with Franck-Condon (FC) and Franck-Condon-Hertzberg-Teller (FCHT) calculations. A summary of these results will be presented. The future perspectives of this methodology will be also discussed.