FEATURED LAB:

The Molecular Spectroscopy Lab was established in the Department of Chemistry in 2005 through a number of competitive grants, both from national and international sources. It specializes in vibrational spectroscopy, and particularly Resonance Raman spectroscopy. The primary goal of the Molecular Spectroscopy Laboratory is the detailed understanding of the interactions between various molecules and their environment which hold the key to their function. Of particular interest are conjugated polymers used as active layers in optoelectronic devices, small molecules used as pharmaceuticals, as well as conjugated polyelectrolytes used in bioelectronics. Our main tool, Resonance Raman (RR) spectroscopy, is a direct structural probe, with selectivity that allows us to uncover important structural information for chromophores of interest in complicated sample blends with unmatched ease.
UV and Visible Resonance Raman Spectroscopy

A vibrational spectroscopic method with high selectivity for the chromophore of interest due to resonance enhancement when excited within the absorption band of the molecule. Two high power Q-switched Nd:YAG lasers, equipped with all the harmonic generation crystals, and three Raman shifters are available for generation of a large range of excitation wavelengths from 190 nm - 1.9 μm. These are complemented by three solid state lasers with emission at 407, 473 and 532 nm. This large array of excitation wavelengths makes the setup suitable for any type of molecular system, from DNA and proteins with UV excitation to conjugated molecules and polymers with visible to near-IR absorption. The scattered light collected from the sample is analyzed by a high-resolution dispersive spectrograph equipped with three different diffraction gratings for choice of spectral resolution, and detected by high quantum efficiency CCD cameras for a large range of wavelengths (deep UV - near IR), which are liquid-nitrogen cooled for the collection of dark noise-free Raman spectra. A cryostat is available for solid state measurements down to 10 K. A specially designed sample holder can also be used for temperature-dependent liquid phase measurements.

Raman microscopy

A custom-made Raman microscope enables collection of Raman spectra from solid state samples with excitation at 532 nm. The microscope is equipped with a volume Bragg grating filter that permits the collection of low-frequency Raman spectra (down to 50 cm⁻¹). The sample is placed on an XYZ stage that enables surface and depth mapping.

Photoluminescence spectroscopy

A spectroscopic method that measures emission from liquid and solid-state samples with laser excitation that spans the above range of wavelengths. An intensified CCD camera enables the collection of nanosecond time-resolved PL.
FEATURED CURRENT PROJECTS:

Organic Electronics

The structure conjugated molecules and polymers assume in thin films, as a result of the interactions with their neighbors and the film processing conditions, plays a central role in the optoelectronic behavior of these materials. Using RR spectroscopy, we strive to elucidate the effect of structure on the photophysics of these materials gaining insights that directly impact their application suitability. Some examples from our work can be seen below.

**Figure 1:** Effect of the contrasting polarity between side chains and conjugated backbone on the optical and structural properties. (left) Absorption spectra of three different polythiophene-based polymers indicating that the polar side-chain induce disorder in the backbone. (middle) RR spectra probing primarily disordered (top) or ordered (bottom) polymer populations. (right) Quantification of the peak areas and location indicate that matching the environmental polarity with that of the side chains, but contrasting it with the polarity of the backbone, induces torsional order along the polymer backbone.

**Figure 2:** Effect of adding additives to the active layer that segregate to the interface with the metal electrode changing its work function. We used Surfaced enhanced Raman spectroscopy (SERS) to probe the structure of P3HT in neat and blend thin films with the electron acceptor PCBM and the additive HEG-DT on Ag. In the presence of the additive the polymer assumed a significantly more torsionally ordered conformation.

**Figure 3:** (Left) Wavelength-dependent excitation RR spectra of the efficient photovoltaic polymer PCE11. (Right) Effect of temperature on the structure of the polymer. Lowering the temperature seems to increase the torsional disorder, with a phase transition visible around 200 K.

Biophysics

Resonance Raman spectroscopy helps us uncover the interactions between small molecules and DNA. These molecules are intended for the stabilization of the special DNA secondary structure called G-quadruplex for the development of cancer drugs.

**Figure 4:** Modification of the UVRR DNA spectra after addition of platinum complexes, revealing the specific interaction sites.
Biosensors and Conformational templating

Conjugated polyelectrolytes can complex with DNA to detect e.g. base pairing mismatches, viral DNA, etc. but at the same time to template specific polymer conformations for nanotechnology. In both cases, uncovering the interactions between the two macromolecules is key to understanding the function of the polymers as sensors and the DNA as a conformational scaffold.

Figure 5. Complexation of the cationic polythiophene with single-stranded DNA changes both the optical properties (left), as well as the conformation of the polymer (right).

Collaborators:

Funding Sources:

LAB MEMBERS:

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PhD Students:

Eliana Nicolaidou
“Binding interactions of DNA with small molecules and polymers”

Nicolas Charalambous
“Effect of Polar Environment on the Conformation of Conjugated Polymers in Thin Films”

MSc Students:

Kyriaki Koumenidou
“Structural investigation of Ternary Non-Fullerene Acceptor Solar cells”

Alexandros Themistokleous
“Small molecule/DNA interactions for the stabilization of the G-quadruplex”

Eleni Mitrakou
“Conjugated polymers in bioelectronics”

Undergraduate Diploma Thesis students:

Anna Kyrri
“Conformational changes upon doping ternary solar cells”

Despoina Kostogloudi
“Conformational Effects upon Blending Conjugated Polymers with Non-fullerene Acceptors in Ternary Solar Cells”

Evgenia Loizou
“Evaluation of pigments in ancient ecclesiastical icons using Raman spectroscopy”