Nano2Fun @ UniPr

Nano2Fun Kickoff Meeting

Parma, September 19-20, 2013

Francesca Terenziani

UNIVERSITÀ DEGLI STUDI DI PARMA

Founded in 962 a.D.

> 30.000 students

> 1.900 faculty and staff members

79 Degree Courses

32 PhD Courses

18 Departments
- Physical & Natural Sciences
- Engineering
- Medical Sciences
- Human & Social Sciences

Department of Chemistry

The first Chemical Institute in Parma dates back to the XIX century

Present building:

Staff
- 49 faculty
- 20 technical & administrative

Department of Chemistry

Bachelor:
Chemistry

Master:
- Chemistry
- Industrial Chemistry

PhD Courses:
- Chemistry
- Materials Science*

TEACHING

Post-bachelor course:
Packaging

** In collaboration with CNR*

Department of Chemistry

First-ranked Department in Italy for research in Chemistry

- Supramolecular Chemistry
- Catalysis
- Biochemistry
- Crystallography
- Green Chemistry
- Theoretical Chemistry
- Food Quality and Safety
- Advanced Materials
- Cultural Heritage Conservation

RESEARCH

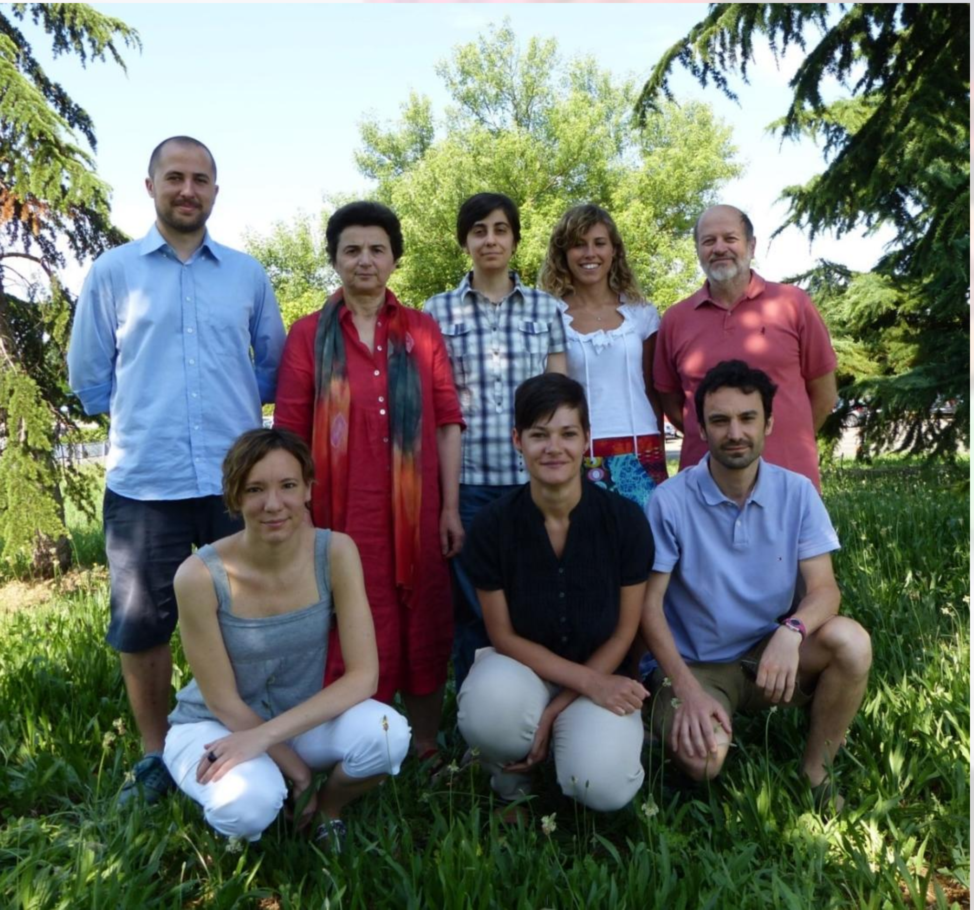
“Advanced Functional Materials” group

Faculty
Anna Painelli
Alberto Girlando
Matteo Masino
Francesca Terenziani

Post-Doc
Cristina Sissa

PhD
Francesca Delchiaro

MATERIALS
- Organic chromophores
- Organic semiconductors
- Charge-Transfer crystals
- Organic nanoparticles



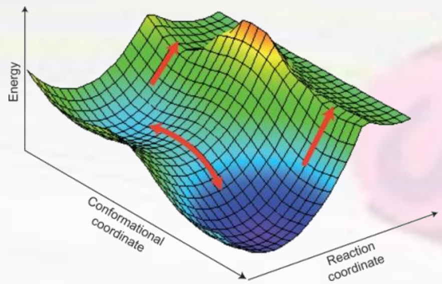
TECHNIQUES

Optical spectroscopy
- UV-Vis
- Fluorescence & lifetimes
- IR & micro-IR
- Raman
- Cryogenic techniques
- High pressure techniques

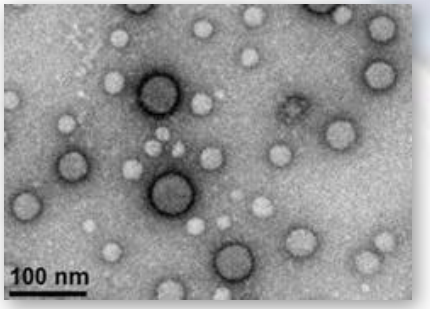
Theoretical models & methods
- Parametric Hamiltonians
- Essential-state models
- Hubbard-like models

Role in the Nano2Fun Project

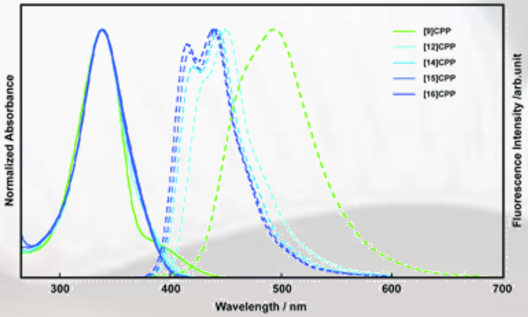
Project Management (administrative and scientific)



Theoretical models
- Medium effects
- Intermolecular interactions
- Charge transfer and energy transfer
- Nonlinear optical responses



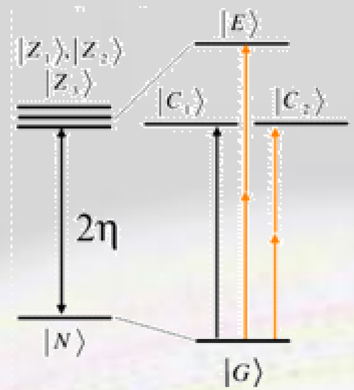
Organic Nanoparticles
- Preparation
- Spectroscopic characterization
- Optimization



Linear optical characterization
of molecules and nanoparticles

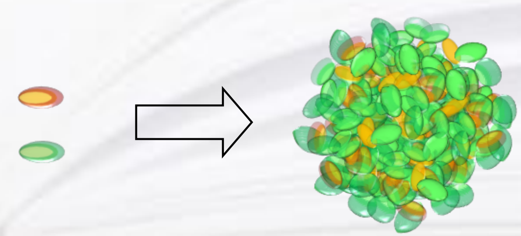
Theoretical models

Essential-State Models
- Minimal electronic basis (main resonating VB structures)
- Coupling with effective molecular vibrations and medium



Key Points
- Some general understanding is gained *at the expense of some details*
- Need for physical-chemical insight (*no black-box*)
- Parameters from experiments or first-principle *(semiempirical)*

Bottom-Up Modeling Strategy
Parameters extracted for chromophores in solution are used to predict the properties for interacting molecules (in multichromophores, solid state, nanoparticles, etc.)

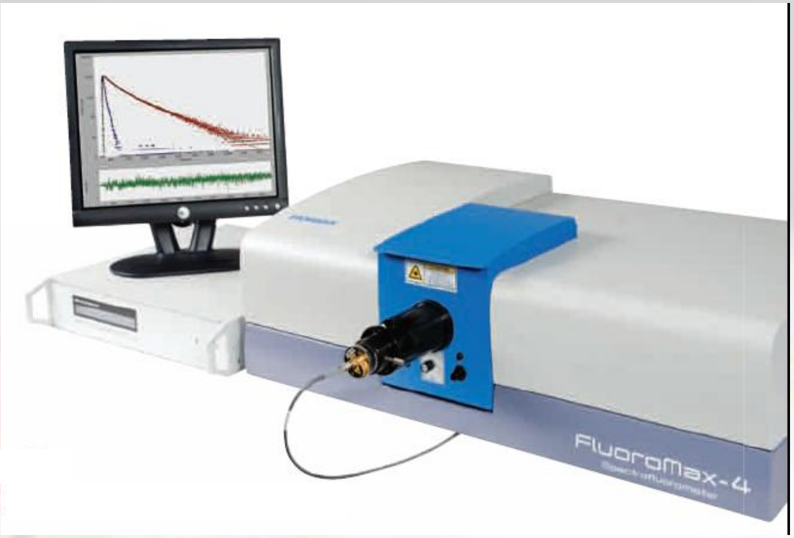


Optical Spectroscopy

Uv-Vis: Perkin-Elmer Lambda 650 with accessory for variable-angle reflectance

FT-IR/NIR: Bruker IFS66 with microscope, setup for luminescence and ATR

Fluorescence: Horiba Jobin-Yvon FluoroMax3 with polarizers and TCSPC for lifetime. Sources: Xe lamp + nano-LEDs



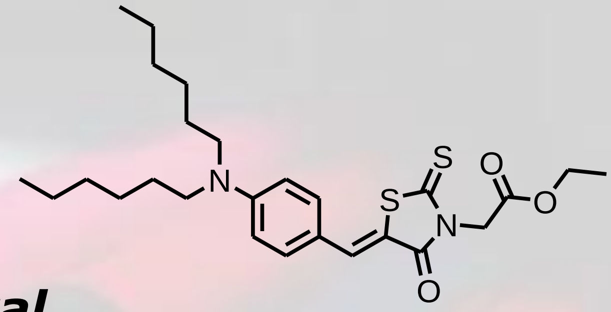
Micro-Raman: Renishaw System-1000 with Krypton laser

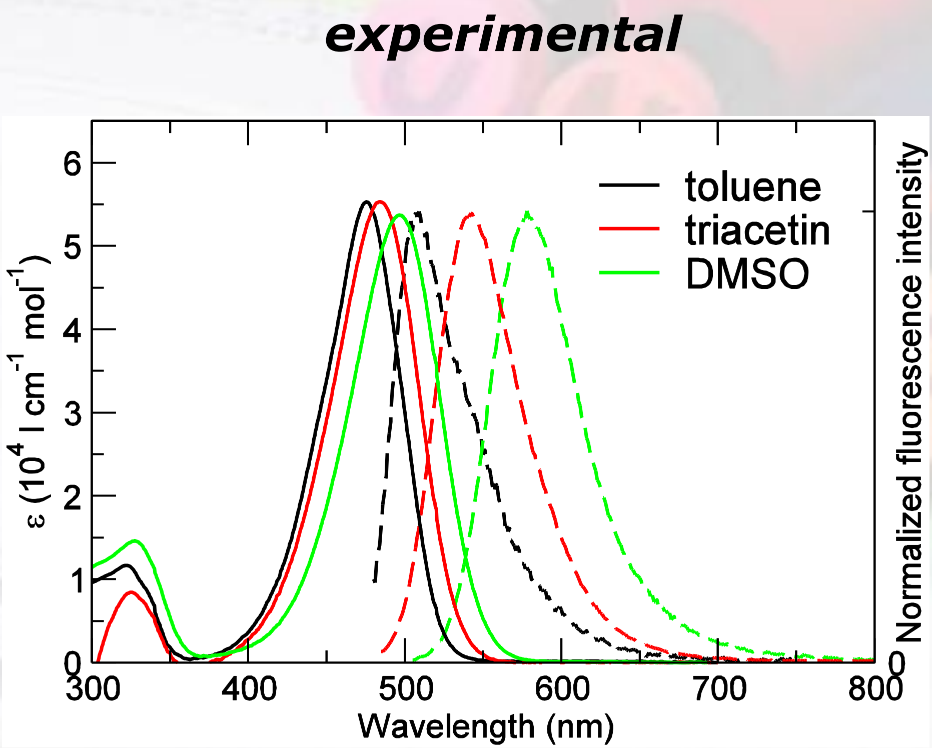
Low-vibration helium-gas closed-cycle micro-cryostat

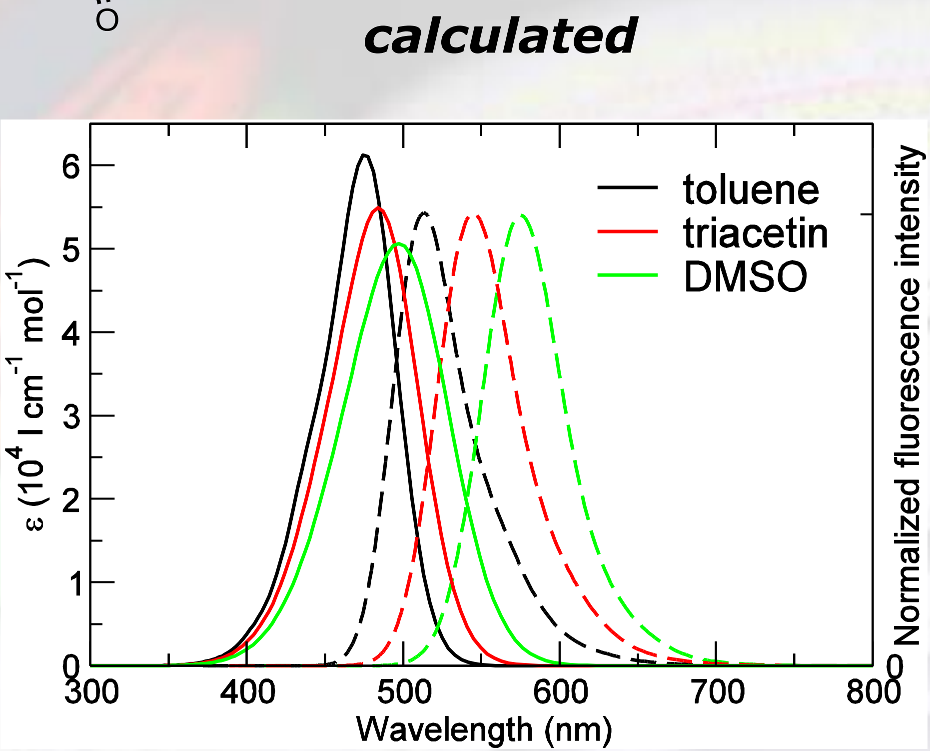
Custom-designed gasketed **diamond anvil cell**, able to fit under the microscope

Cryogenic system for liquid samples: Oxford Instruments (liquid nitrogen, cuvette in exchange gas)

A case study







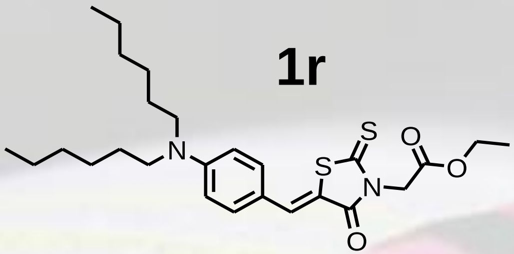
⇓

molecular parameters

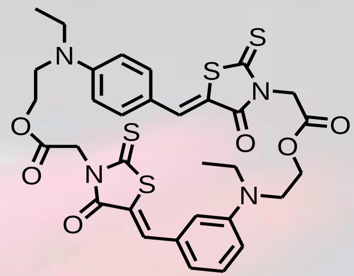
polarizability ⇒ **exportability of parameters**

A case study

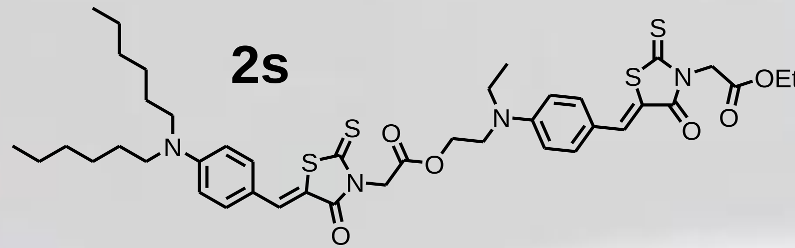
1r



2a

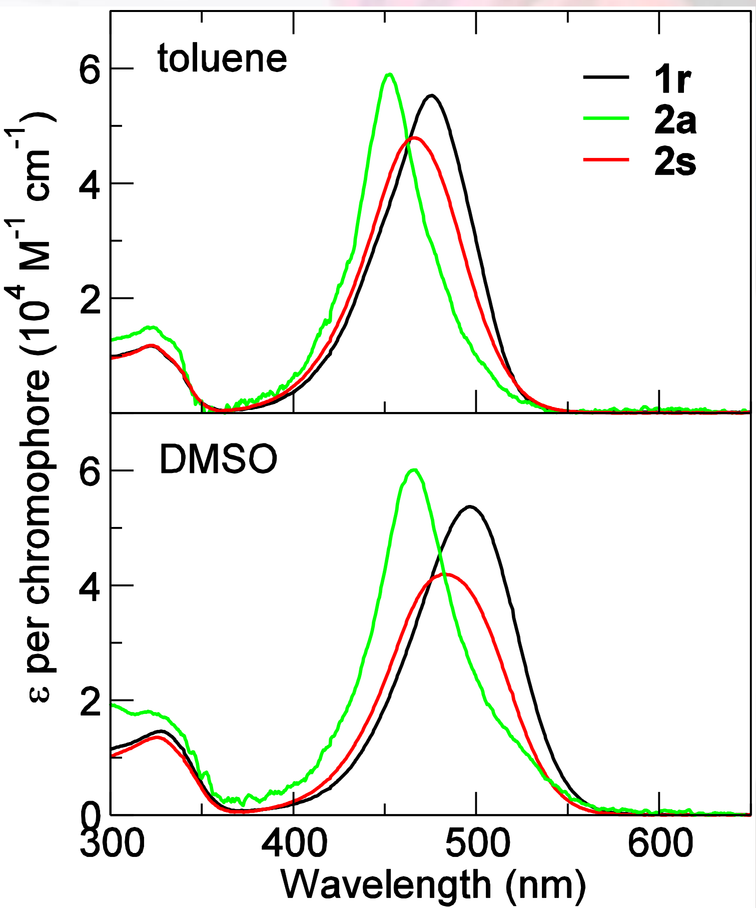


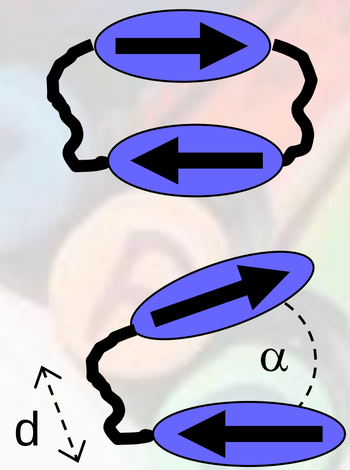
2s



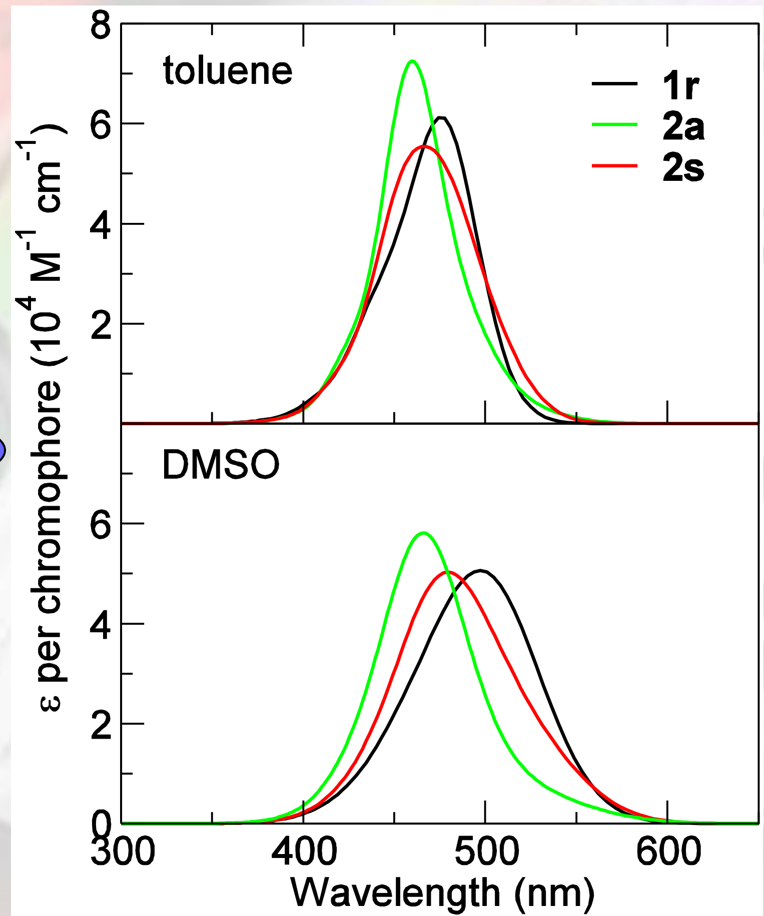
experimental

calculated





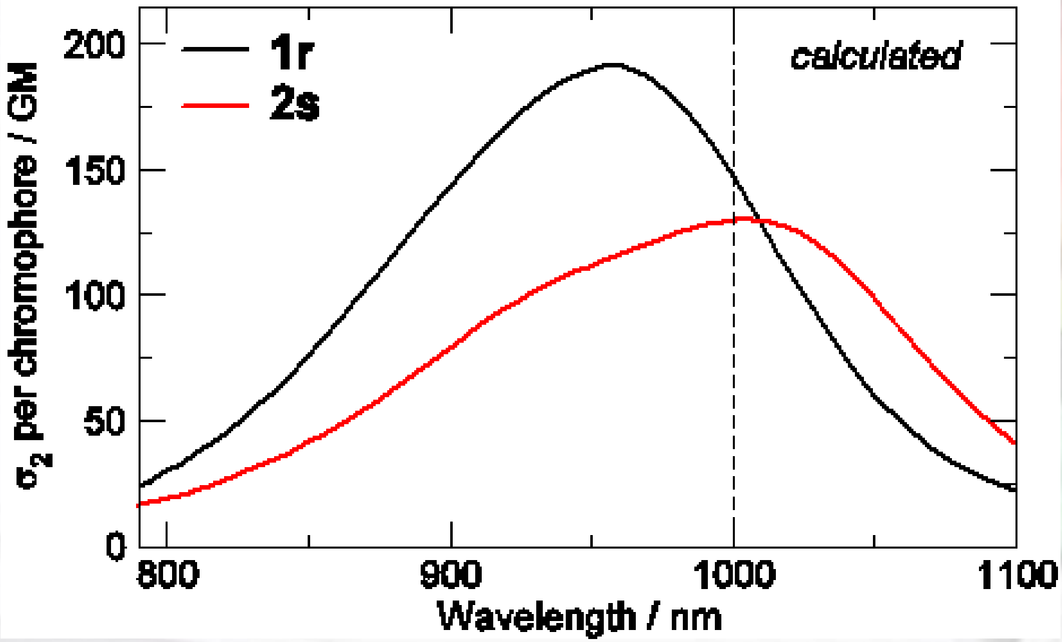
d = 7 Å
α = 40°



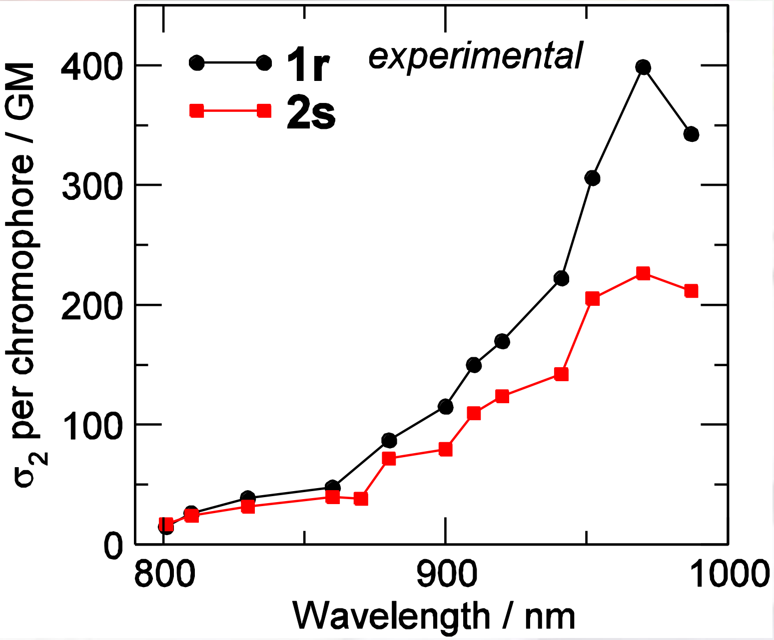
A case study

Two-Photon Absorption

calculated

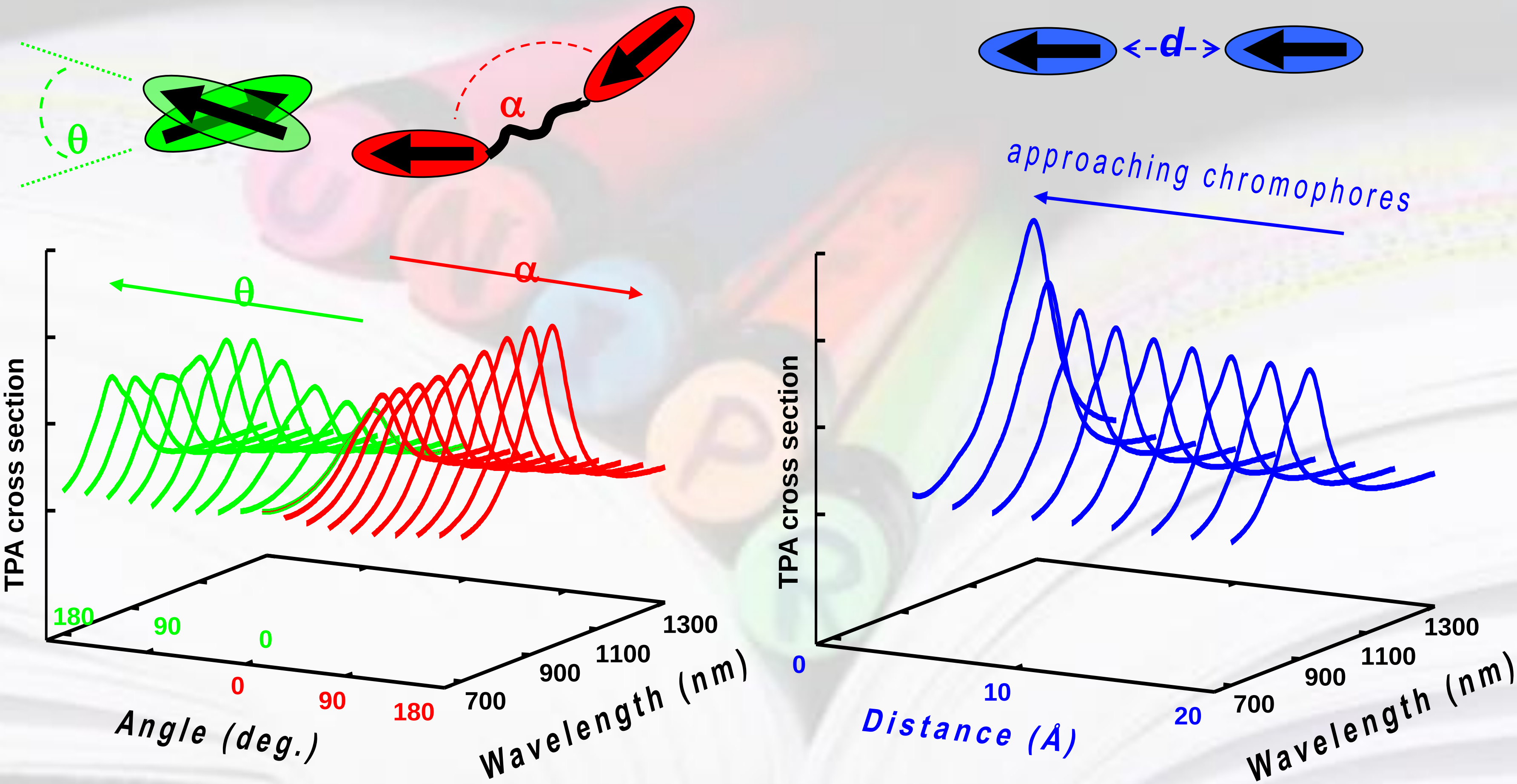


experimental



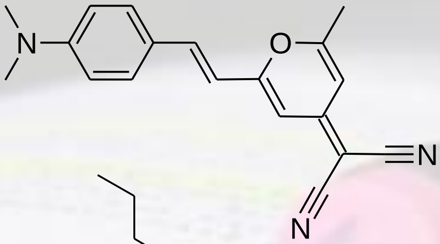
ChemPhysChem **7** (2006) 685

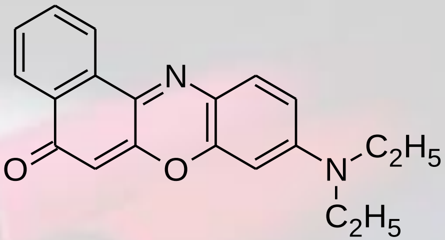
Tuning of NLO responses

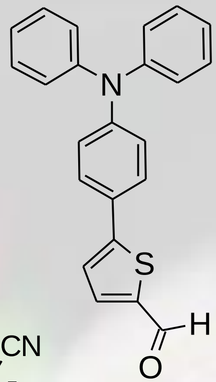


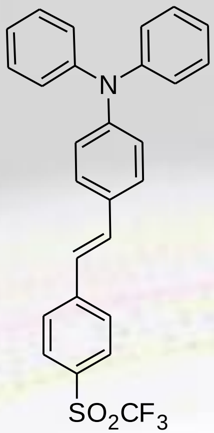
ChemPhysChem, cover March 2006

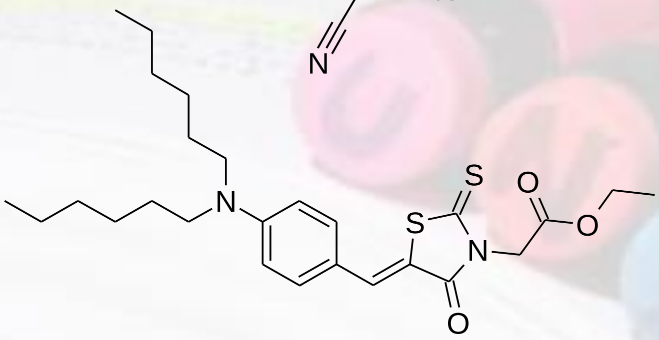
Dipolar chromophores

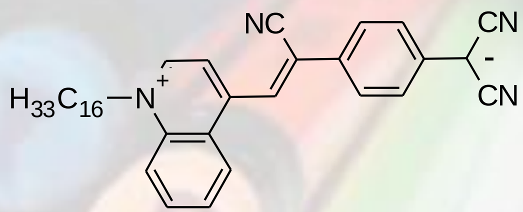


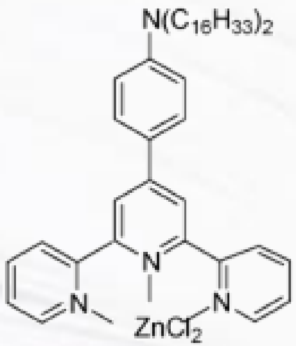


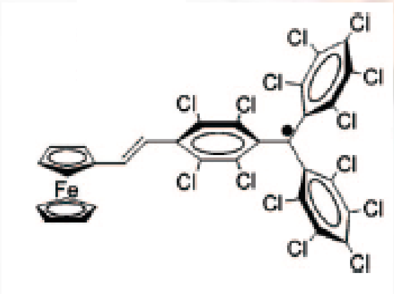










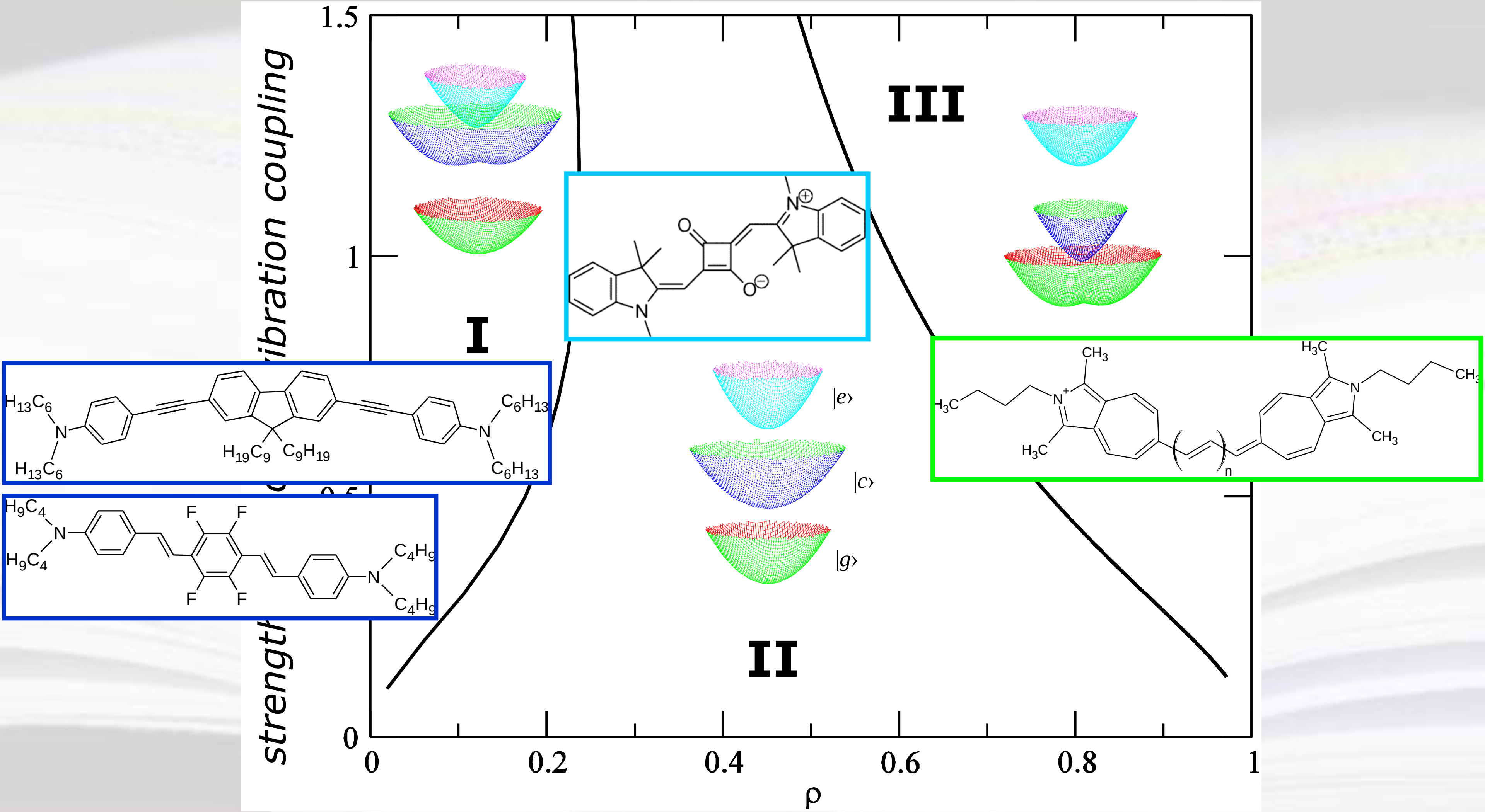


- **Vibronic effects**
- **Solvatochromism**
- **Inhomogeneous broadening**
- **Nonlinear optical properties**

J. Phys. Chem. A 106 (2002) 6286
J. Phys. Chem. B 108 (2004) 10743
Phys. Chem. Chem. Phys. 11 (2009) 9450
…

Quadrupolar chromophores

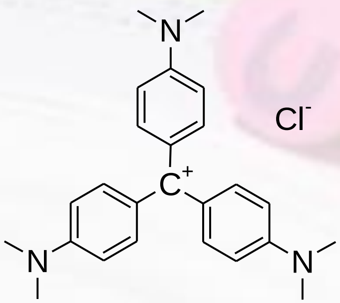
Symmetry breaking

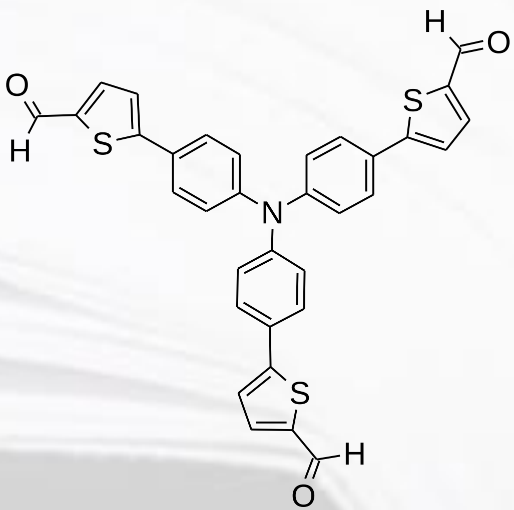


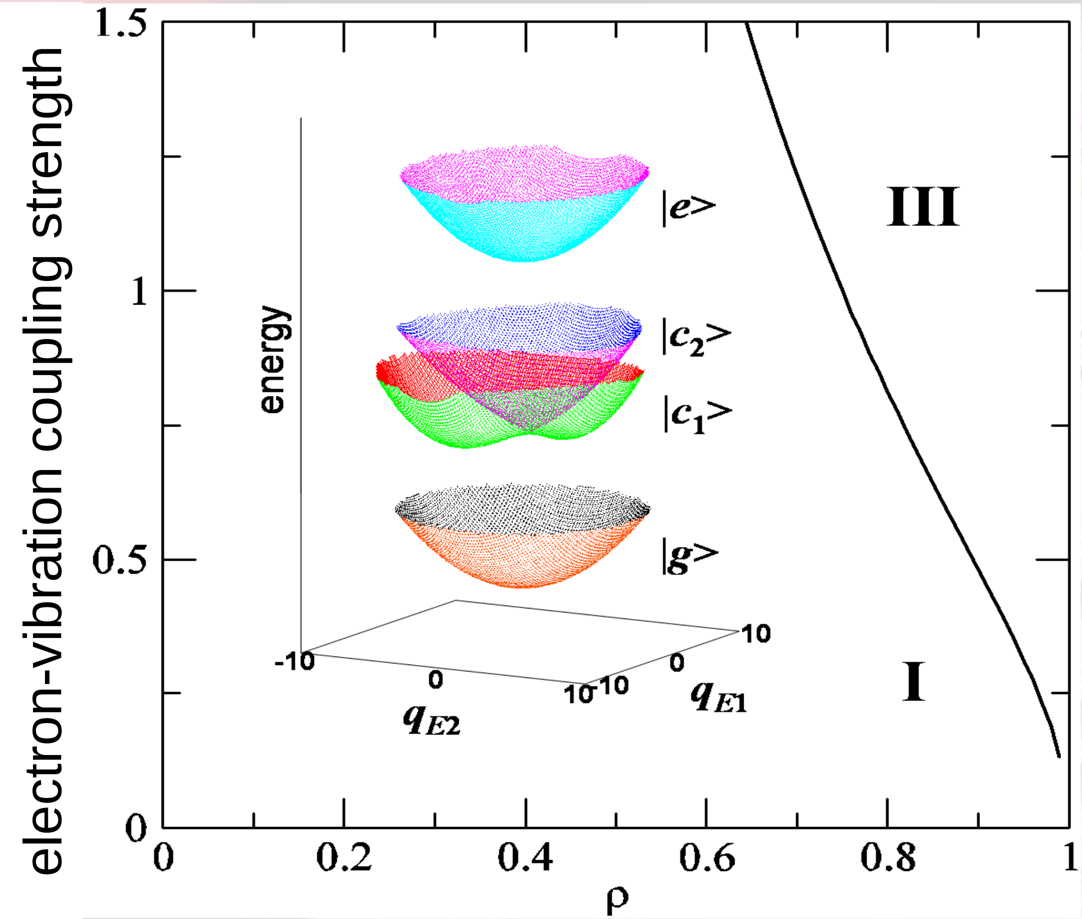
JACS 128 (2006) 15742; *J. Phys. Chem. Lett.* 2010, 1, 1800

Octupolar chromophores

- **Symmetry breaking: conical intersection**
- **Inhomogeneous broadening: fluorescence anisotropy**
- **Nonlinear optical responses**



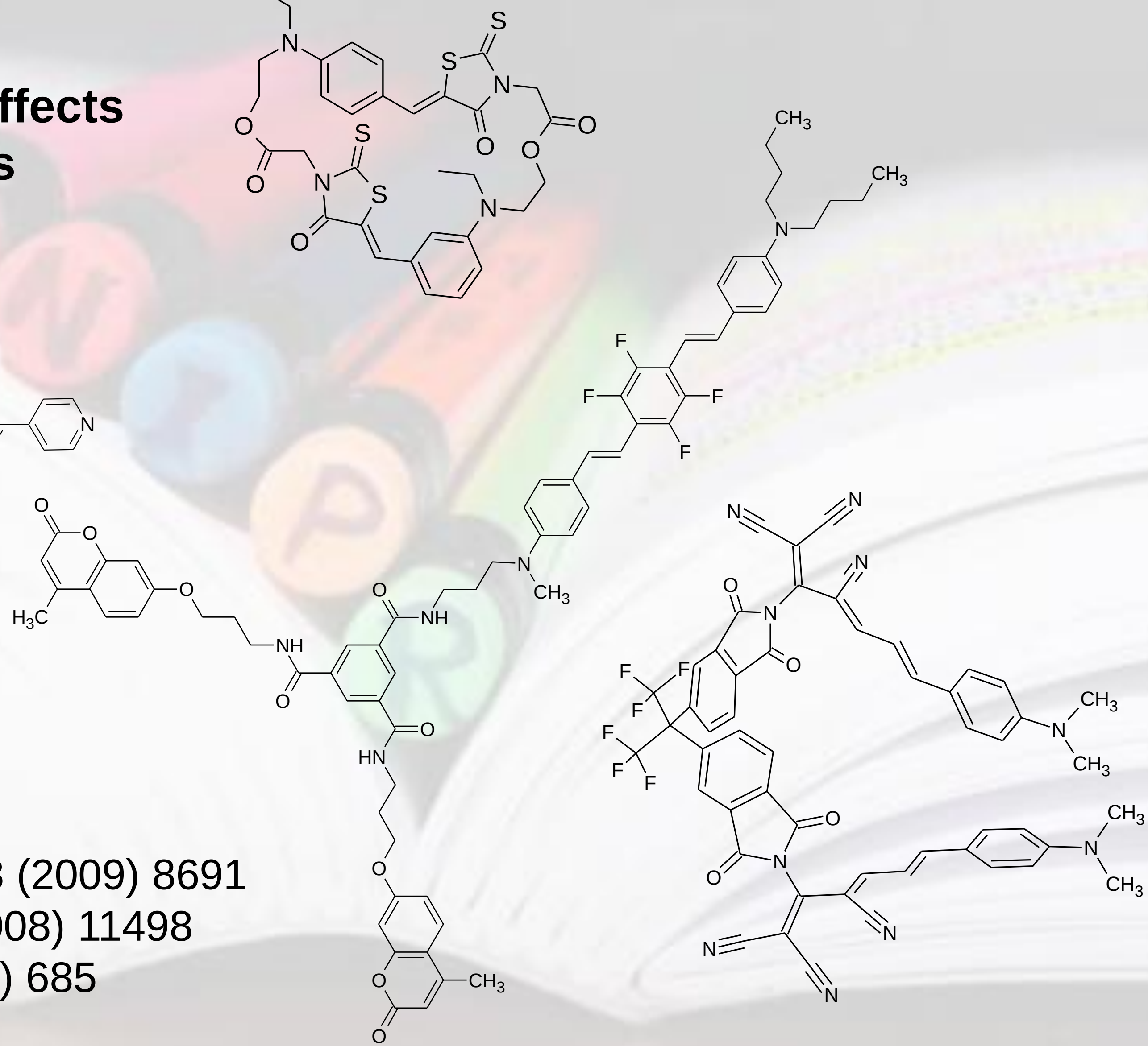


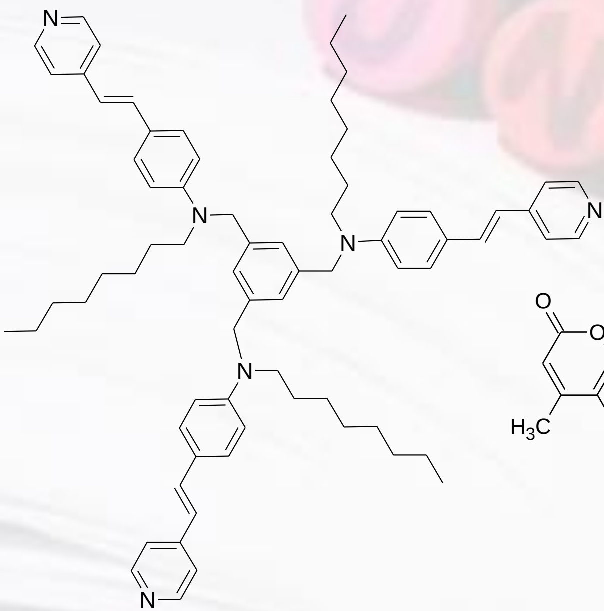


J. Phys. Chem. B 112 (2008) 5079; *JACS* 132 (2010) 16467

Multichromophores

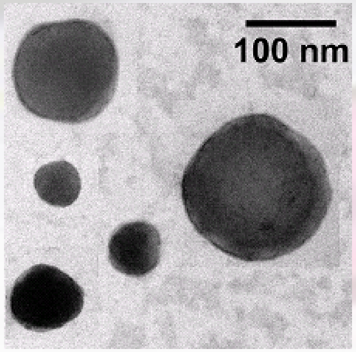
- **Excitonic effects**
- **Energy transfer**
- **Unconventional effects on NLO properties**





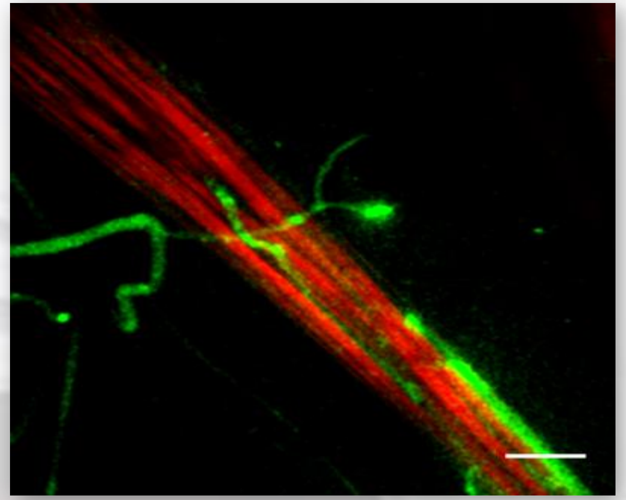
Angew. Chem. Int. Ed. 48 (2009) 8691
J. Phys. Chem. B 112 (2008) 11498
ChemPhysChem 7 (2006) 685
…

Organic Nanoparticles

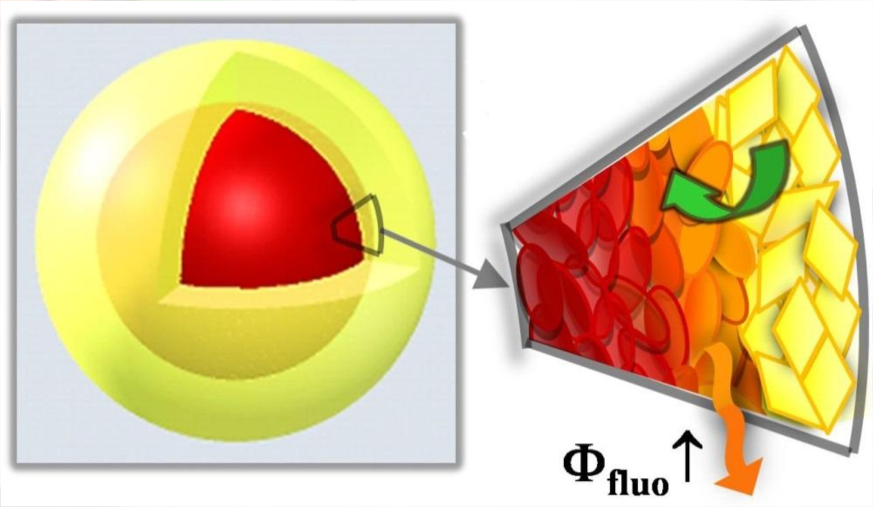


Enforcing Luminescence at Organic Nanointerfaces: Luminescence Spatial Confinement and Amplification in Molecular-Based Core-Shell Nanoparticles

Bioimaging



Small 7 (2011) 3219



Small 9 (2013) 1982

Recruitment

3 PhD positions (for non-italian students)

1.
Optical spectroscopy of organic nanoparticles: models and computations

<u>Aim:</u>
- Definition of reliable essential-state models for dyes and interacting dyes in organic nanoparticles
- Validation against spectroscopic data

<u>Means:</u>
- Theoretical optical spectroscopy, quantum-chemical calculations & molecular dynamics
- Some basics of experimental optical spectroscopy

<u>Secondments</u>:
- JNCASR, Bangalore, India (8 months, molecular dynamics and TD-DFT calculations)
- Nanomol Technologies, Spain (1 month, design of dyes for the growth of organic nanoparticles & experience with industrial research practices)

Recruitment

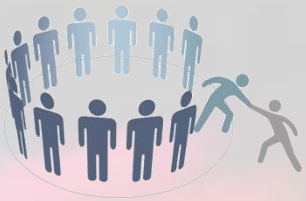
2.
Organic Nanoparticles: design, growth and characterization

<u>Aim:</u>
- Growth and complete spectroscopic characterization of organic nanoparticles
- Dye-design and supramolecular interaction control to obtain nanoparticles with sought optical properties

<u>Means:</u>
- Reprecipitation technique
- Spectroscopic characterization

<u>Secondments</u>:
- Bordeaux University (2 months, design strategies of dyes and organic nanoparticles)
- Physics Ukraine (4+2 months, two-photon absorption characterization)
- Antwerp University (2 months, spectroscopic measurements)
- Hannover Lazer Zentrum (1 months, design strategies for dyes and organic nanoparticles for two-photon polymerization)

Recruitment



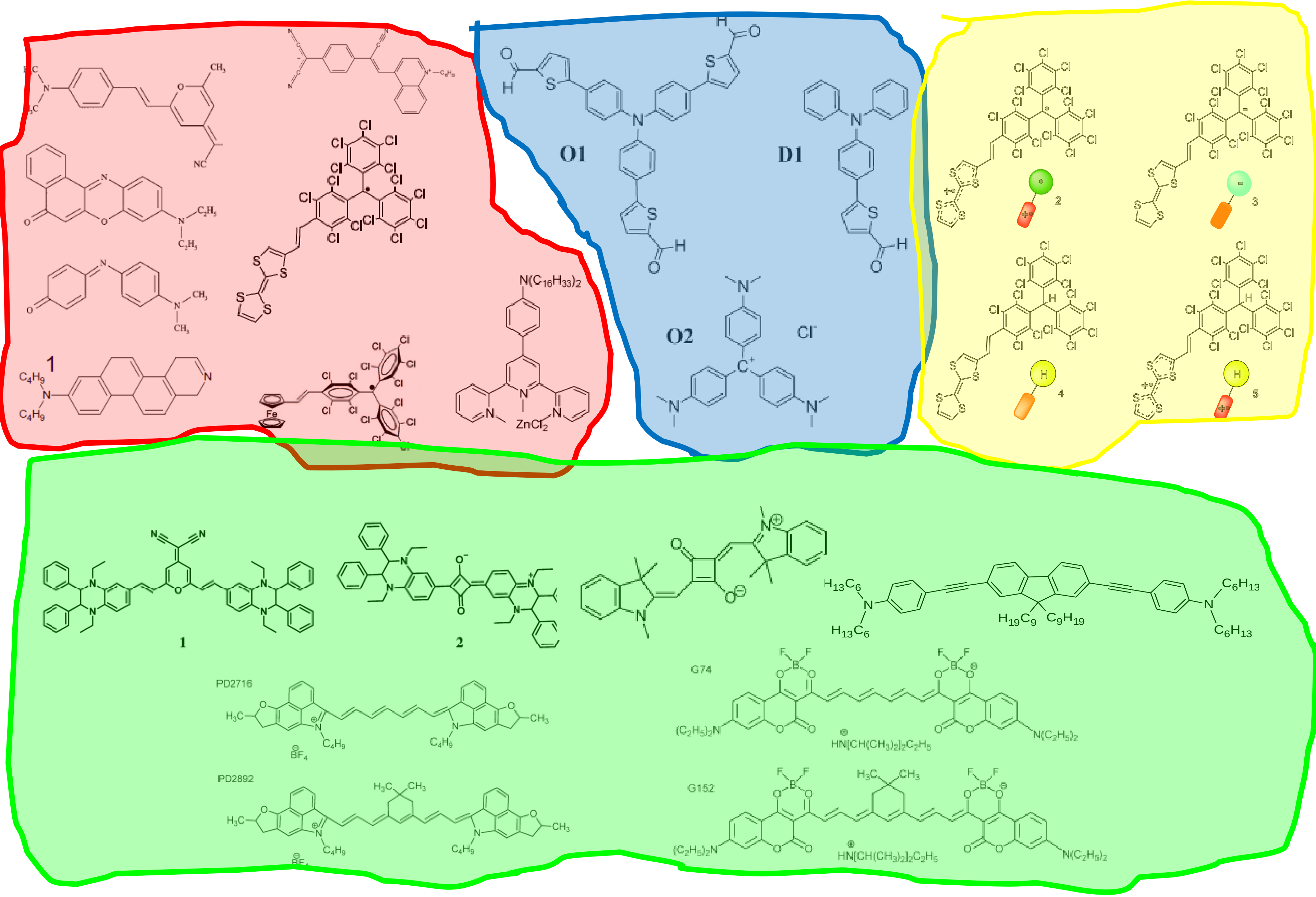
3.
Nonlinear spectroscopy, two-photon microscopy and STED-enhanced two-photon microscopy

Aim:
- Linear and nonlinear optical characterization of organic molecules and their nanoparticles
- Use of the samples as probes for two-photon microscopy (2PM) and its STED-augmented counterpart (STED = Stimulated Emission Depletion)

Means:
- Advanced linear and nonlinear spectroscopic characterization techniques
- Time-resolved studies

Secondments:
- University of Central Florida (5 months, two-photon absorption measurements by Z-scan technique, 2PM and STED-2PM)
- Institute of Physics Ukraine (4+2 months, two-photon absorption and time-resolved measurements)

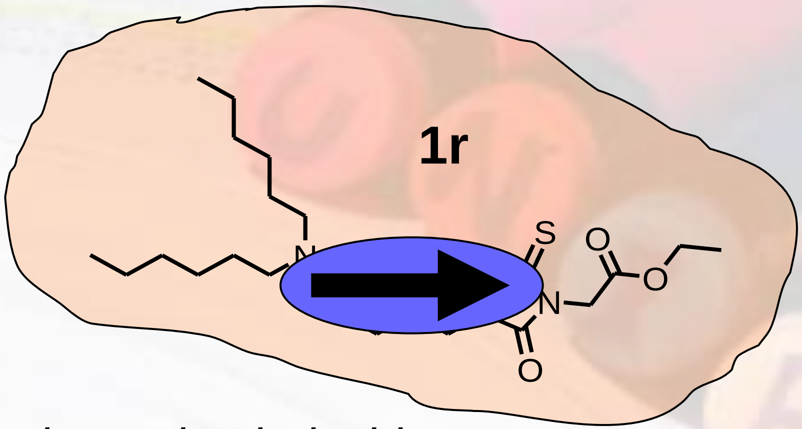
Systems: organic functional chromophores (CT chromophores)

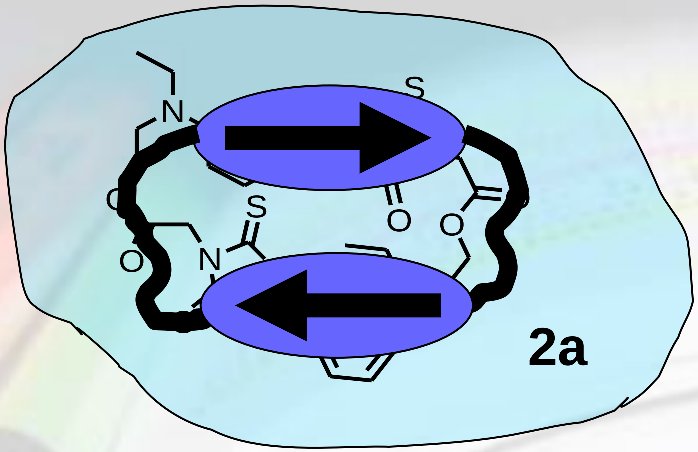


How can we make sense of the variegated properties & behavior of such a large variety of systems?

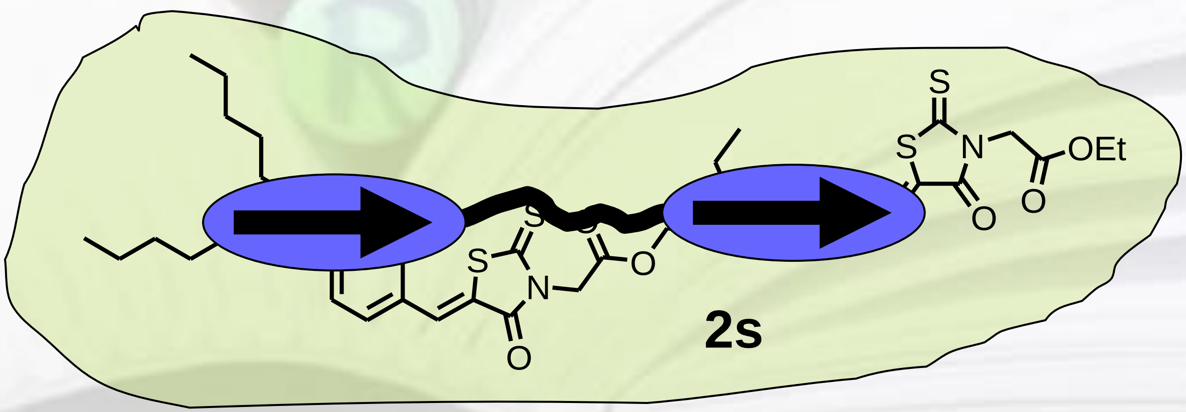
How can we guide the synthesis of molecular materials with required properties?

Optical Spectroscopy





polar and polarizable chromophore



mimic highly concentrated samples

Systems:
organic functional chromophores (CT chromophores)

Phenomena:

- optical spectra in solution, solvatochromism & symmetry breaking
- excitonic effects in optical spectra
- multistability & multiexciton generation in condensed phases
- energy transfer

Conclusions

Essential state models

- offer a powerful tool to rationalize optical spectra of families of dyes in solution
- explain symmetry-breaking in multipolar dyes
- account for multistability induced by electrostatic interactions in crystals of DA molecules
- can be adopted to describe the behavior of interacting chromophores in aggregates, crystals, etc and offer a quantitative basis to describe resonant energy transfer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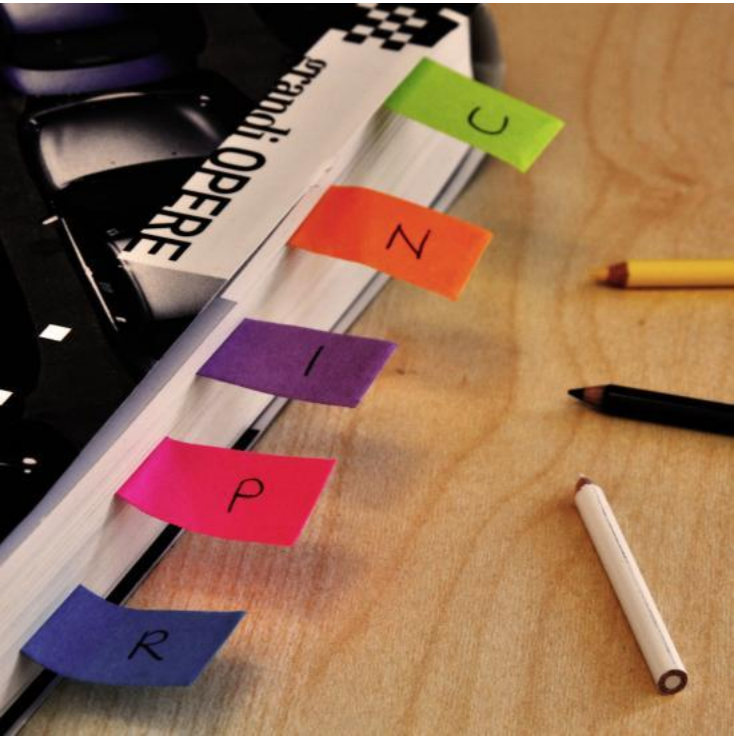
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