Spectroscopic and ellipsometric approach to polymer and hybrid thin films

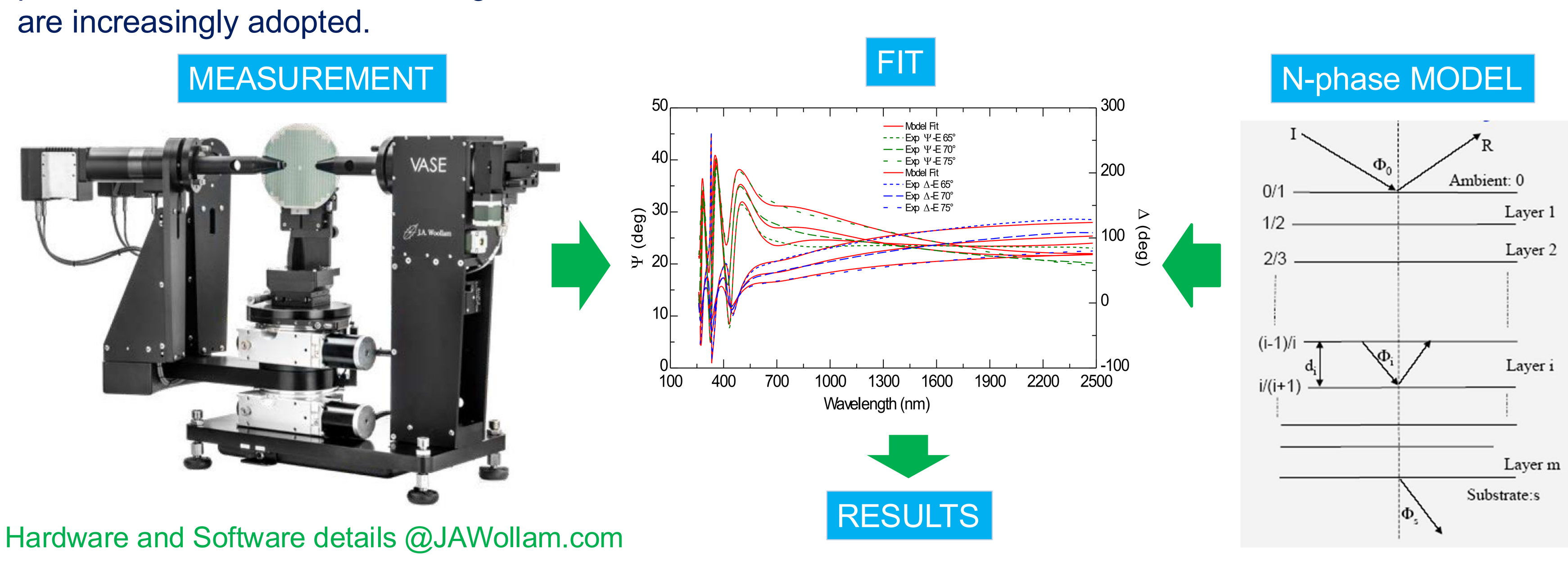
Maddalena Patrini[1], Paola Lova[2], Davide Comoretto[2] and RELY-Photonics Lab. staff[2]

[1]Dipartimento di Fisica 'Alessandro Volta' e Centro Interdipartimentale MADE, Università degli studi di Pavia
[2]Dipartimento di Chimica e Chimica Industriale, Università degli studi di Genova

Thin films of polymers and organic compounds deposited on solid substrates are of high technological importance due to their potential for applications in multidisciplinary micro- and nano-technologies. Their characterization methods must be refined appropriately to obtain information and databases useful in the design and modelling of devices. Spectroscopic Ellipsometry (SE) methodology has technically improved, becoming the method of choice for the optical response of materials, determining both dielectric dispersion and absorption contributions in the UV-vis-IR spectral range.
Advanced modelling allows for investigating conduction properties, structural conformation, all-polymer heterostructures and emitting devices.

SE approach

SE is an optical technique that measures the change in polarization of light after radiation/sample interaction at wavelengths from UV to IR. The parameters often reported are ψ and Δ, which are mainly related to intensity and phase information at variable angles of incidence; other data collection methods such as Jones or Mueller matrix are increasingly adopted.



Hardware and Software details @JAWollam.com

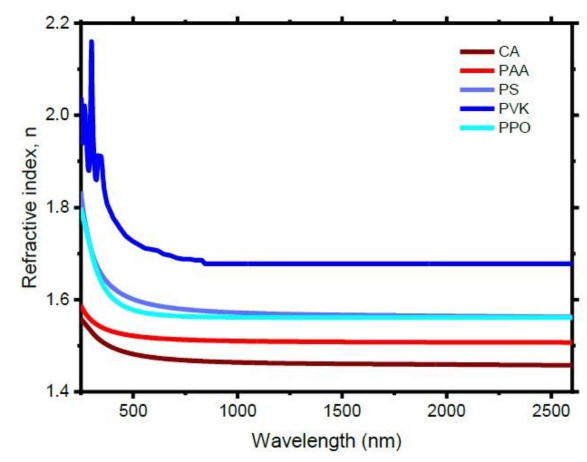
Optical modelling necessary: choosing the wavelength range of interests, start by taking measurements, and build the optical model to describe the layer structure. Request info: substrate, estimates on film thickness and dielectric response or just guesses. The software calculates SE spectral output based on the model and compares it to experimental data; a good match can be achieved through a regression analysis. From the best-fitted physical and unique model, the results are reported, *i.e.*

any PHYSICAL EFFECT or PROCESS that CHANGES MATERIAL DIELECTRIC RESPONSE or THICKNESS

Thickness and Isotropic film *n* dispersion

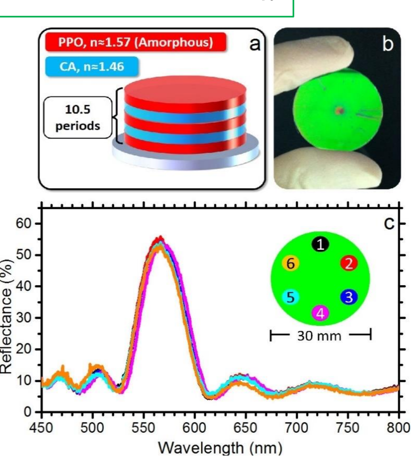
In the transparency spectral region (hyp. $k \cong 0$) SE allows for determining the thickness and refractive index n normal dispersion of deposited thin films, not just the database general material

For isotropic films n can vary due to many factors, such as growth process and conditions, post-treatments, sample structure or even thickness. Surface microstructure (*roughness*) or depth profile of n (*grading*) should be analyzed.



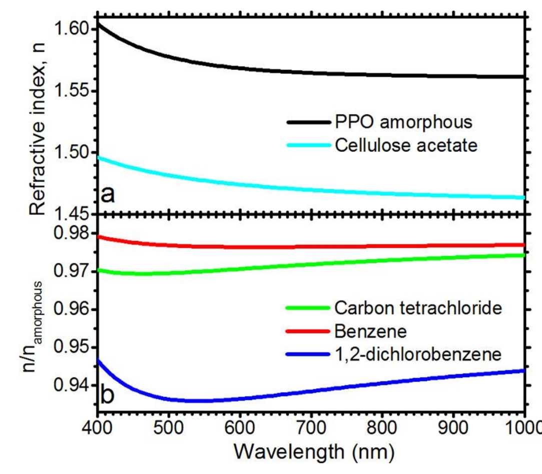
Photonics: search for different polymers that could be dissolved in orthogonal solvents and deposited by spin-coating techniques.[11] The refractive index n dispersion is reproduced using an empirical & few-parameter Cauchy or Sellmeier model, assuming ideal transparency.

$$\varepsilon_1 = n^2 = 1 + \sum_{n=1}^{2,3} \frac{B_n \lambda^2}{\lambda^2 - C_n}$$



Spatial periodic modulation of the dielectric function on a scale comparable to λs of interest has realized highly efficient polymer 1D photonic crystal structures (DBR).[20-22]

Figure of merit is a significant dielectric contrast Δn between the two polymers the *low-n* and the *high-n* material

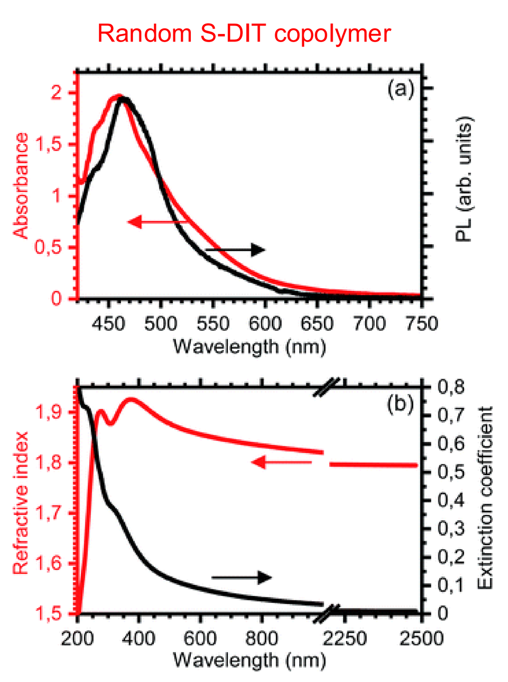


Vapor sensing application: (b) Fractional refractive index variation of PPO thin films after crystallization induced by exposure to different organic guests.[16]

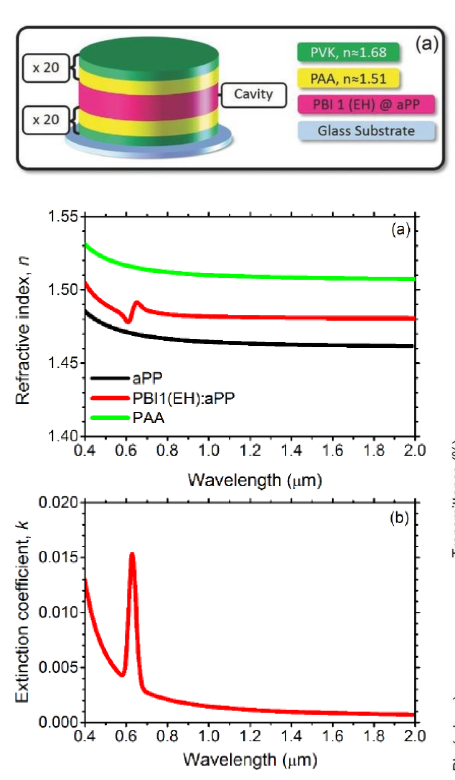
Both Dispersion & Absorption

Extended Wavelength Range and Flexible Measurements at variable angle of incidence give access to the complete material response depending on layer thicknesses and complex dielectric functions

$$\tilde{\varepsilon}(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) = \varepsilon_0\, \tilde{\varepsilon}_r \quad \text{or equivalently} \quad \tilde{n}(\omega) = n(\omega) + ik(\omega) = \sqrt{\tilde{\varepsilon}_r(\omega)}$$

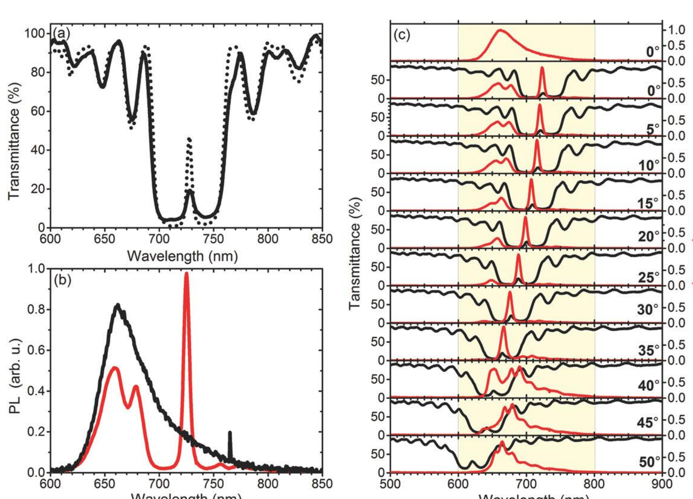


Spectral extension to the ultraviolet (UV) region is desirable because of characteristic electronic resonances or absorption available. The analytical potential in near infrared (NIR) range is based on the extensive radiation penetration depth, strengthening optical modelling of layers, multilayers and interfaces.



SE measurements in strict correlation with optical theory allow a careful design of PhCs.

In the PhC gap region, the photonic DOS is tunable by introduction of a defect layer - an active material is embedded – in between two DBRs. A planar Microcavity is realized, where light confinement and emission can be tailored to specific intervals and shapes.



Electronic and vibrational resonances require modelling by physical Oscillators - Kramers Kronig consistent - including Harmonic, from Lorentzian to Gaussian and intermediate lineshapes.

Simultaneous modelling with Reflectance/Transmittance and PL data is welcome to determine a unique solution.

Blends and Hybrids

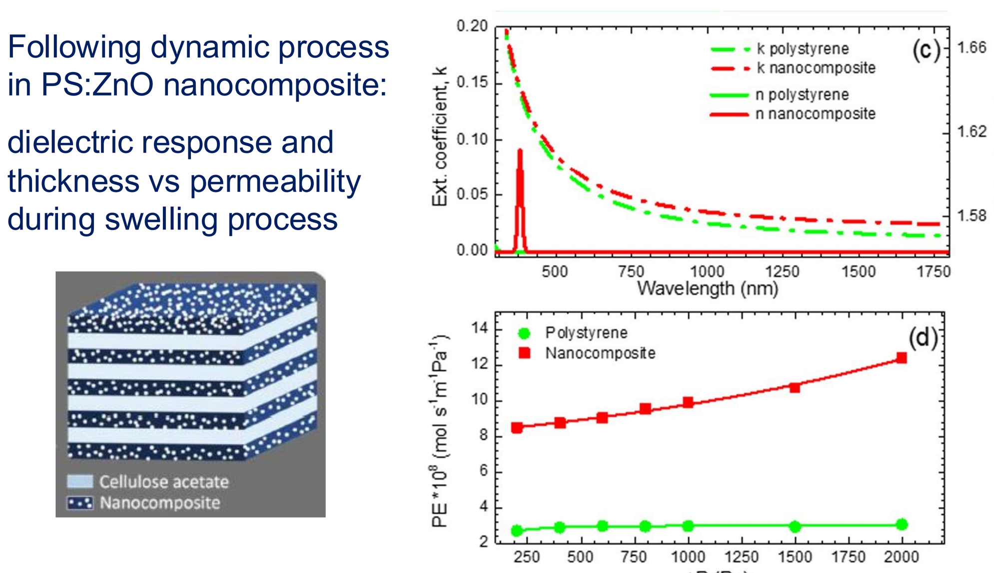
Amplitude and phase information at multiple angles of incidence allow investigation of crystallinity and composition miscibility in more complex systems

Determine the dielectric response of polymer or hybrid mixed blends through previously analyzed single phases and Effective Medium Approximation models
Maxwell Garnett or Bruggeman ($\tilde{\varepsilon} = \tilde{\varepsilon}_A$) with depolarization factor (0 ÷1)

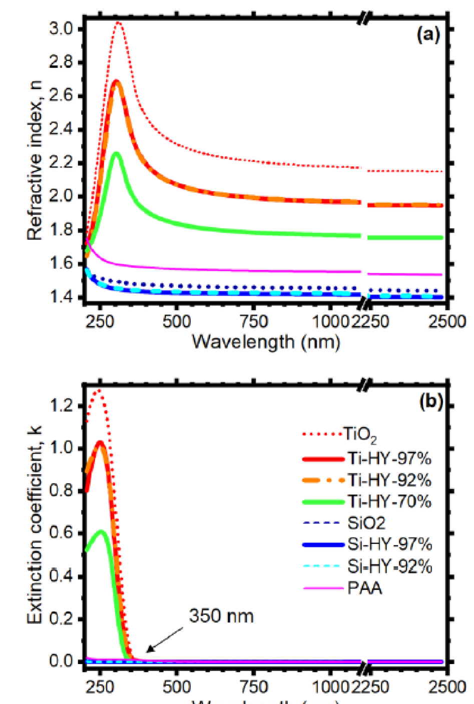
$$\frac{\tilde{\varepsilon} - \tilde{\varepsilon}_A}{\tilde{\varepsilon} + 2\tilde{\varepsilon}_A} = f_B \frac{\tilde{\varepsilon}_B - \tilde{\varepsilon}_A}{\tilde{\varepsilon}_B + 2\tilde{\varepsilon}_A} + f_C \frac{\tilde{\varepsilon}_C - \tilde{\varepsilon}_A}{\tilde{\varepsilon}_C + 2\tilde{\varepsilon}_A}$$

Following dynamic process in PS:ZnO nanocomposite:

dielectric response and thickness vs permeability during swelling process



Hybrids from a polymer matrix and a variable percentage inorganic filler: a low-temperature sol–gel route between the alkoxides of Si and Ti and PAA leads to stable polymer−inorganic hybrid materials with tunable refractive index.



Alternating thin films of the two hybrids allows planar PhC with high optical quality and dielectric contrast as large as 0.64.

Overall trend for single-λ values of n_D versus the Abbe number V_D, an approximate measure of the material's dispersion

$$V_D = \frac{n_D - 1}{n_F - n_C}$$

D,F, C point to 656.3 nm, 587.6 nm, and 486.1 nm λs

Conductivity matters

The basic optical conductivity model is the Drude-Sommerfeld one, which should be applied to explain the optical response of electrically conducting polymers

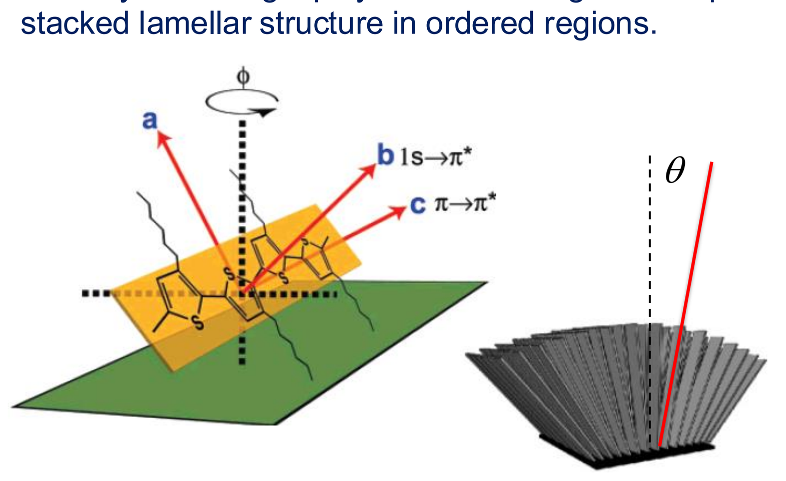
The additive σ_D or permittivity ε_D term from the Drude model is described by the plasma frequency (ω_p) and the momentum-averaged scattering time (τ), alternatively by the charge density (n) and the mobility (μ).
m stands for the effective mass of the charge carries.

$$\tilde{\varepsilon}_D(\omega) = \varepsilon_\infty - \frac{\omega_p^2 \tau}{\omega^2 \tau + i\omega} = \frac{ne\mu}{\varepsilon_0(\omega^2 m\mu/e + i\omega)}$$

The overall Drude-Lorentz model provides accurate values for the electrical properties of the material, including electrical DC conductivity, charge carrier density, and anisotropic mobility.

Among synthetic metals, different formulations of poly(3,4-ethylenedioxythiophene) (PEDOT) have been synthesized and compared to the commercial PEDOT:PSS (Sigma-Aldrich, Ossila Ltd.) when cast as thin films on different substrates.

Semicrystalline rigid polymers are thought to adopt a stacked lamellar structure in ordered regions.



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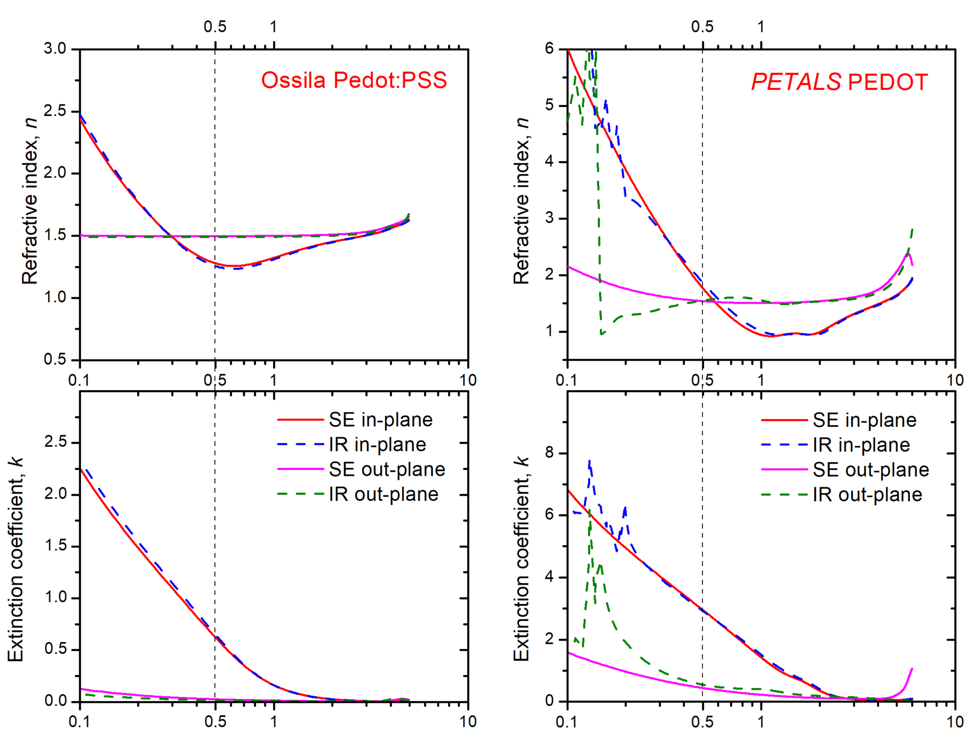
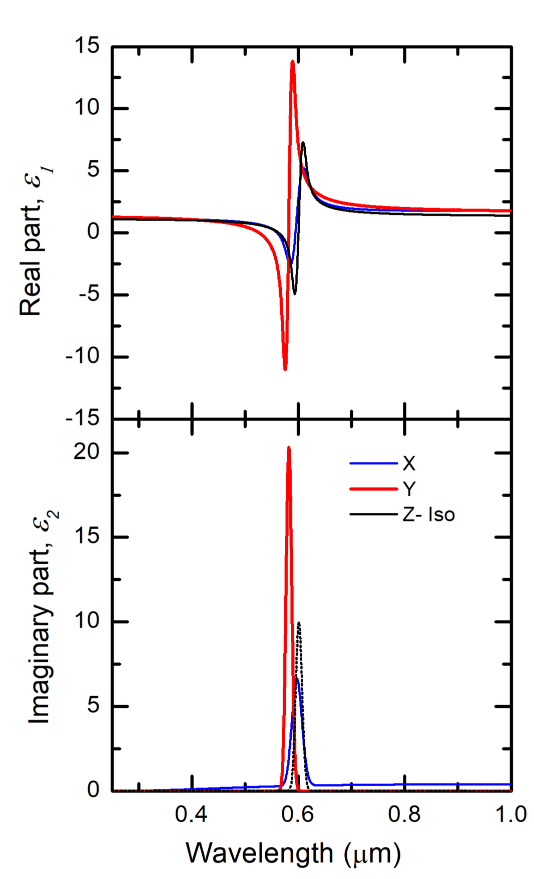


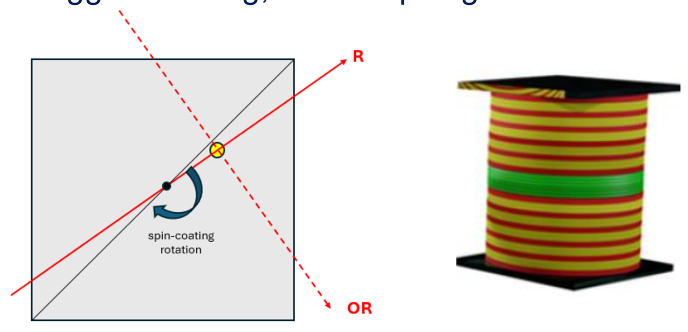
Uniaxial scheme, with top-hat spread in θ of ± 26°

Exploiting Anisotropy

Generalized Ellipsometry data types (Jones & Mueller Matrix elements) expand the SE sensitivity in the case of intrinsically anisotropic material or preferential molecular orientation
Determination of a complete and consistent set of uniaxial or biaxial dielectric functions with Euler angles θ, ψ, ϕ

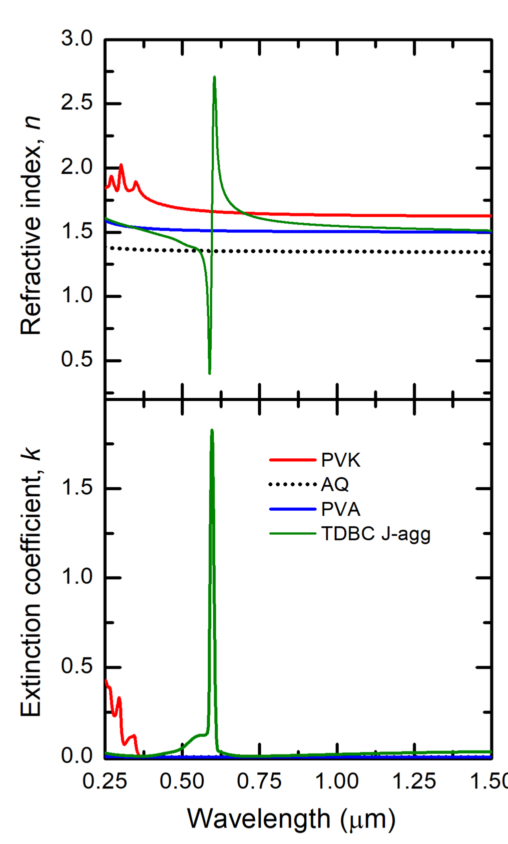


Molecular planarity of TDBC facilitates an ordered and rigid sheet-like structure in the j-aggregates of cyanine dye with an aggregation number of about 10.
Modulating spin-coating growth conditions allows both isotropic and anisotropic *J*-agg structuring, with a slip angle of θ~20°.



Two all-polymer multilayer DBRs with high dielectric contrast have been realized by alternating PVQ/AQ thin films. They are not absorbing visible light and act as dielectric mirrors for a TDBC *j*-aggregate doped PVA film, realizing a PhC planar microcavity.

Thanks to PhC design control, PL spectrum of *j*-agg at λ ~ 585 nm is spectrally overlapped to DBR stop band.



TDBC doped PVA films with peak absorption coefficient 10^6 cm^{-1} and thickness of 10s nm are well-suited for strong coupling optoelectronic applications, realizing exciton-polariton microcavities operating at RT. Rabi splitting energies depend on dye concentration and light polarization.

Regione Lombardia

MUR

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