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Excited States Photoreactions Study and Multiparametric Probing by Fluorescent Methods

Vladimir Tomin

Słupsk location

Słupsk

Sity Hall

Pomeranian University
Main Building

Institute of Physics
Pomeranian University in Słupsk
76-200 Słupsk, POLAND

Institute of Physics

Specialities for undergraduate students:

Physics and Technical Physics

Sections:

Environmental Physics

Applied Physics

Experimental Physics

Environmental Physics Section

Head prof. Bogdan Wóźniak

Development of a satellite methods for the Baltic Ecosystem monitoring.

Focus on aquaring information concerning physical, chemical i biological properties of sea waters and accompaning processe

SatBałtyk project funded by EU via European Regional Development Fund (contract No. POIG.01.01.02-22-011/09

Applied Physics Section

Head prof. A. Jaworek

Electrospraying and Electrospinning applications for nanotechnology:

-thin solid film deposition, porous microlayers deposition, nanofibers production, nanocomposite materials

Spectroscopy of electrical discharges in gases, water klasters and H-bond complexes

Experimental Physics Section

prof Vladimir Tomin

Marie Curie Actions
Nano²fun
Initial Training Network

Fundamentals of CT (Charge Transfer) and ESIPT (Excited State Internal Proton Transfer) photoreactions in organic solutions (benzonitriles and 3-hydroxychromones, systems with dual fluorescence):

-mechanisms of electronic spectra broadening due to intermolecular interactions;

-photoreactions from different states of heterogeneity;

-simple tests of excited-state reactions character verification (kinetic or thermodynamic);

-study of aprotic forms of ESIPT solutes as additional instrument for probing complex systems;

-generation of white light with one solute in sample.

Our aim is to develope efficient and reliable spectroscopic tools for visualization and sensing different sites of probe incorporation with two-color and multicolor fluorescent probes

Research Facilities and Infrastructure

-Spectrofotometers and fluorometeres for basic spectroscopy: HITACHI F2500, F7500, U3900H, U 2810 (equipped with polarizes and thermoregulation), compact spectrometeres (Maya 2000, Spectra Laser) with fiber optic connectors;

-Lab of kinetic measurements with OPG-401 tunable in UV/VIS (45 ps pulse), streak camera HAMAMATSU C4334-01 on registration;

-Microscope Olympus CKX41 with CCD registration;

-Gaussian package and hardware facilities for quantum chemical calculations, access to PL-Grid project with advances facilities for simulations.

Research Facilities and Infrastructure

Regional Laboratory for Fluorescence Kinetics Study

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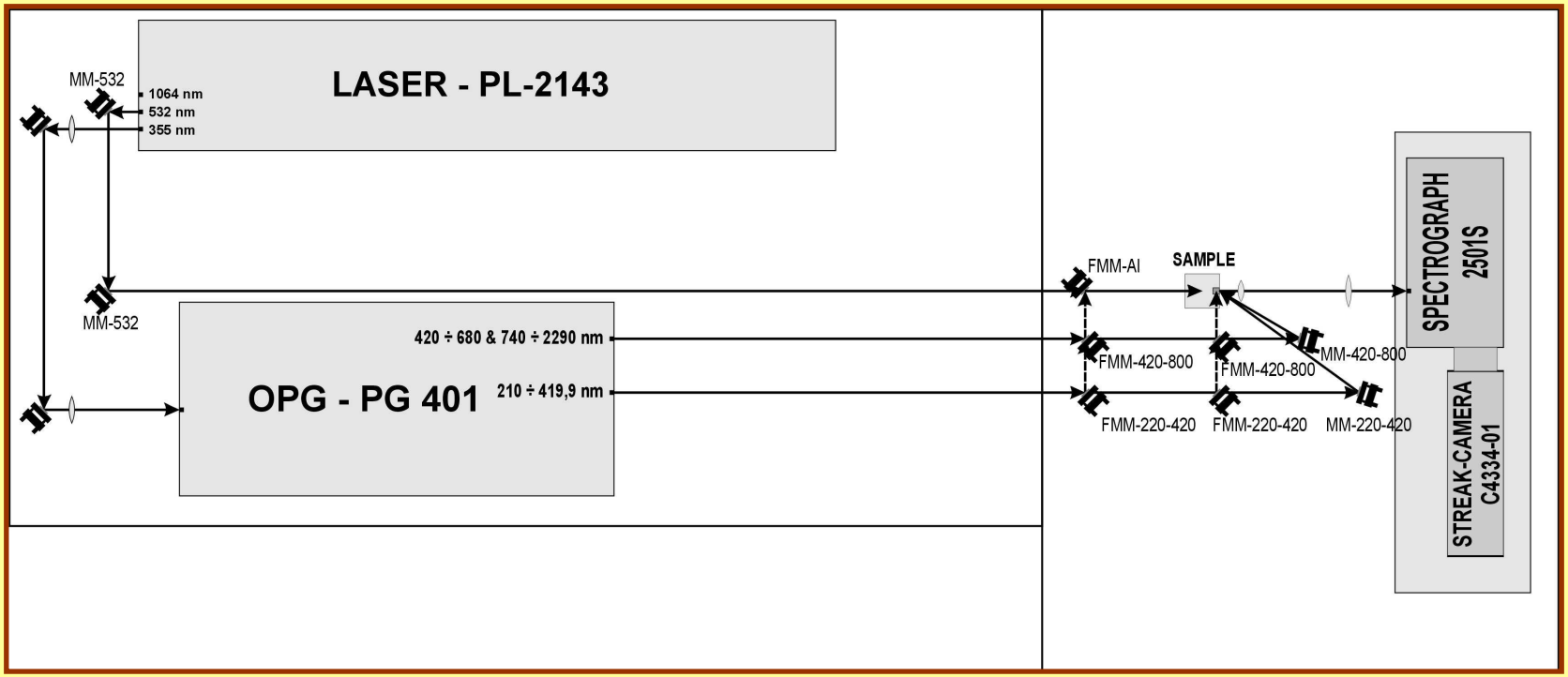


Optical Parametric Generator (OPG) pulse duration $t_{0.5}$=44 ps,

Excitation Spectral Range A (210-419 nm)~ 70-130μJ;

Excitation Spectral Range B (420-2200 nm) ~300-1000μJ

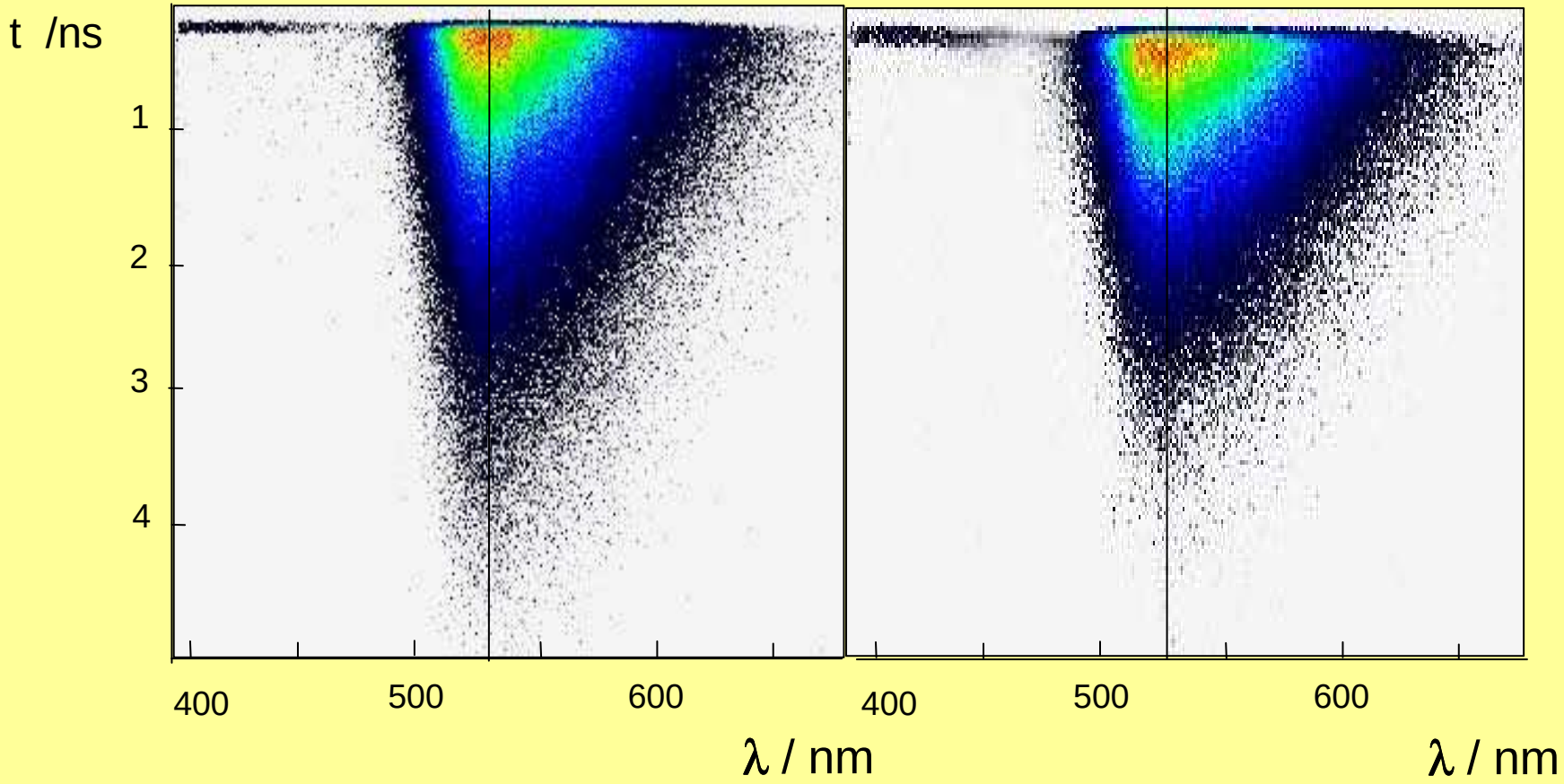
Hamamatsu C4334-01 Streak Camera, $\Delta\lambda$~0.5-0.02nm; Δt from 2 ps/pixel

ESIPT reaction from the S_2 state

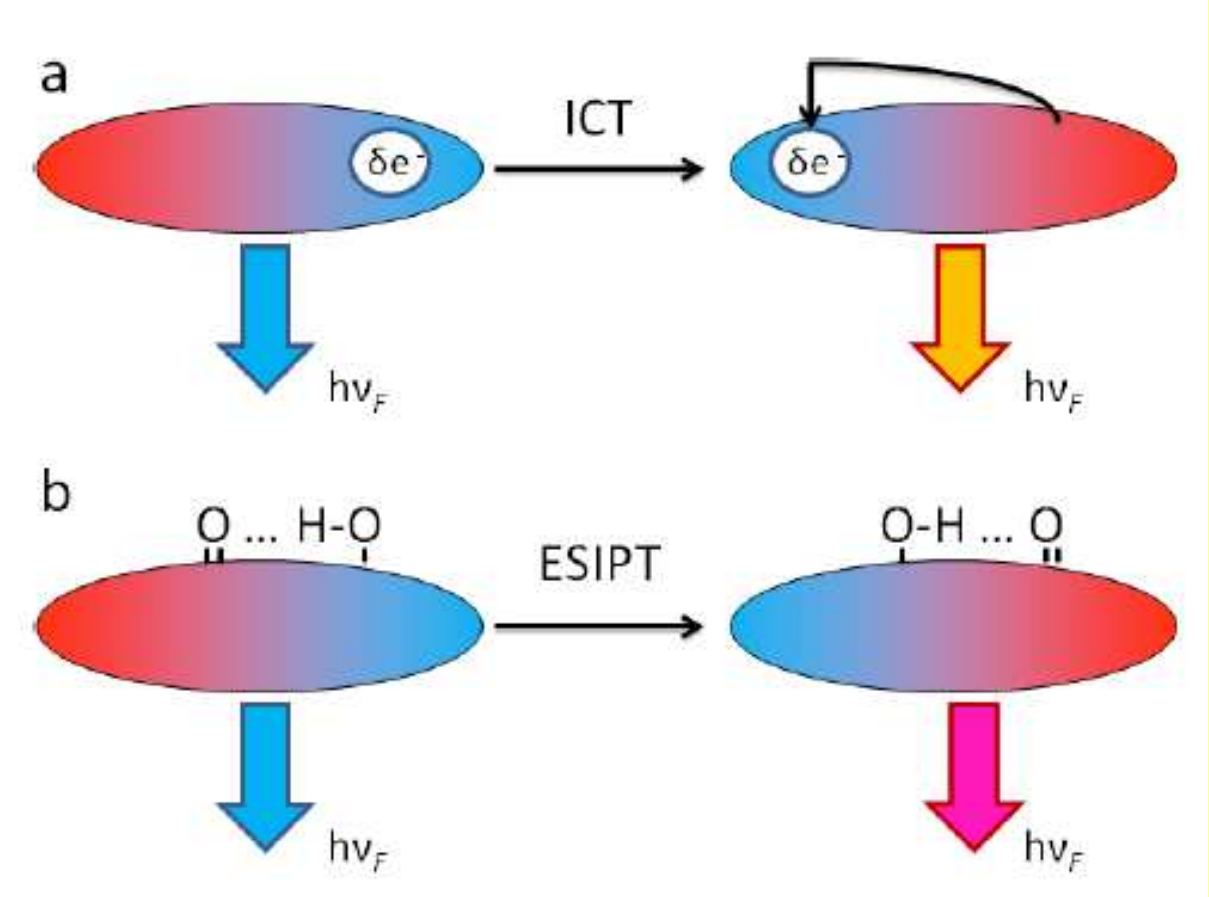
(The matrices of 3-HF flourescence in ethyl acetate)

λ_{ex} = 300 nm

λ_{ex} = 340nm



The mechanisms of generation of spectral shifts in the cases of ICT and ESIPT

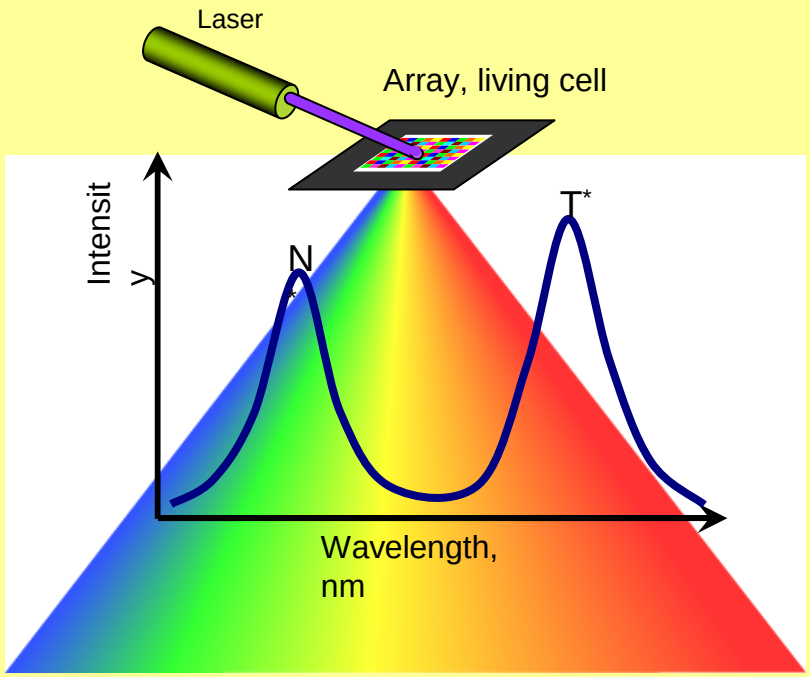


Demchenko A.P. Methods Appl. Fluoresc. 1 (2013) 022001

Two-band ratiometric detection

Ratiometric dual wavelength measurements (λ-ratiometry) are very popular, particularly in case of nanosensors combining both an indicator and a reference dye in the same sample or in a single bead.

Two-band ratiometric detection



ESIPT molecular probes are practically ideal for λ-ratiometry with *single* emiter.

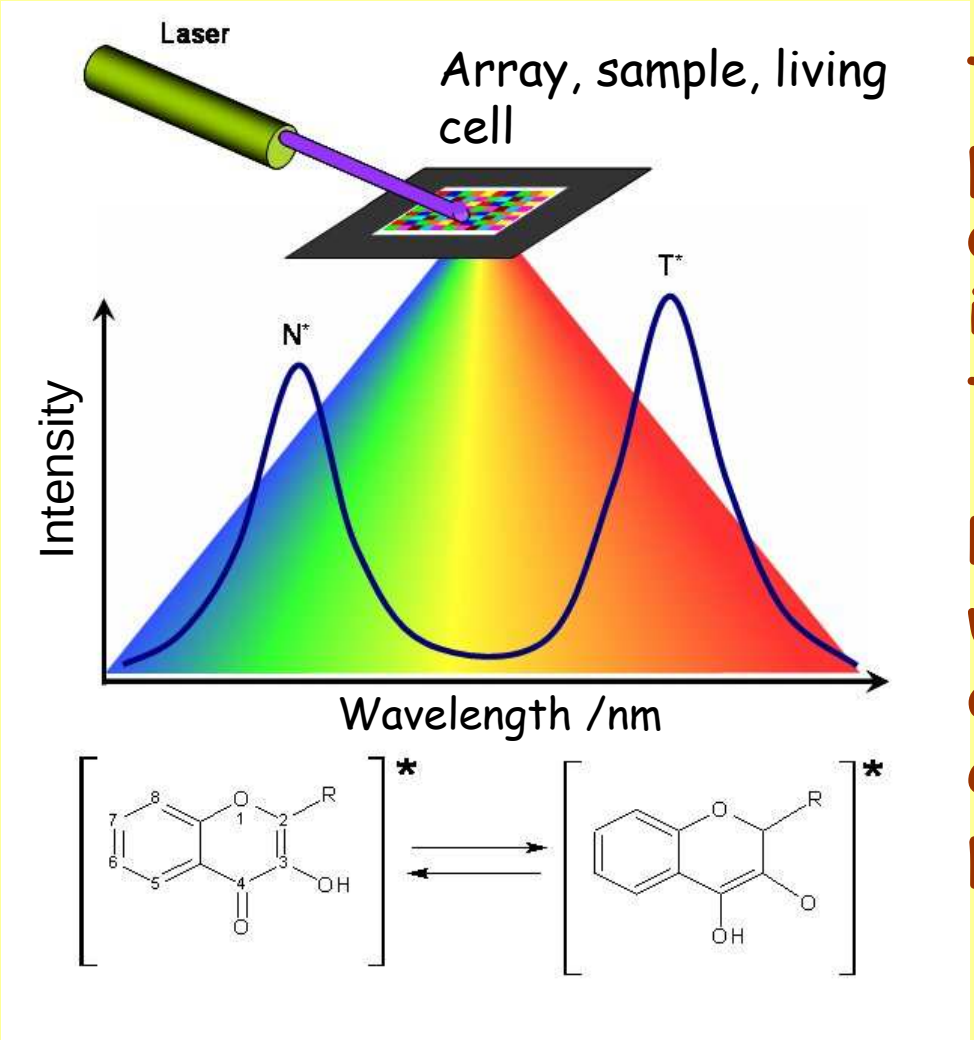
Ratio I_N/I_T is self or internal calibration parameter:

-insensitive to instrumental factors,concenration of probe, uncontrolled quenching by impuruties;

-high sensitivity to intermolecular interactions controlling ESIPT rate

A.Demchenko,Introduction to Fluorescence Sensing (Springer, 2009).

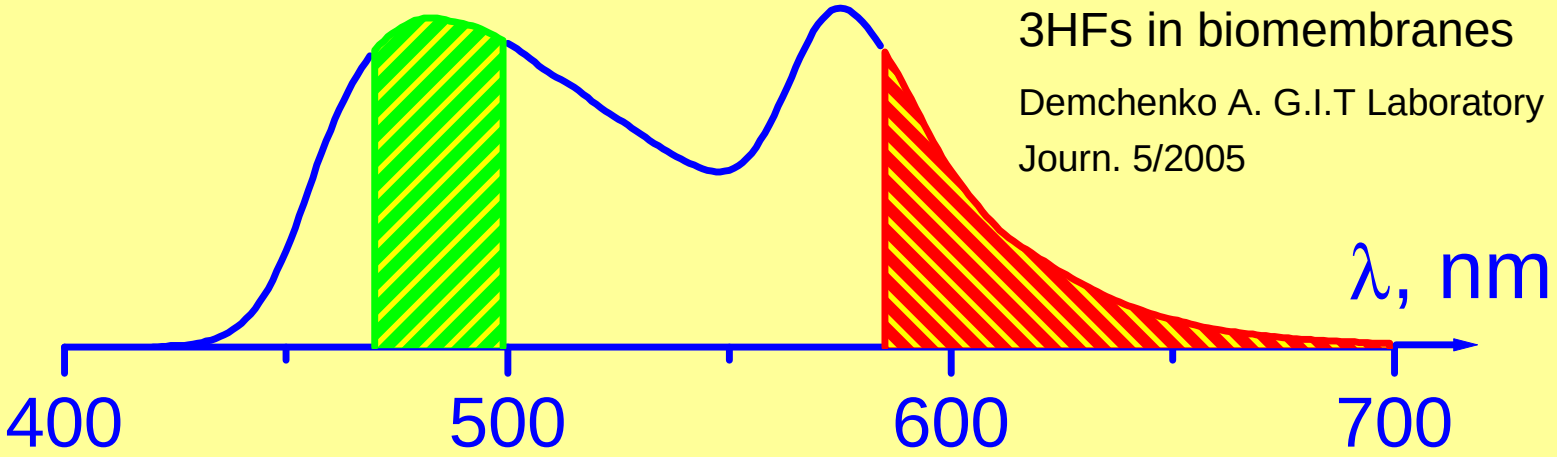
Two-band ratiometric fluorescence detection

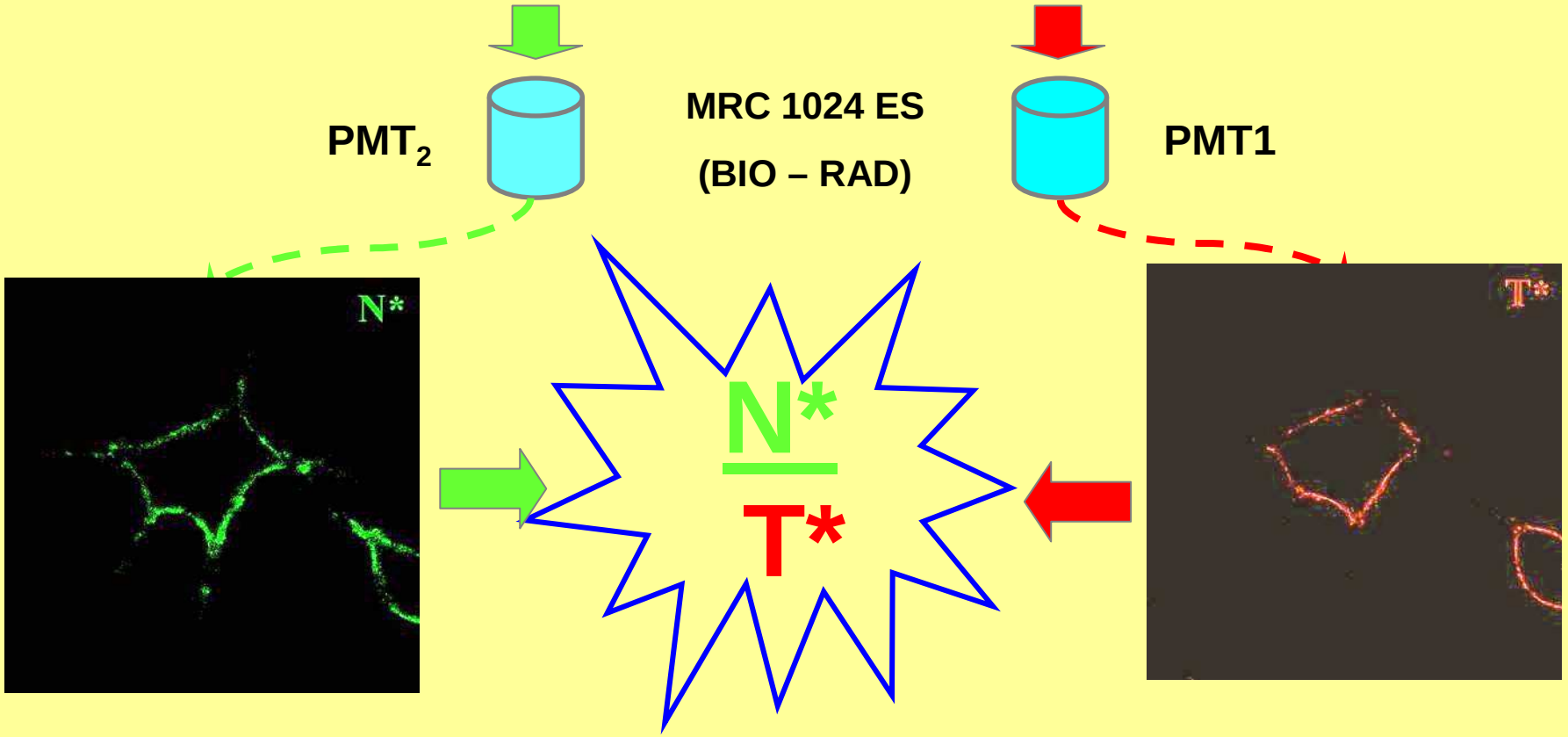


The sensing signal is produced by the changing of I_N / I_T even when there is no solvatochromism for the bands!

Ratio I_N / I_T is associated with fluorescence colour and, therefore, visual estimation of environment properties is possible!

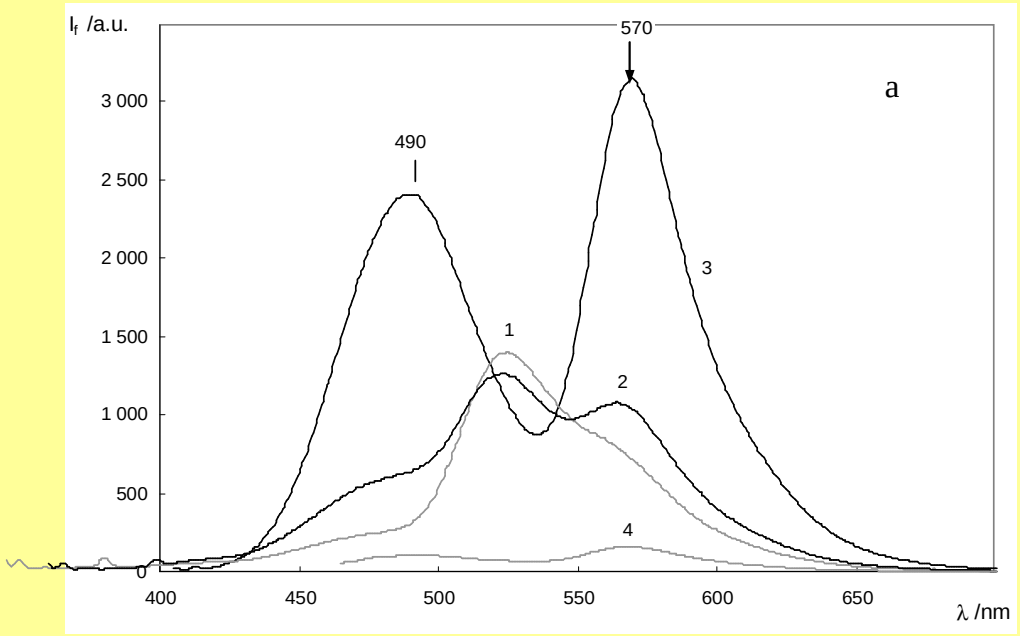
Ratiometric image by confocal microscopy





FET (diethylamino-3HF) in dichloromethane .

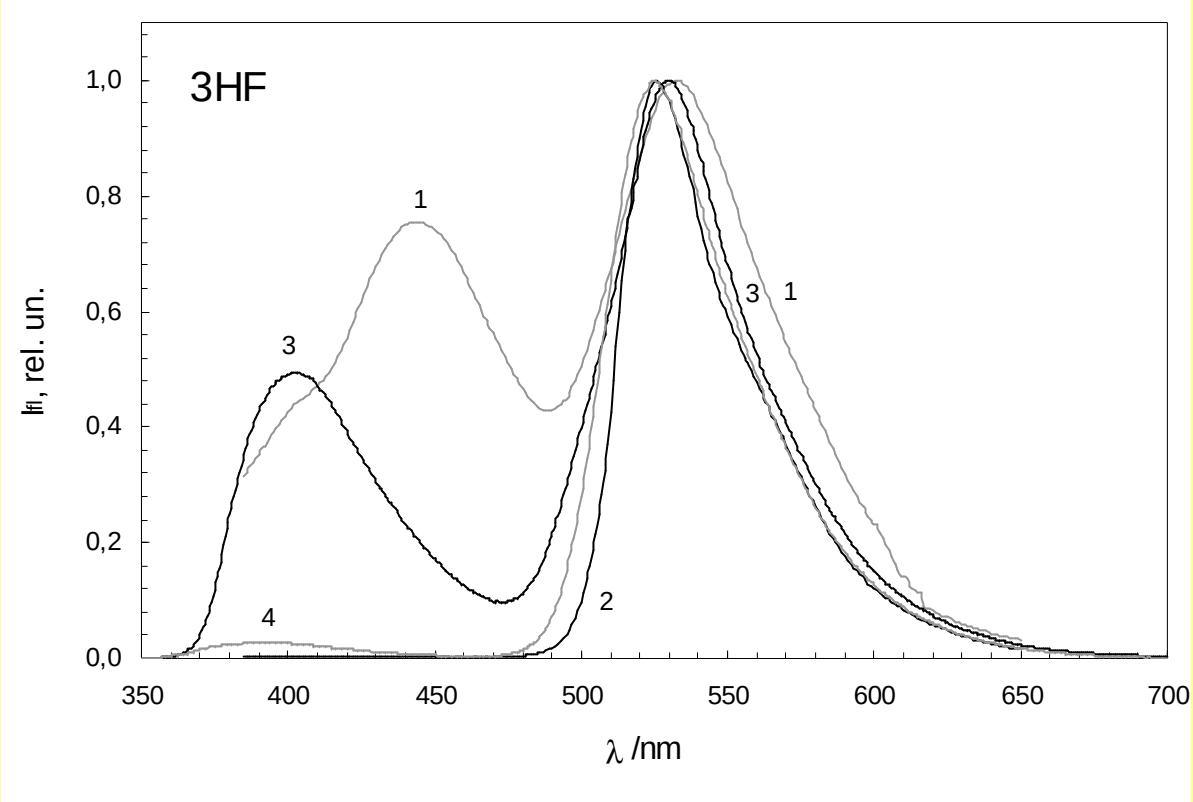
λ_{ex}: 340 (1), 355 (2), 400 (3) and 460 (4) nm T=20°C,



Control of ESIPT rate by streching samples

Fluorescence spectra of 3-HF in (*1*) unstretched and (*2*) two, (*3*) four, and (*4*) sixfold stretched PVA films.

Excitation 350 nm.

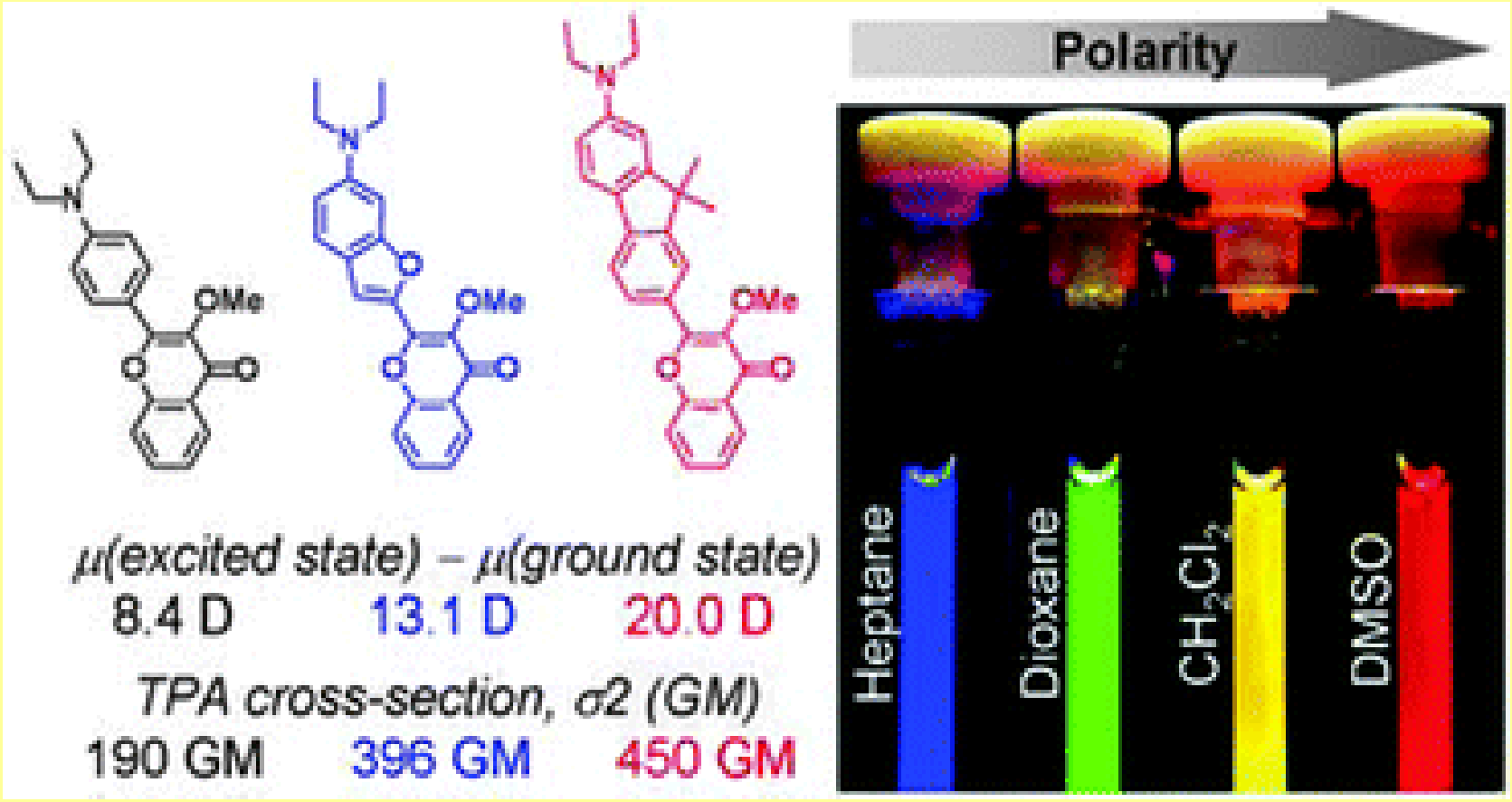


Applications of CT and ESIPT probes

Monitoring such parameters as polarity, viscosity, temperature, local electric field, pressure, pH, H bonds, stretching of films doped with dye.

Obviously, *there are no universal probes* and, hence, in each case one needs in special chose of proper probe

3-methoxychromones CT probes with strong solvatochromism and 2ph absorption cross section



O.A. Kucherak et al, ***PCCP***, 2012,**14**, 2292-2300

Multiparametric fluorescence probes

ESR 12 PhD student

Objectives:

microcharacterization of systems for 2 ph applications with CT and ESIPT probes;
developing of spectroscopic methods for characterization and modelling organic materials for 2-ph applications

Tasks and methodology:

monitoring of main physico-chemical properties molecular and polymer samples doped with dyes and ONP;
methods of fluorescence, polarization and laser picosecond spectroscopy, exploration of the model of inhomogeneous broadening of dye electronic spectra and REE effects

Participants & Cooperation

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Prof. Jacek Fisz
Lab for Biomedical Photonics and Nanotechnology, Faculty of Health Sciences, Collegium Medicum N. Copernicus University, Bydgoszcz, POLAND

publications

V. I. Tomin. Proton Transfer Reactions in the Excited Electronic States. In: Hydrogen Bonding and Transfer in the Excited State. Wiley@Sons. Ltd, N. York, ed. Ke-Li-Han

V.I. Tomin. Physical Principles Behind Spectroscopic Response of Organic Fluorophors to Intermolecular Interactions

in: Springer series on Fluorescence, Methods and Applications. V.8. Advanced Fluorescence Reporters in Chemistry and Biology Springer. Heidelberg Dordrecht London New York 2010 Ed. A. Demchenko.

Thank you for your time!