ORGANIC & HYBRID PHOTONIC CRYSTALS

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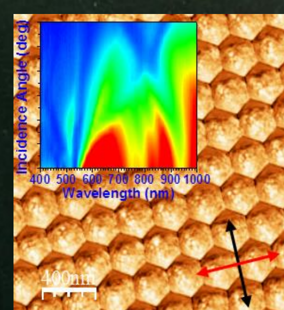

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GNSR – the former GISR

C. N. R.
CONSIGLIO NAZIONALE DELLE RICERCHE
ISTITUTO DI METODOLOGIE AVANZATE INORGANICHE
AREA DELLA RICERCA DI ROMA
E
CONSORZIO ROMA RICERCHE

XIII MEETING
DEL GRUPPO NAZIONALE DI DISCUSSIONE
PER LE SPETTROSCOPIE RAMAN
E GLI EFFETTI NON LINEARI
(GNSR)

1-2 DICEMBRE 1994
AREA DELLA RICERCA DI ROMA

PROGRAMMA

Balzanelli - Tel. e Fax 906.99.66

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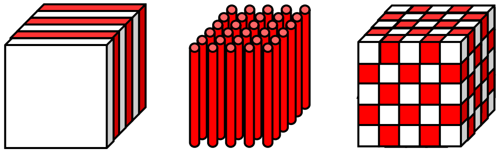
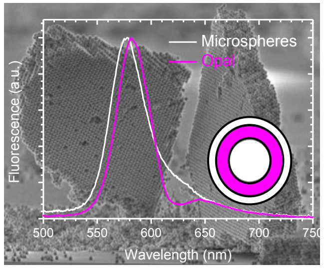
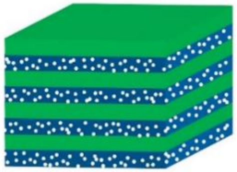
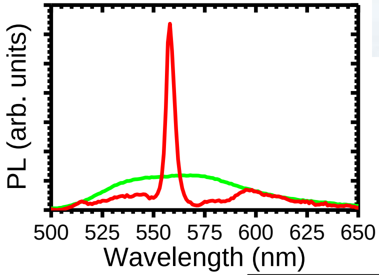
TALK OUTLINE

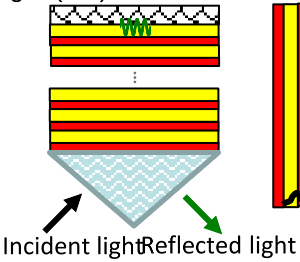
- Introduction to Photonic Crystals
- Fluorescence Enhancement in Engineered Opals
- Hybrid Plasmonic-Photonic systems (2D-3D)
- All-Polymer Distributed Bragg Reflector Sensors
- Polymer & Hybrid Microcavities for Lasing & Switching
- Bloch Surface Waves: Polaritons & Light Localization

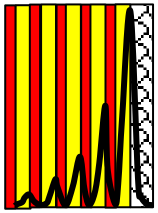




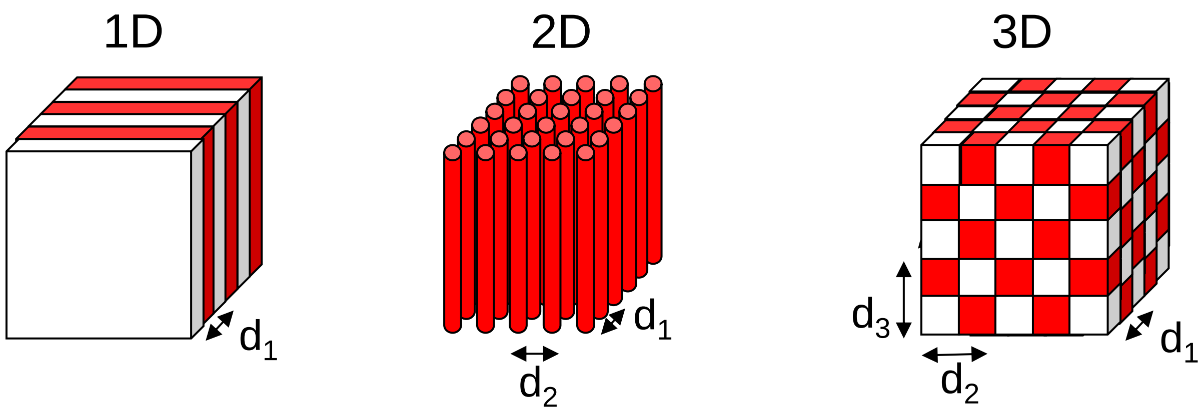








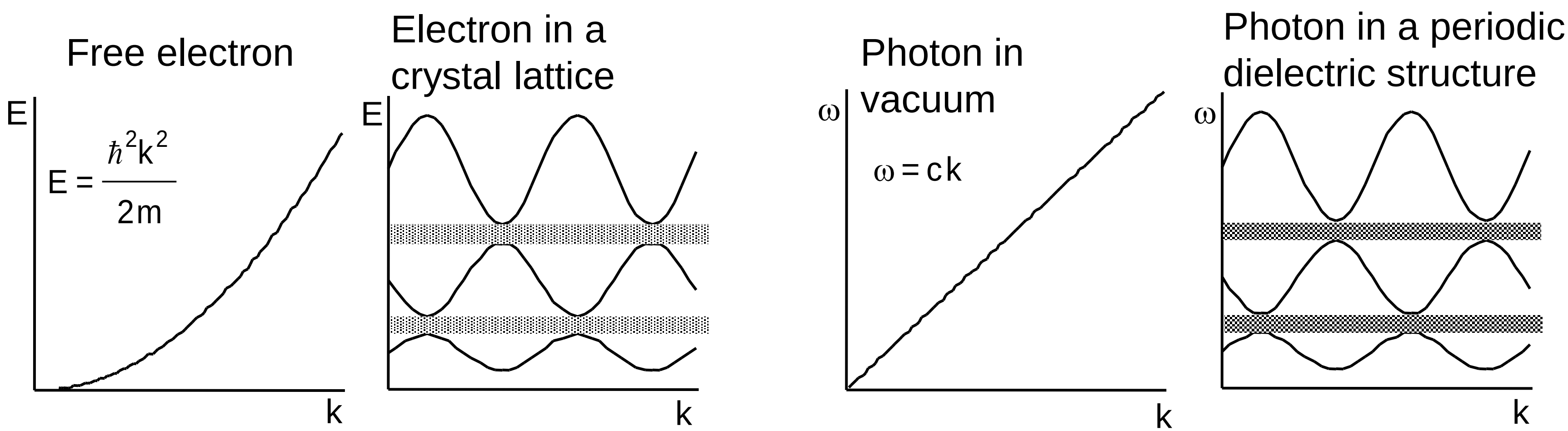
PHOTONIC CRYSTALS



$d_j >> a_0$ (Bohr's radius)

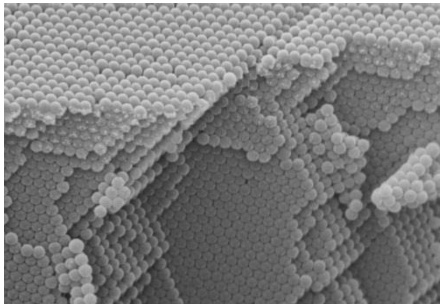
$d_j \sim \lambda$ of visible light

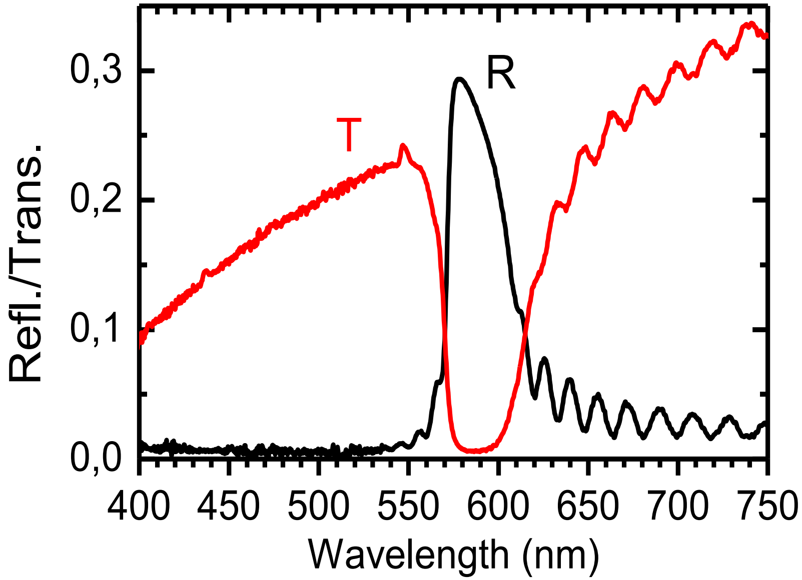
The dielectric constant (ε) must be considered (dielectric lattice)



OPTICAL EFFECTS IN PHOTONIC CRYSTALS

polystyrene opal film (Ø 260 nm)





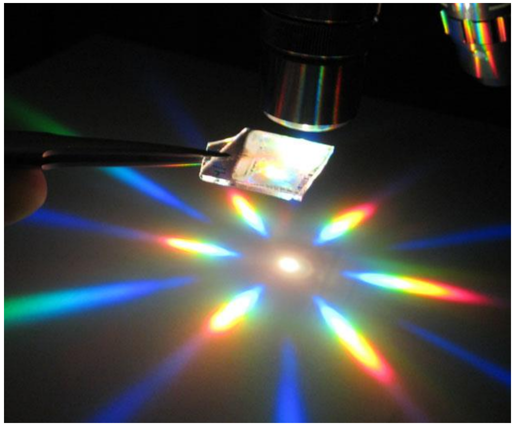
- Photons having energy within the PBG cannot propagate into the PhC being backward diffracted.
- Dielectric lattice geometry and dielectric contrast allow to engineer the PBG.

E. Pavarini, Phys. Rev. B72, 045102 (05)

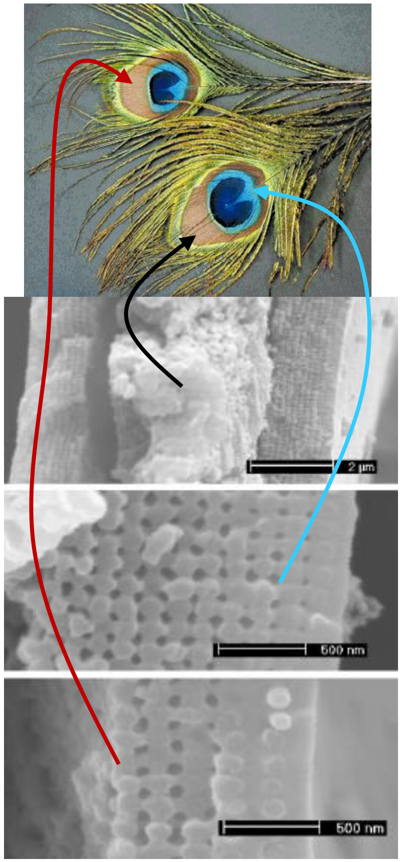
STRONG LIGHT DIFFRACTION EFFECTS

- Bright colors.
- Iridescence (color change by orientation).
- Chromatic effects depend on the dielectric environment - applied stimuli.

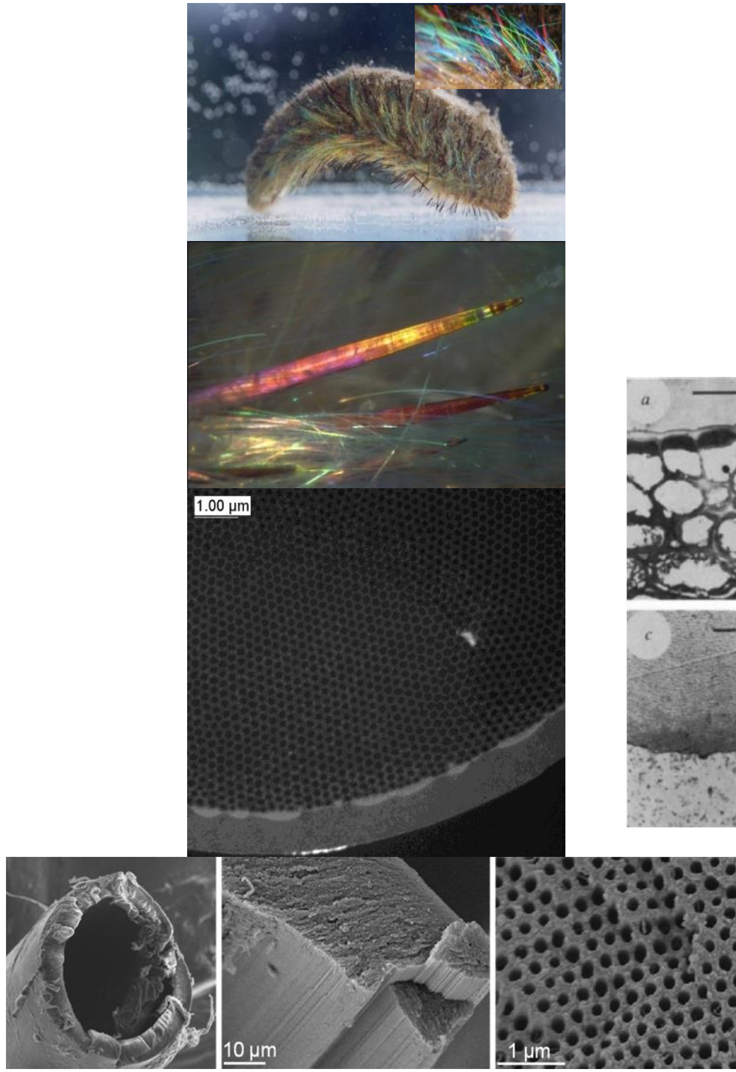
$$\lambda = 2\boldsymbol{D}\sqrt{\boldsymbol{n_{eff}^2} - sin^2\boldsymbol{\theta}} \qquad D = \boldsymbol{a}\sqrt{\frac{2}{3}}$$



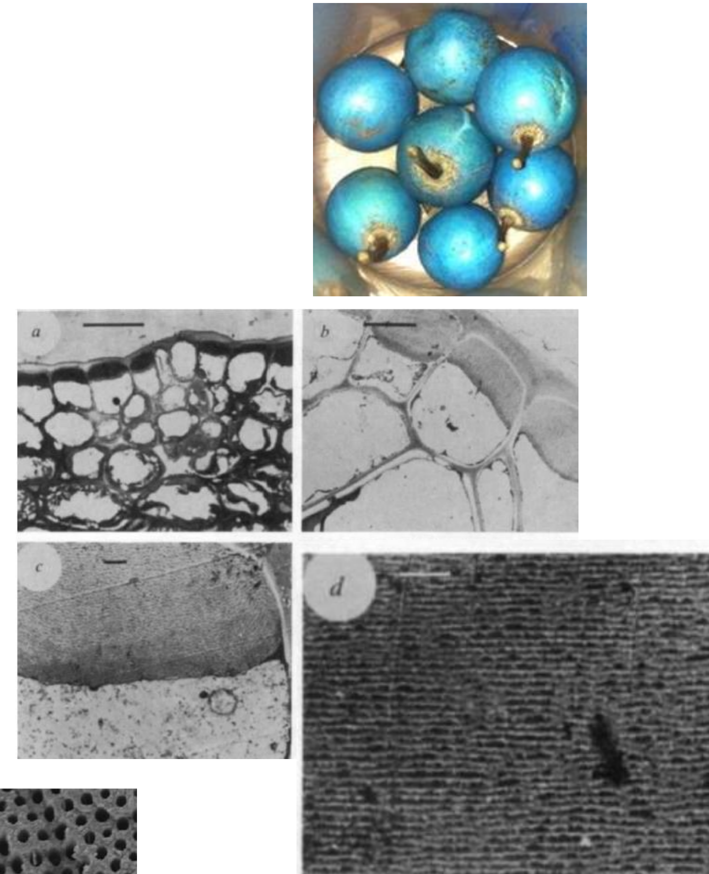
NATURAL PHOTONIC CRYSTALS



Peacock feathers



Sea mouse



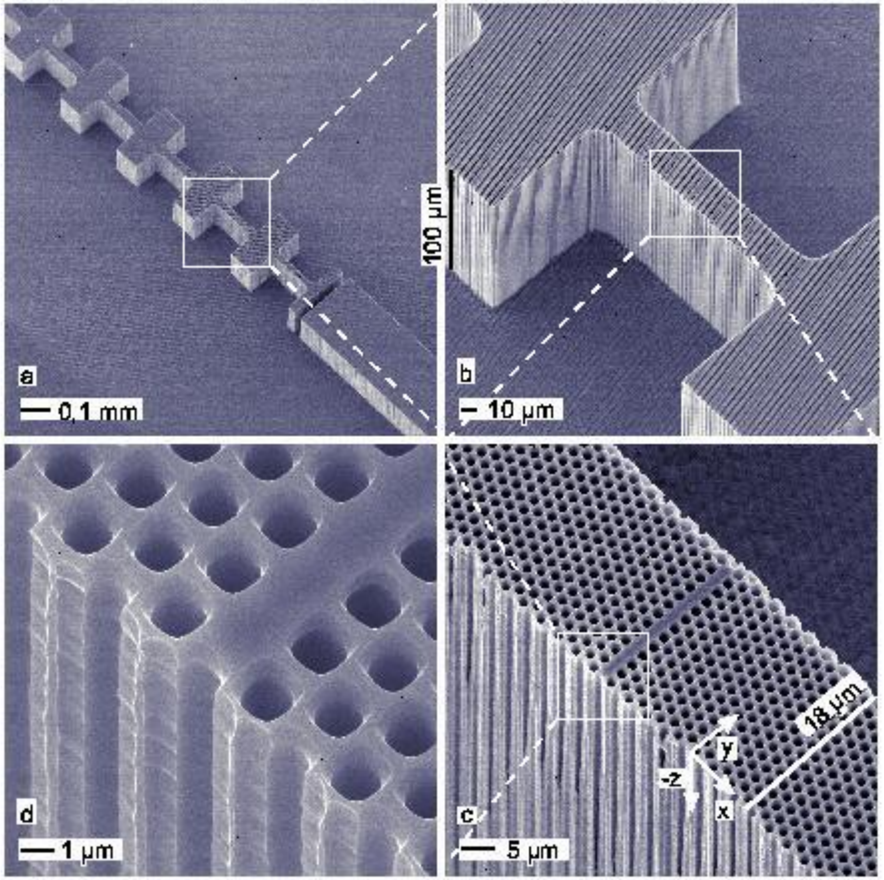
Photonic berries
(Elaeocarpus fruits)

PHOTONIC FOODS

Photonic™ Chocolate, © morphotonix

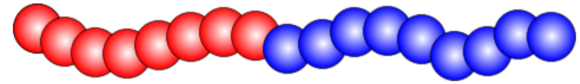
PHOTONIC CRYSTALS GROWTH

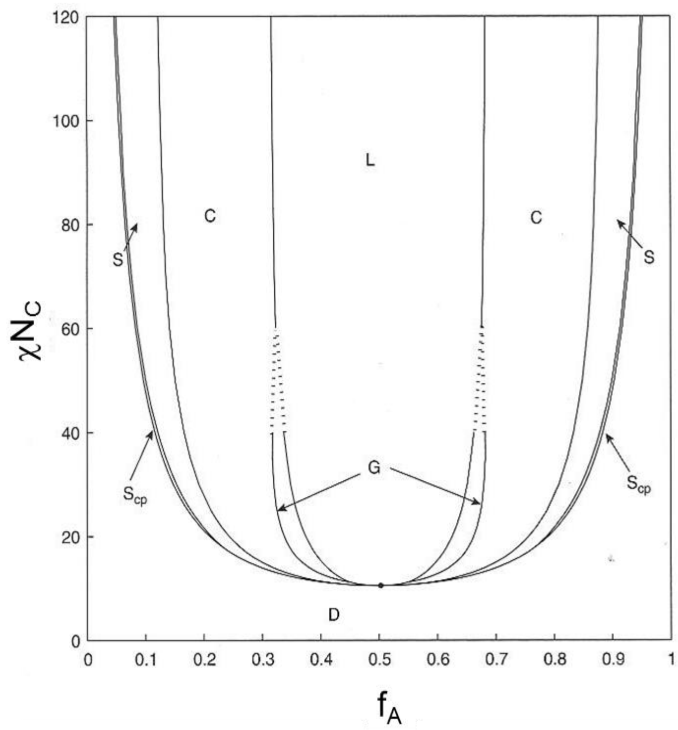
Inorganic materials
TOP-DOWN



F. Müller et al., J. Porous Mater. 7, 1/2/3, S. 201 (00)

Organic materials
BOTTOM-UP

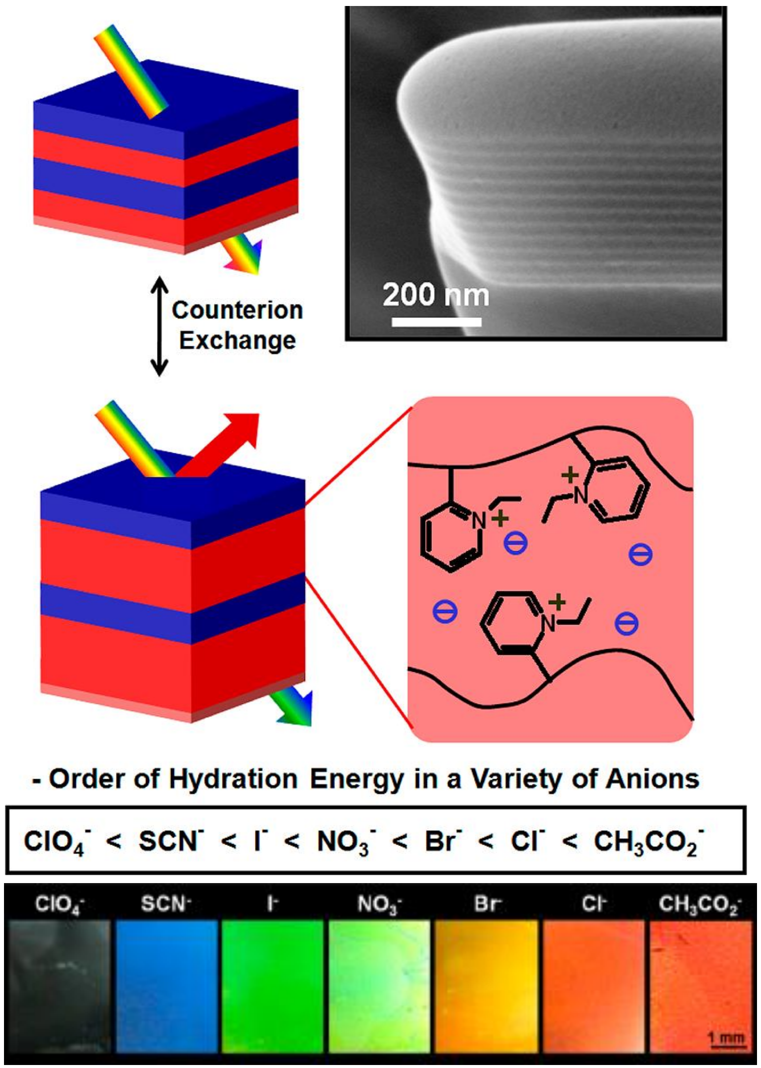




E.L. Thomas group. Polymer 44, 6725 (03)

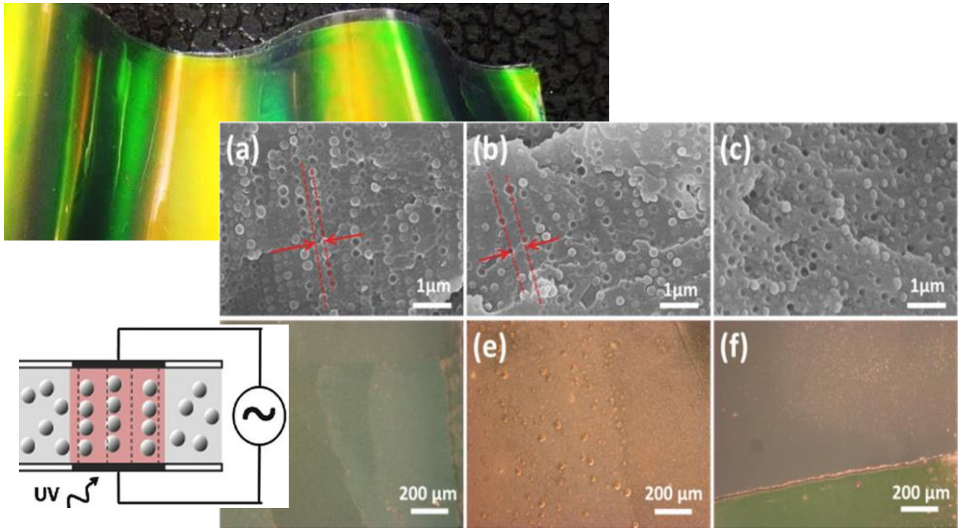
POLYMER PHOTONIC CRYSTALS @ WORK

Polymer photonic crystal sensors



E.L. Thomas group, ACS Nano 6, 8933 (12)

Polymer opals fabric

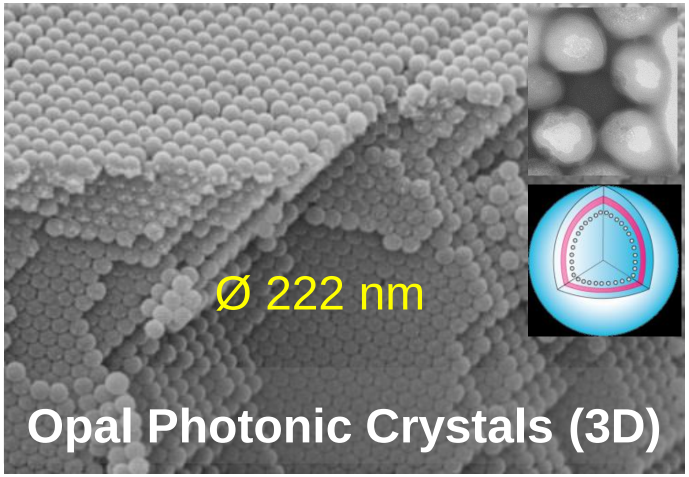


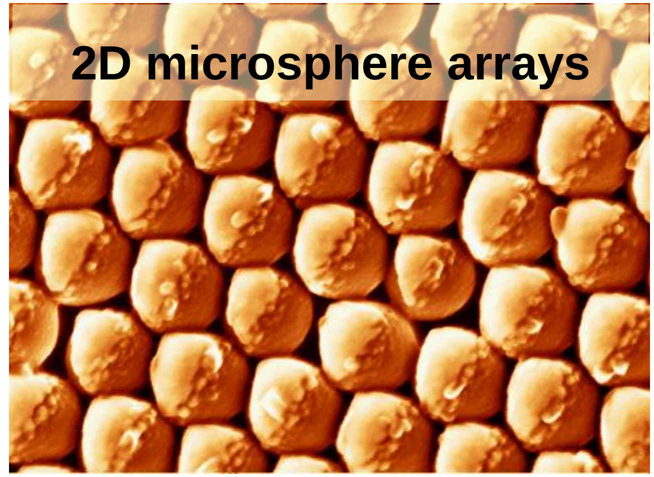
http://www.np.phy.cam.ac.uk/research-themes/polymer-opals

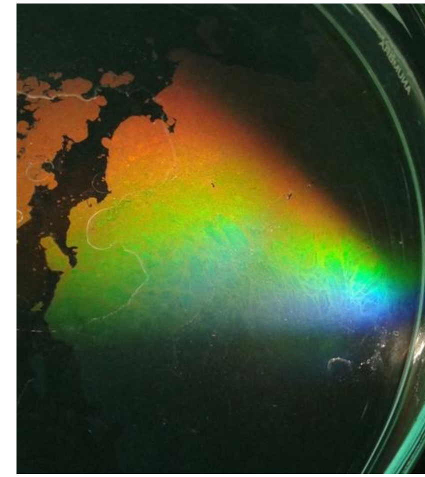
Adv. Engin. Mater. 15, 948 (13)

http://www.thegenteel.com/articles/design/rainbow-winters

PHOTONIC CRYSTAL IN GENOVA



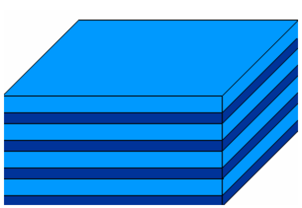




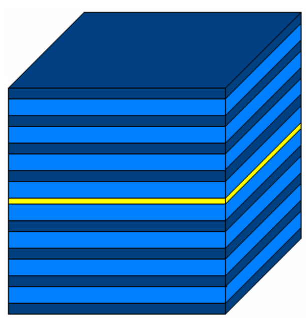
L. Berti, J. Phys. Chem. C114, 2403 (10)
D. Antonioli et al., Polym. Int. 4206 (12)
K. Sparnacci et al., J. Nanomat. 2012, 980541 (12)
D. Comoretto et al. Polym. Comp., 34, 1443 (13)
F. Di Stasio et al. APL. Materials 1, 042116 (13)

V. Robbiano et al. Adv. Optical Mater. 1, 389 (13)
A. Belardini et al. Adv. Optical Mater. 2, 208 (14)

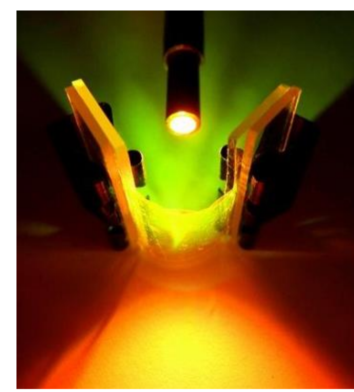
Polymer multilayers and microcavities (1D)



Distributed Bragg Reflectors (DBR)



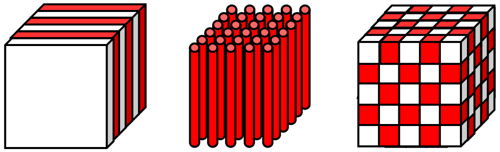
Microcavity

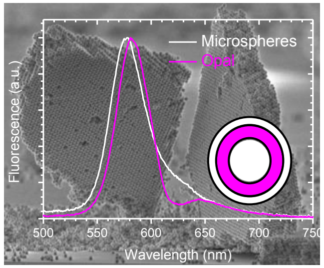


L. Frezza et al., J. Phys. Chem. C115, 19939 (11)
G. Canazza et al. Laser Phys. Lett. 11, 035804 (14)
S. Pirrotta et al., Appl. Phys. Lett. 104, 051111 (14)
C. Toccafondi et al. J. Mater. Chem. 2, 4692 (14)

TALK OUTLINE

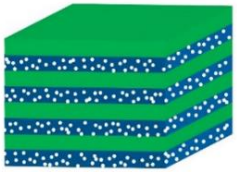
- Introduction to Photonic Crystals



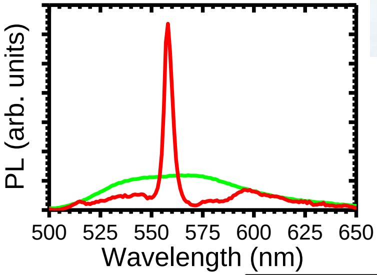


- Fluorescence Enhancement in Engineered Opals

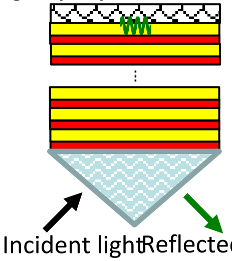
- Hybrid Plasmonic-Photonic systems (2D-3D)

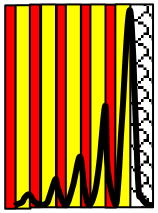


- All-Polymer Distributed Bragg Reflector Sensors



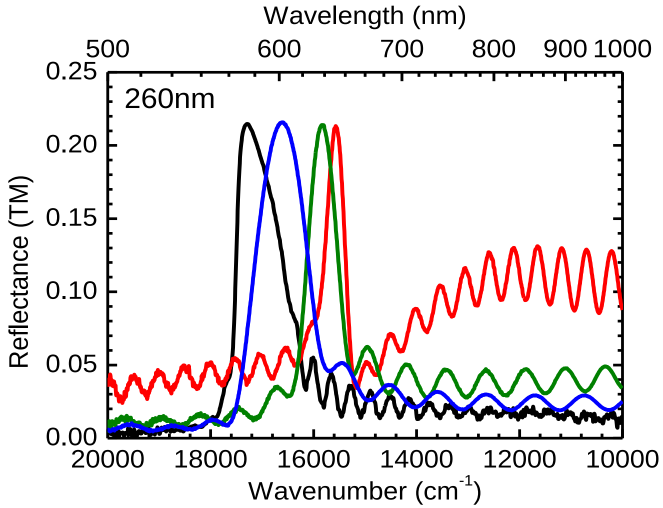
- Polymer & Hybrid Microcavities for Lasing & Switching

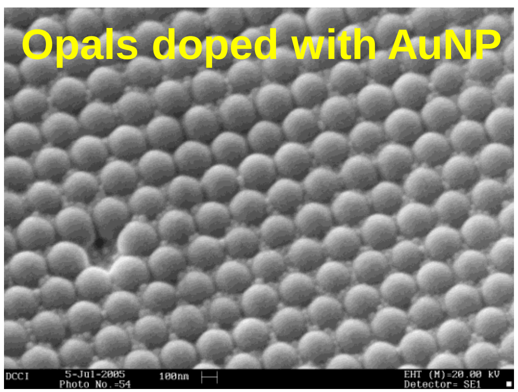




- Bloch Surface Waves: Polaritons & Light Localization

HYBRID PLASMONIC-PHOTONIC SYSTEMS





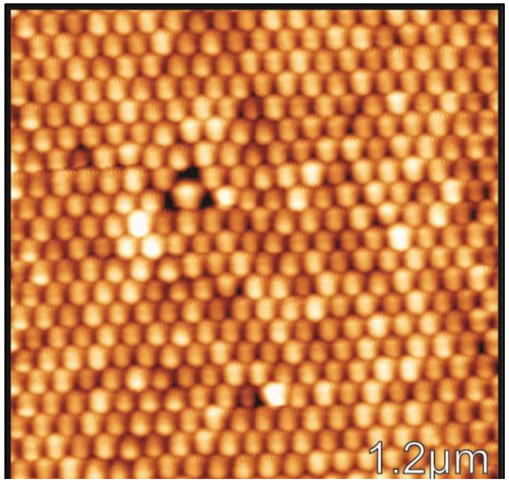
Bare Opals: Phys. Rev. B72, 045102 (05)

Gold nanoaprticles doped opals

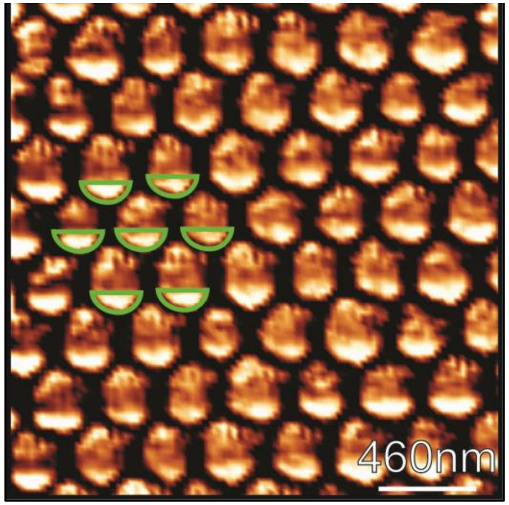
Optical Switching: Adv. Funct. Mater. 17, 2779 (07)

Light Localization: J. Phys. Chem. C, 112, 6293 (08)

Fine Band Gap Tuning: Appl. Phys. Lett. 93, 091111 (08)



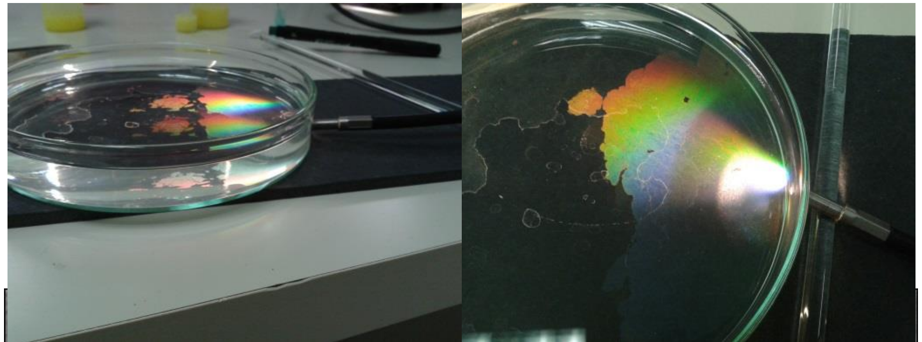
Nanocrescents@Opals

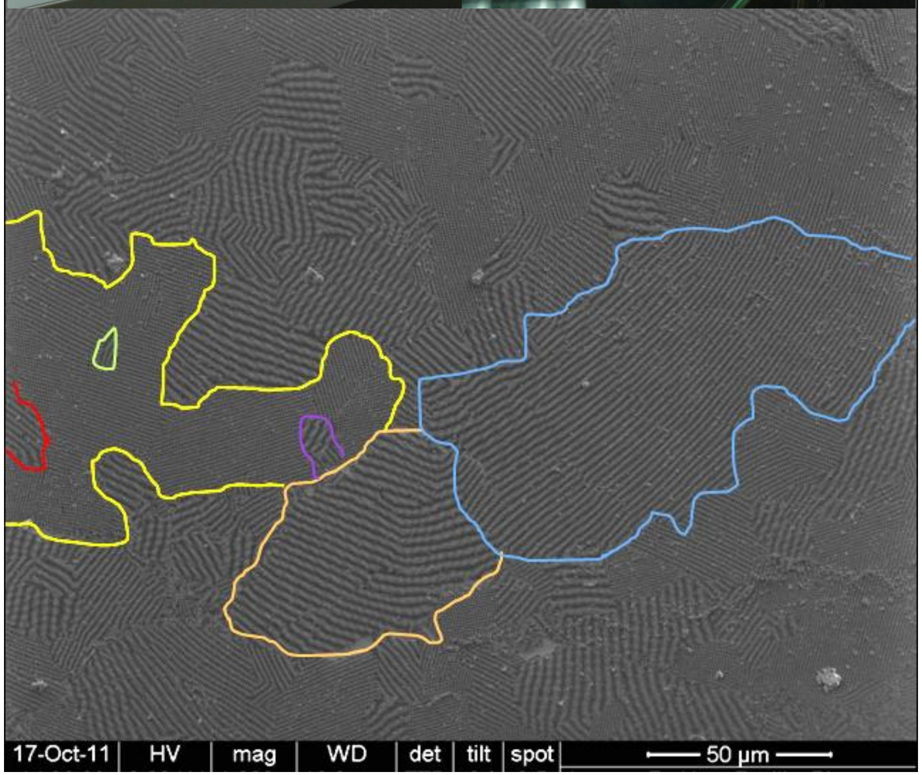


V. Robbiano et al. Adv. Optical Mater. 1, 389 (13))

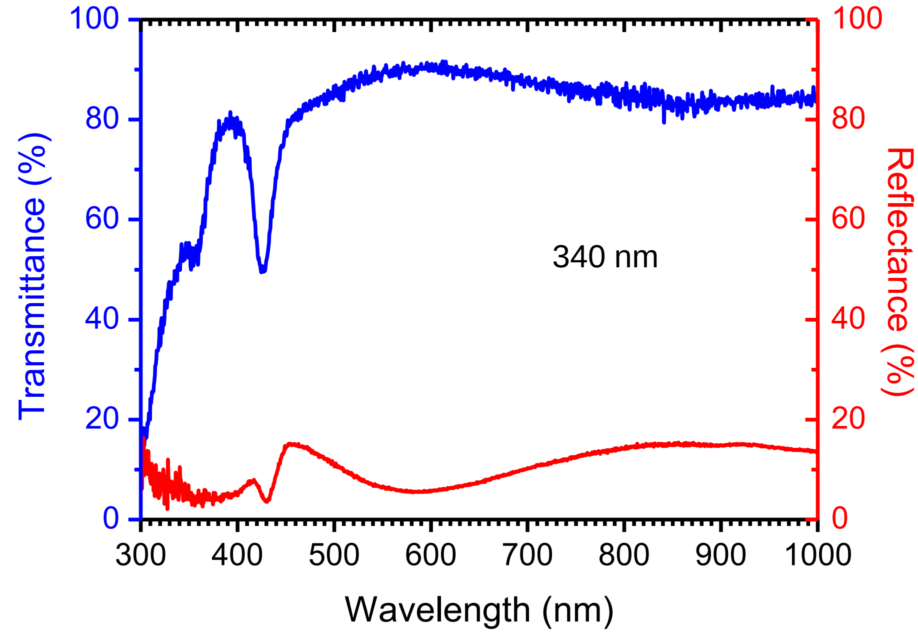
A. Belardini et al. Adv. Optical Mater. 2, 208 (14)

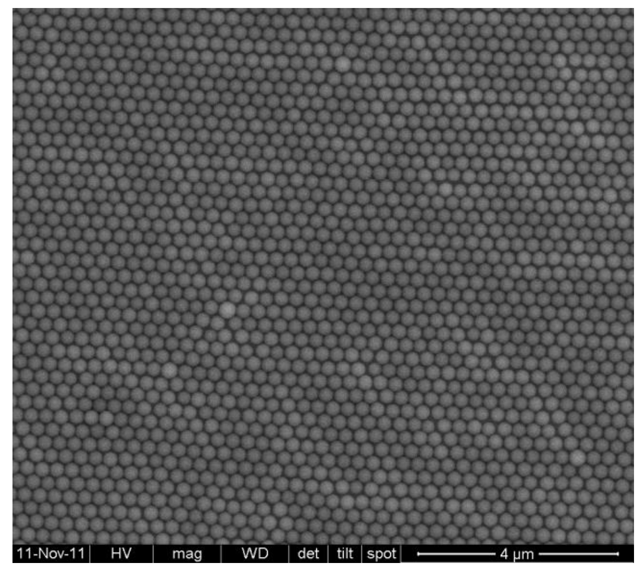
MICROSPHERE MONOLAYERS





V. Robbiano et al. Adv. Optical Mater. 1, 389 (13)





NANOCRESCENTS ON MONOLAYER

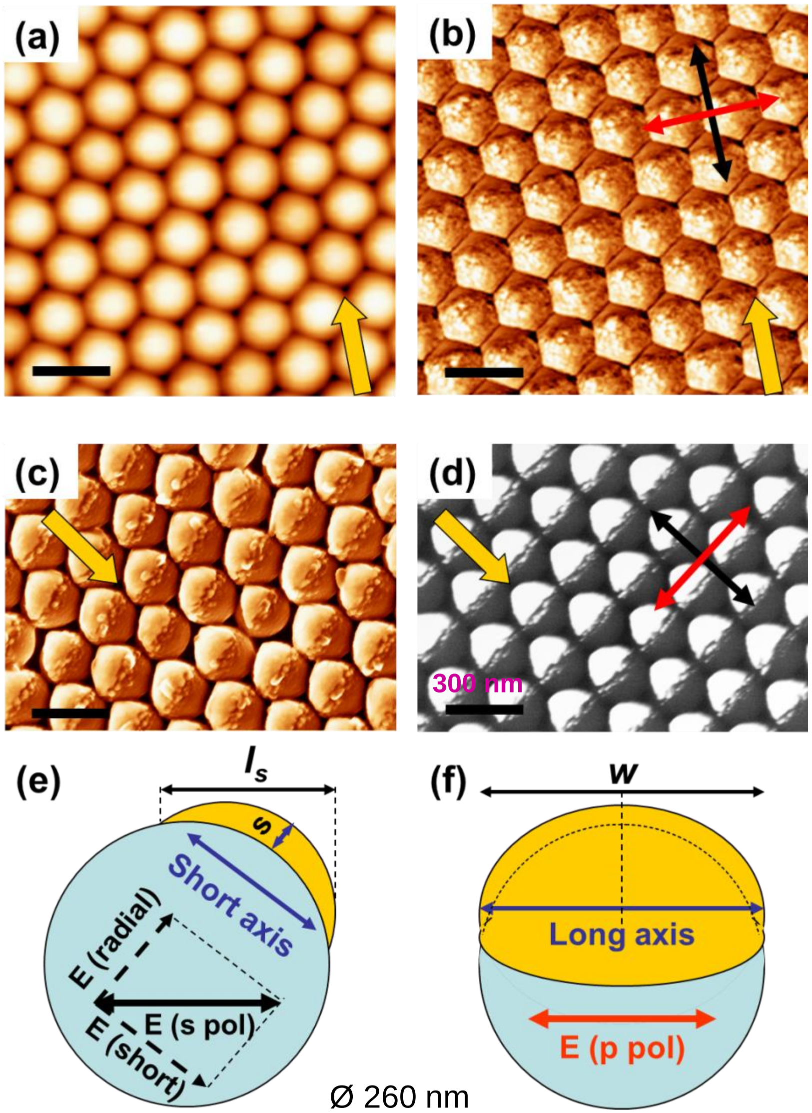
AFM topography
(intermitted contact)

AFM
(phase-contrast)

Microsphere diameter [nm]	w [nm]	ls [nm]	s [nm]
260	231 ± 11	198 ± 10	34 ± 2
340	302 ± 15	250 ± 13	34 ± 2
426	378 ± 19	304 ± 15	34 ± 2

SEM
(secondary electrons)

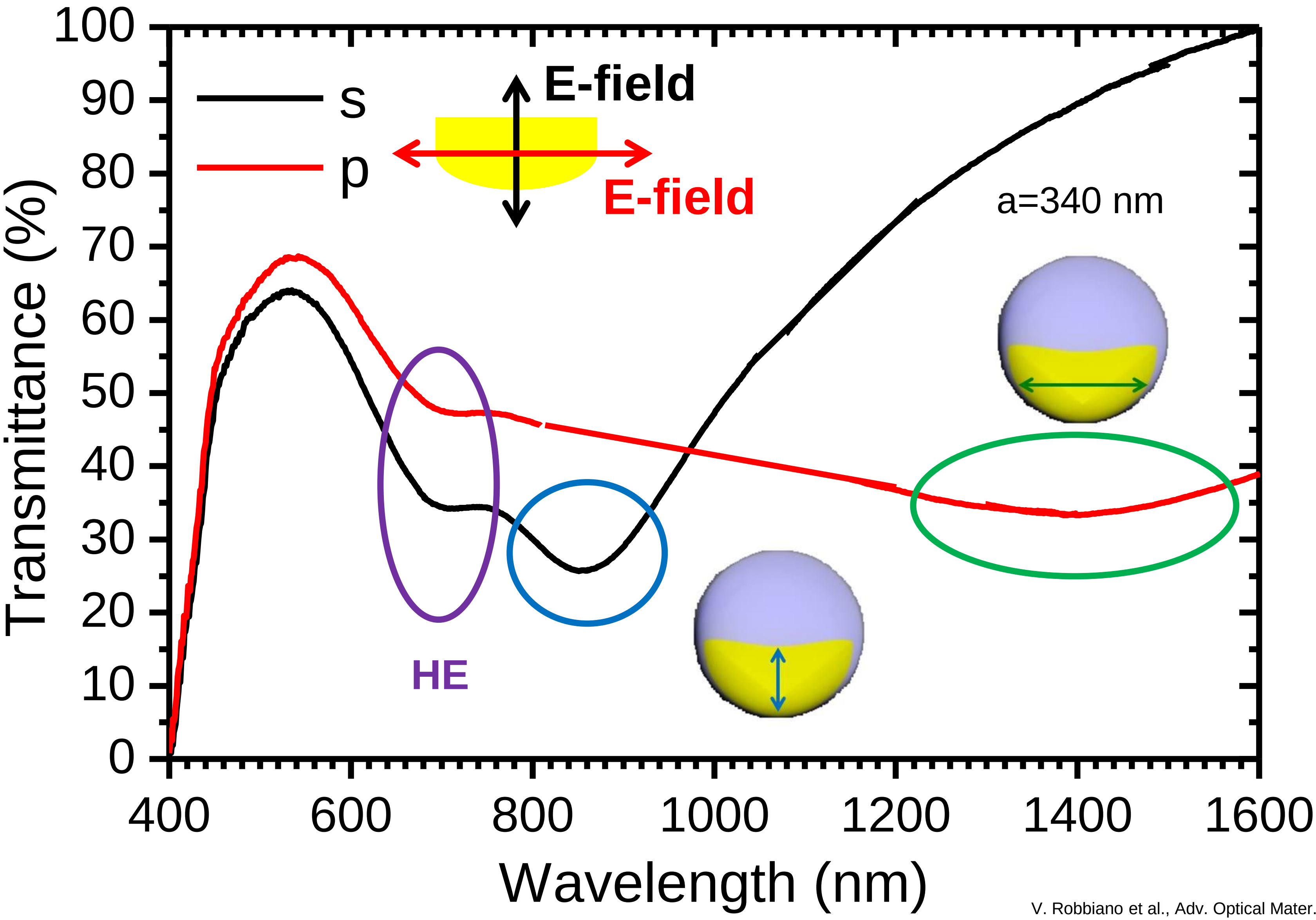
SEM
(back-scattering)



- Grazing (20°) evaporation incidence.
- Polycrystalline Au.
- Disconnected crescents.
- Strongly anisotropical system (long axis: diameter; short axis: arc; variable cortex thickness).
- Curved crescents.

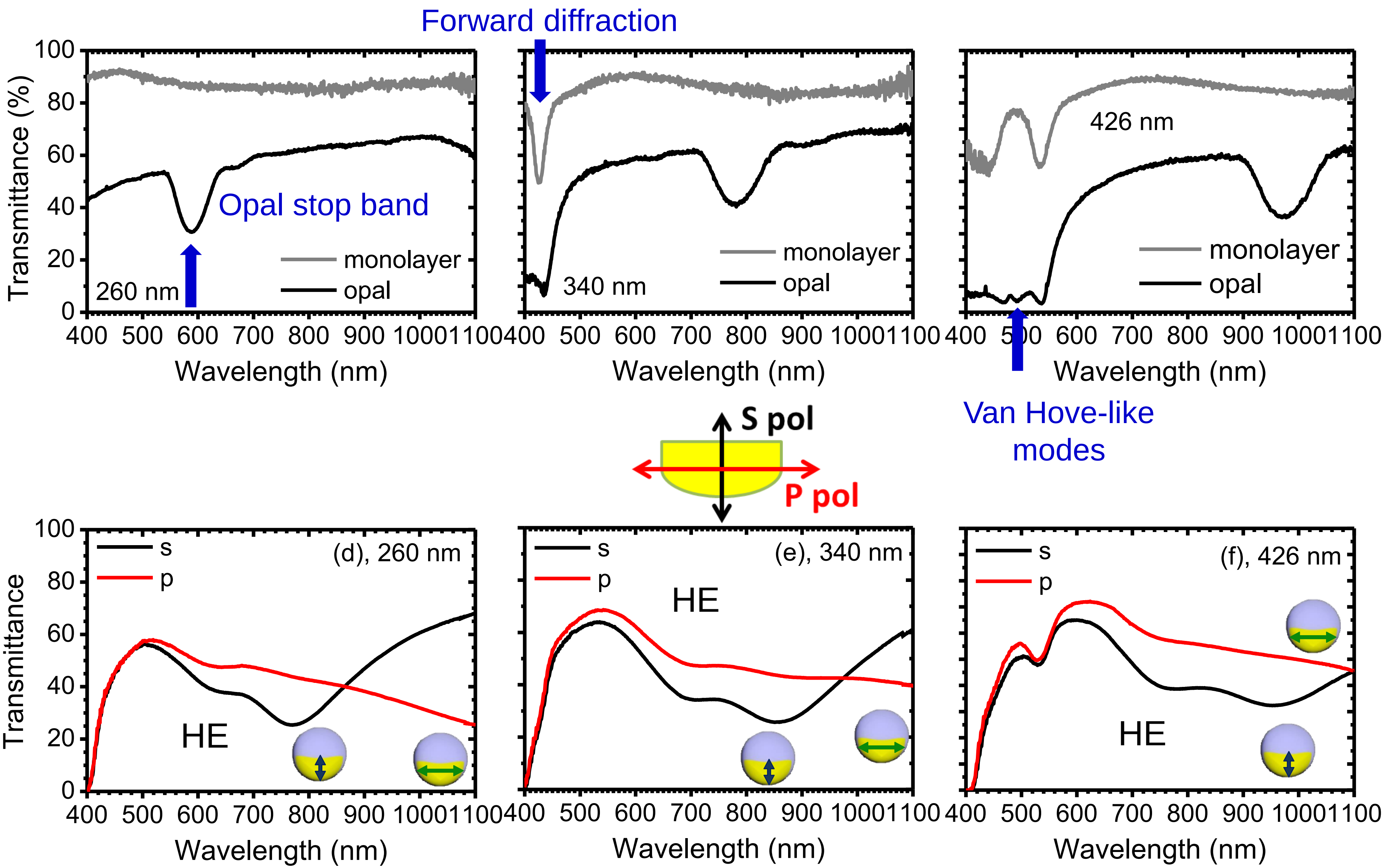
- The morphological analysis suggests the assignment of plasmonic modes

OPTICAL RESPONSE OF NANOCRESCENTS

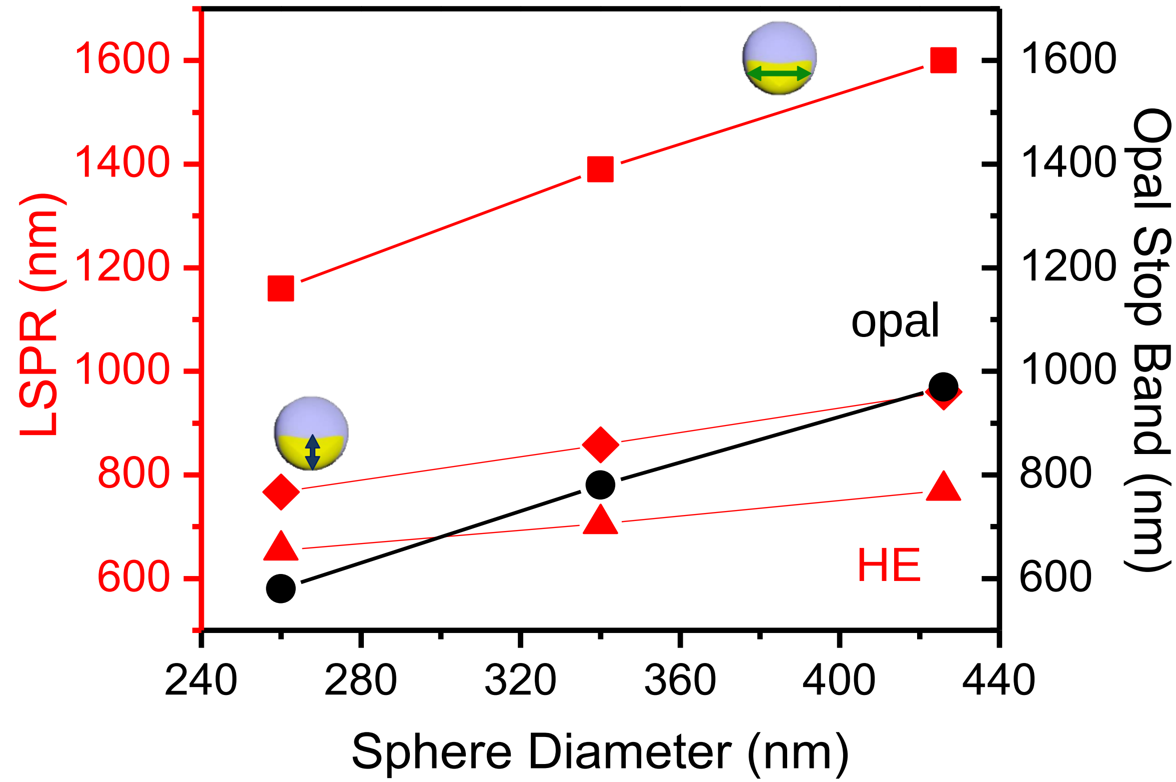


V. Robbiano et al., Adv. Optical Mater. 1, 389 (13)

MONOLAYER vs OPAL vs NANOCRESCENTS



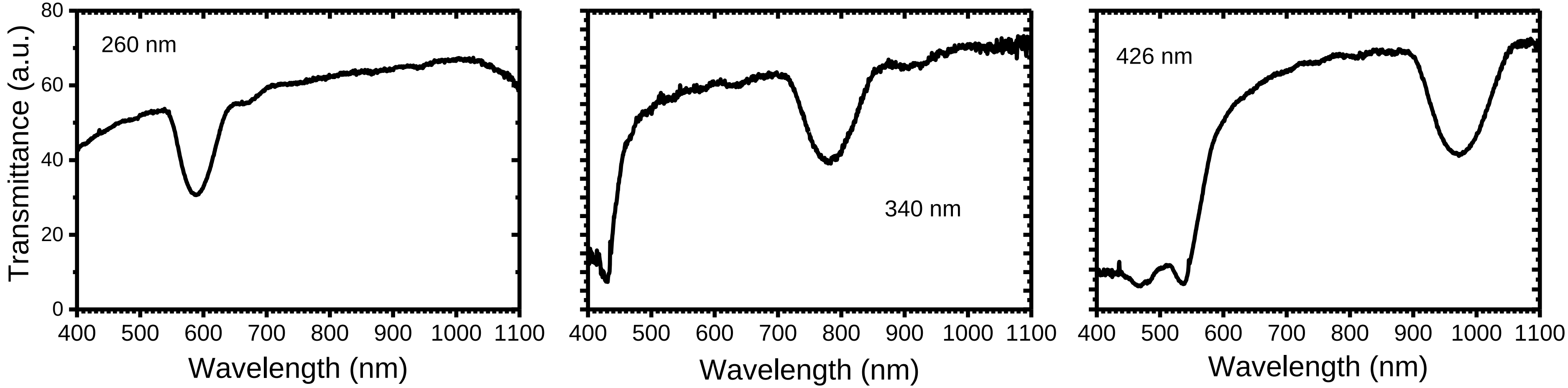
SCALING PROPERTIES OF NANOCRESCENTS



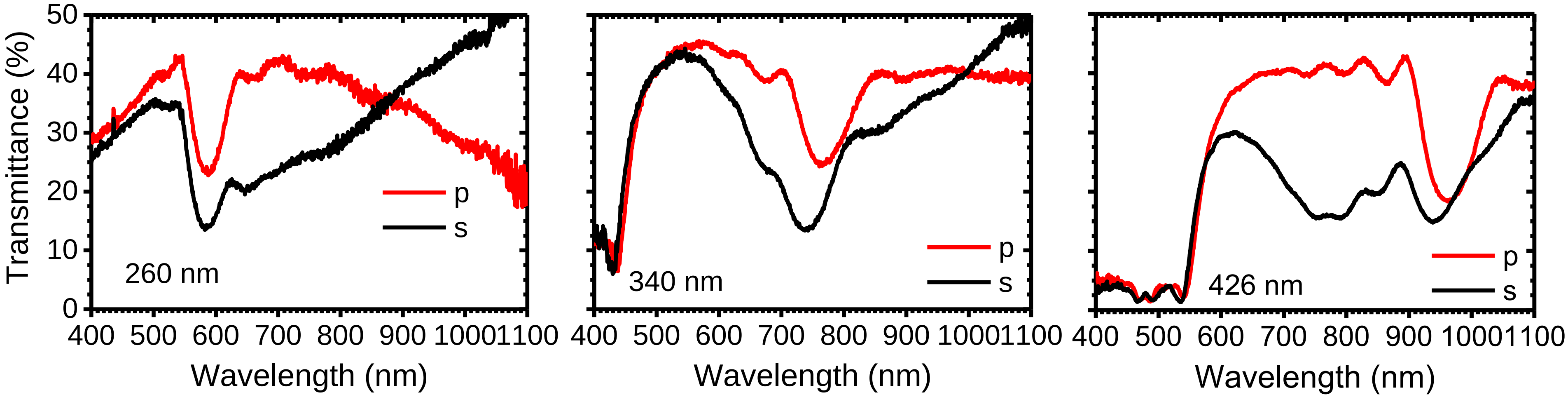
- **Opal stop band** and **LSPR along the long axis** have almost the same scaling thus making impossible their spectral overlap.
- Resonances along the **nanocrescent short axis** and the **HE** have a **reduced dependence on microsphere diameter:**
- **Overlap is expected in particular for light polarised along the short nanocrescent axis (S).**

OPALS vs NANOCRESCENTS@OPALS

OPALS



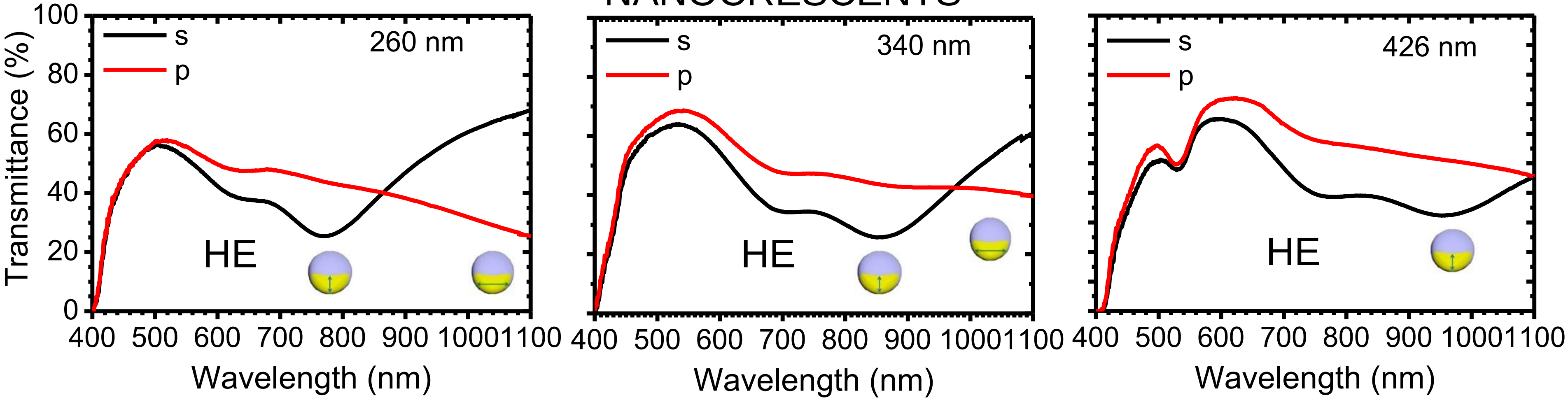
NANOCRESCENTS @ OPALS

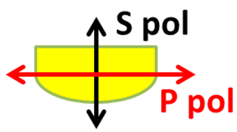


- depending on microsphere diameter and light polarization (S), a “mixing” between the PhC modes and the LSPR can be suggested.

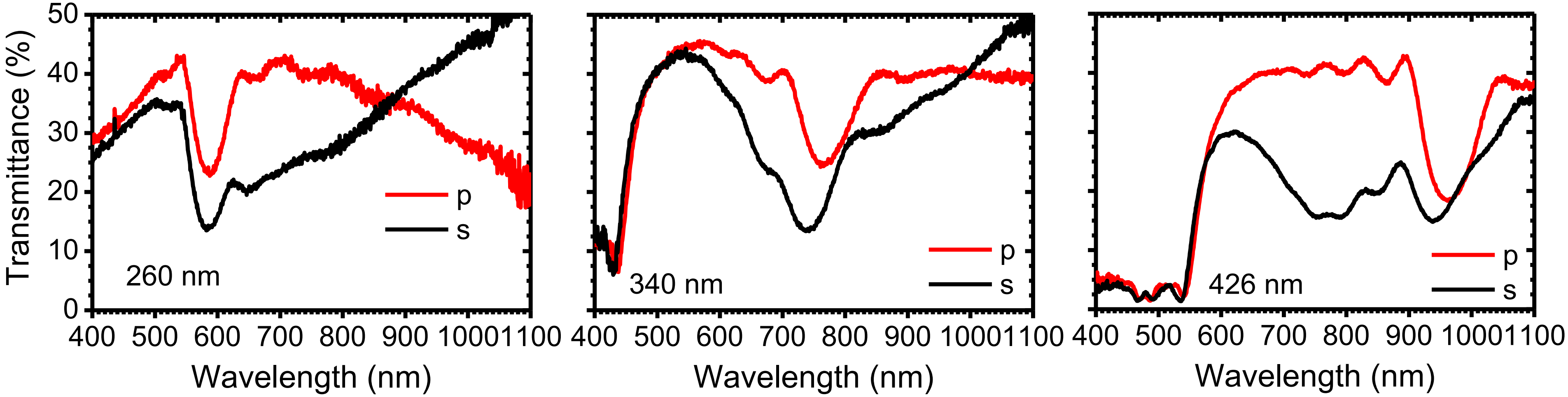
NANOCRESCENTS vs NANOCRESCENTS@OPAL

NANOCRESCENTS

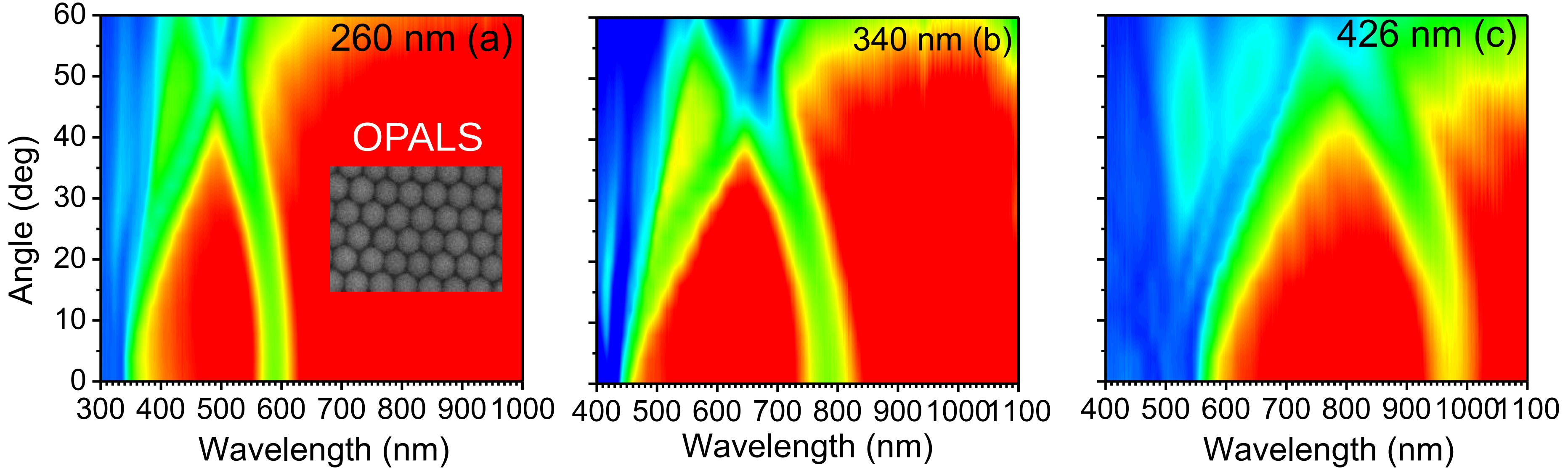




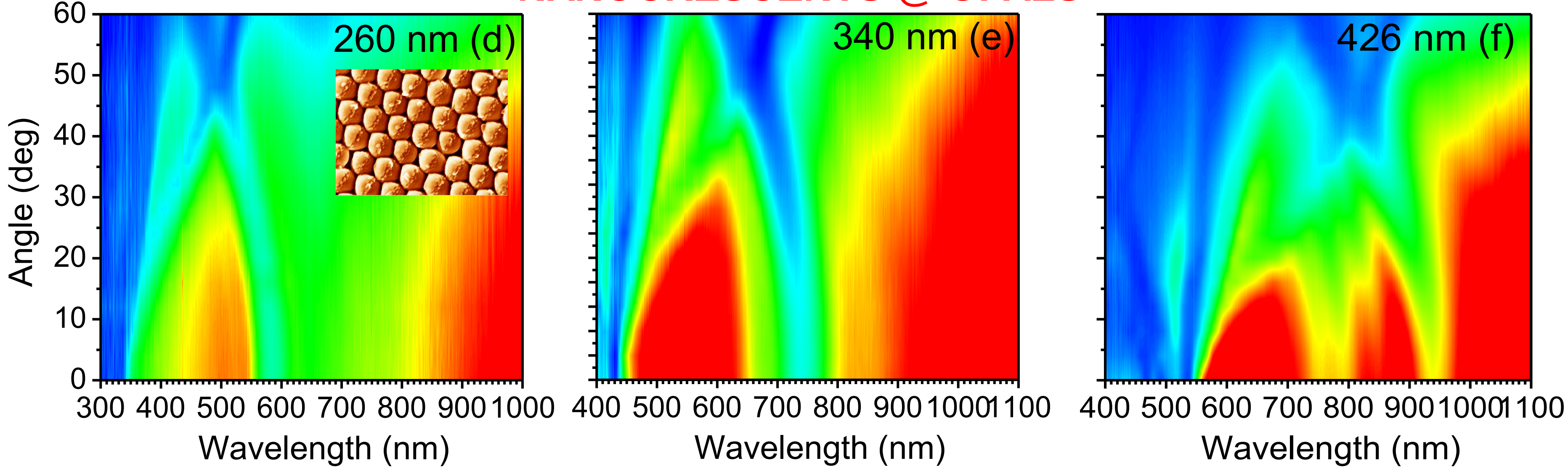
NANOCRESCENTS @ OPALS



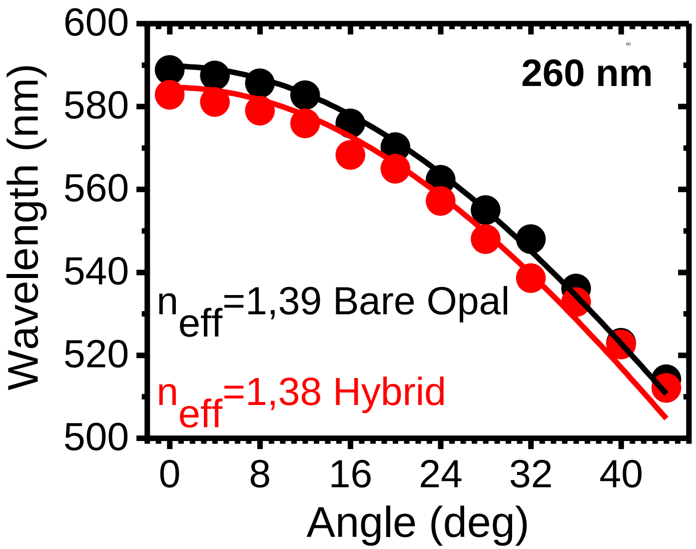
OPALS & NANOCRESCENTS@OPALS



NANOCRESCENTS @ OPALS

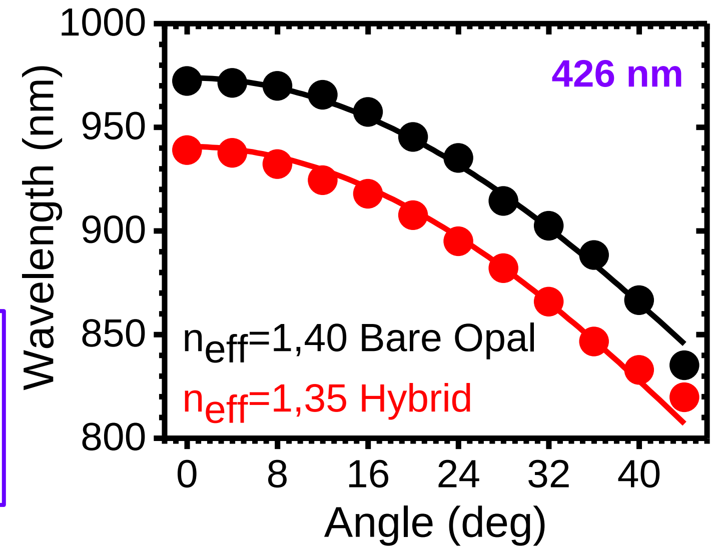


DISPERSION PROPERTIES OF HYBRID SYSTEM



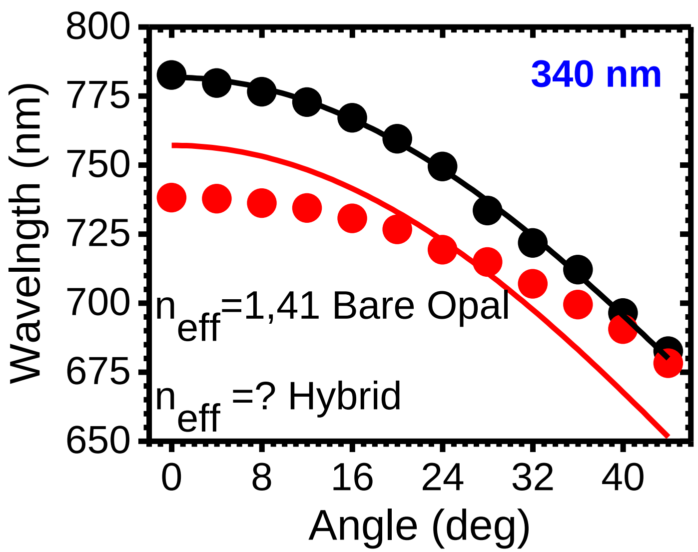
- No spectral shift
- Unchanged dispersion

- Spectral Shift
- Unchanged dispersion



$$m\lambda = 2D\sqrt{n_{eff}^2 - sin^2\vartheta}$$

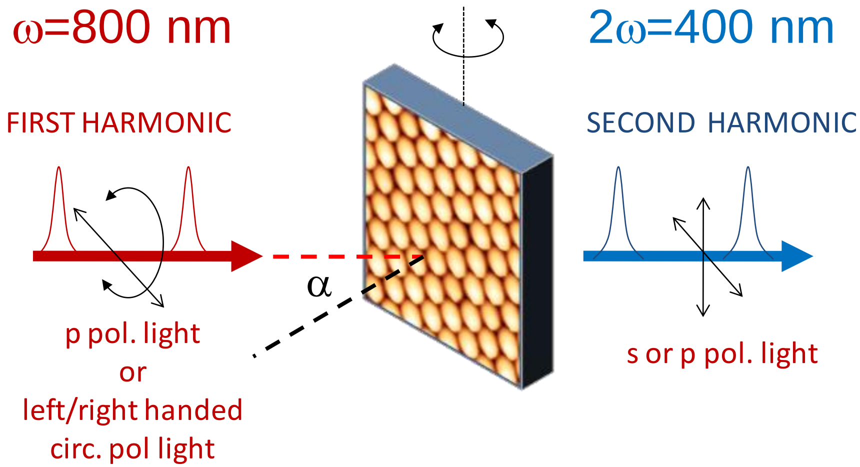
$$D = a\sqrt{\frac{2}{3}}$$



- Spectral shift
- Strongly modified dispersion

- Photons lose their wavevector dependence by transferring it to localised plasmons.
- **An HYBRID PLASMONIC-PHOTONIC EXCITATION is created.**

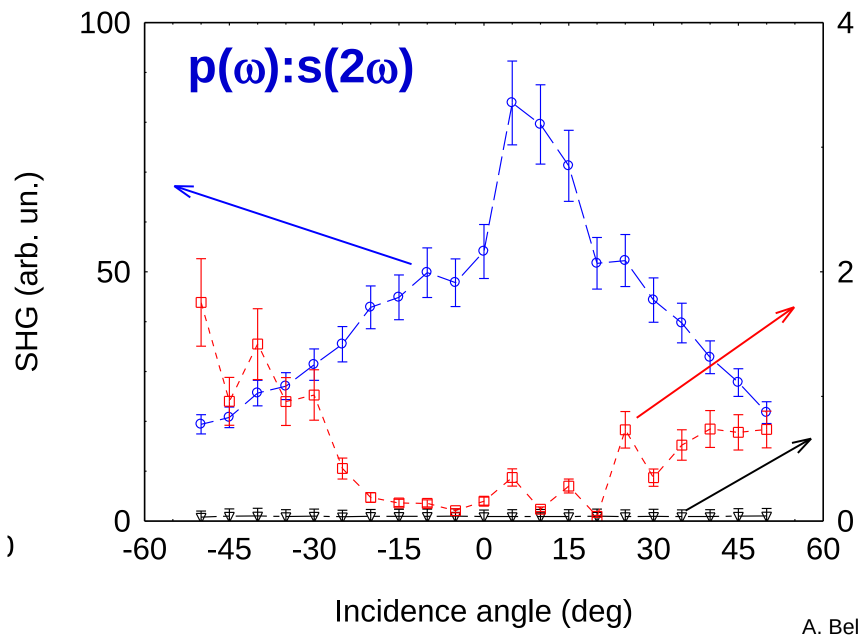
SECOND HARMONIC GENERATION CIRCULAR DICHROISM IN NANOCRESCENTS

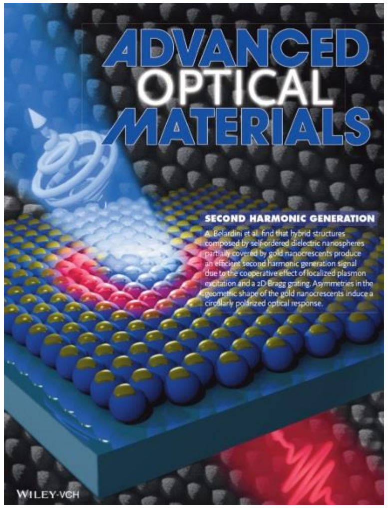


Sample 2: 340 nm + gold nanocrescents

Sample 4: 340 nm nanocrescents

Sample 5: gold film



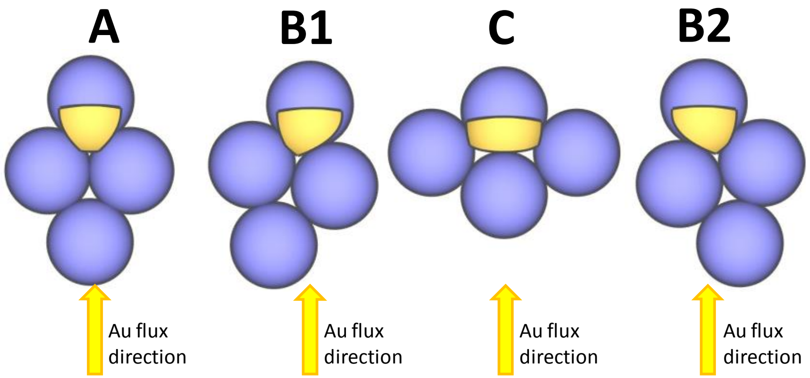


<u>Anisotropical response strongly dependent on the microsphere diameter</u>

A. Belardini et al. Adv. Optical Mater. 2, 208 (14)

SECOND HARMONIC GENERATION CIRCULAR DICHROISM IN NANOCRESCENTS

A. Belardini et al. Adv. Optical Mater. 2, 208 (14)

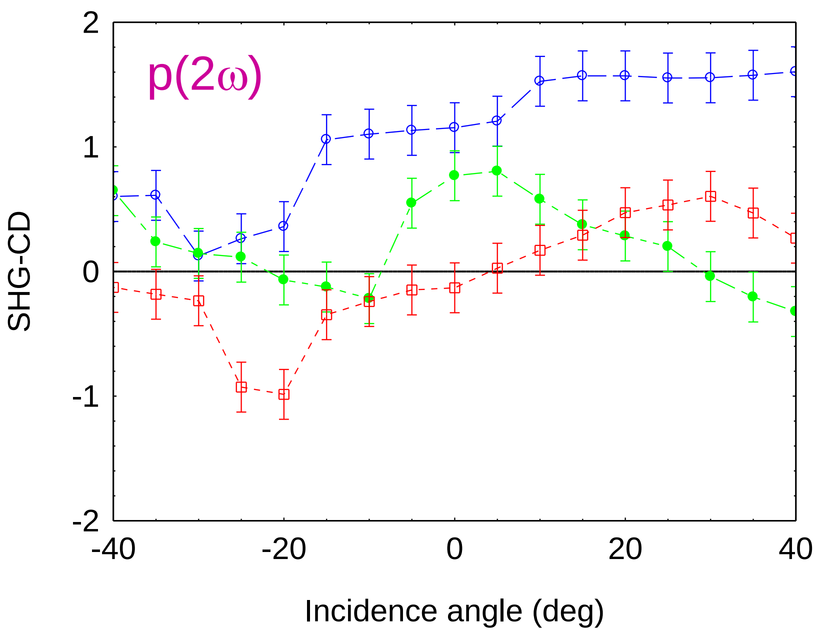


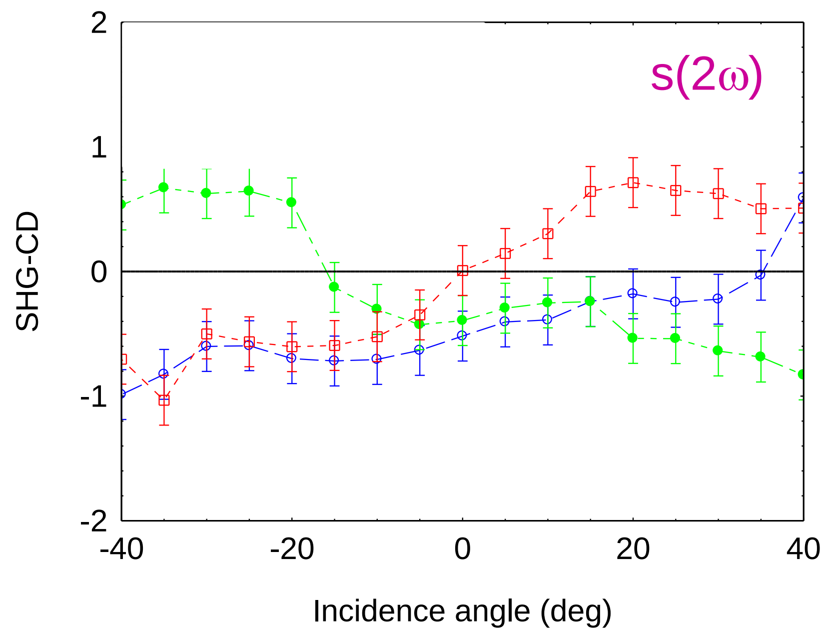
Sample 1: 260 nm + gold nanocrescents

Sample 2: 340 nm + gold nanocrescents

Sample 3: 426 nm + gold nanocrescents

$$SHG\text{-}CD = \frac{I_L^{2\omega} - I_R^{2\omega}}{(I_L^{2\omega} + I_R^{2\omega})/2}$$

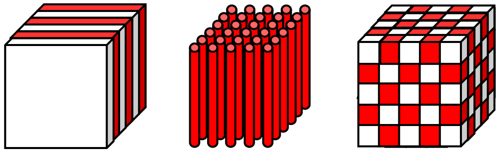




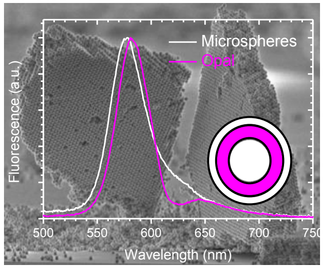
260 nm, chirality θ=0° **340 nm, chirality θ=0°** **426 nm, chirality only for θ≠0°**

TALK OUTLINE

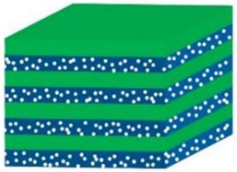
- Introduction to Photonic Crystals



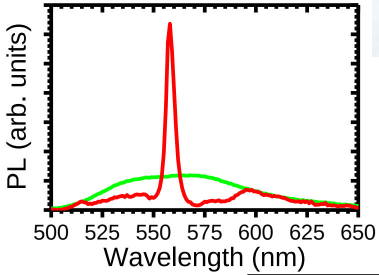
- Fluorescence Enhancement in Engineered Opals



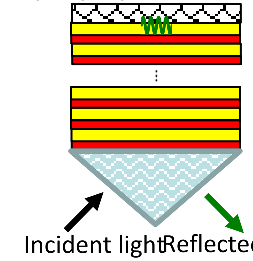
- Hybrid Plasmonic-Photonic systems (2D-3D)

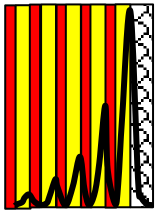


- All-Polymer Distributed Bragg Reflector Sensors



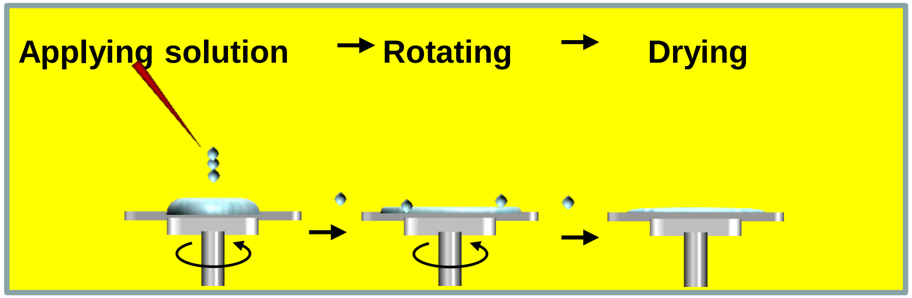
- Polymer & Hybrid Microcavities for Lasing & Switching



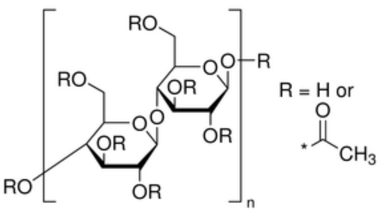


- Bloch Surface Waves: Polaritons & Light Localization

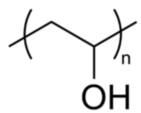
SPIN CAST 1D POLYMER PHOTONIC CRYSTALS



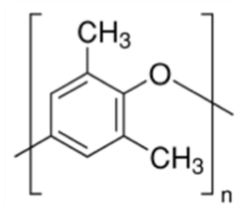
L. Frezza et al., J. Phys. Chem. C115, 19939 (11)
G. Canazza et al. Laser Physics Lett. 11, 035804 (14).



Cellulose Acetate (CA, n= 1,47)

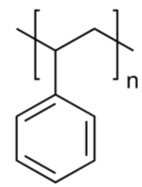


Poly(vinyl alcohol) (PVA, n= 1,5)

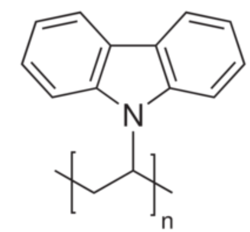


Poly(phenylene-oxide) (PPO, n= 1,57)

G. Guerra - Salerno

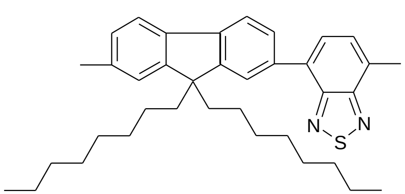


Polystyrene (PS, n= 1,59)

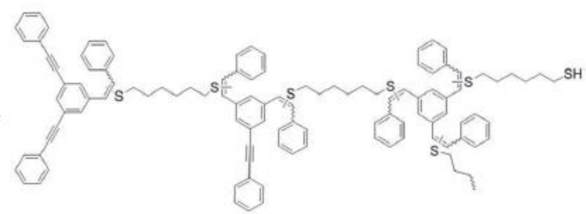


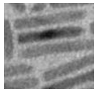
Poly(vinyl carbazole) (PVK, n=1.67)

Fluorescence



Poly(9,9-di-n-octylfluorene-alt-benzothiadiazole) (F8BT)

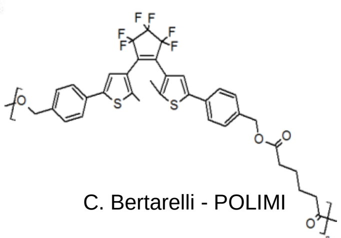




CdSe:CdS dot@rod

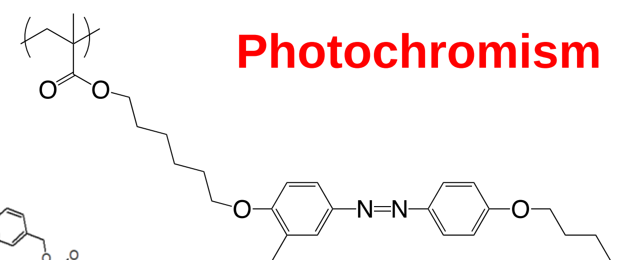
Branched Poly(vinylsulfide) (**n> 1,7**)

B. Voit - Dresden



C. Bertarelli - POLIMI

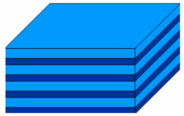
Photochromism

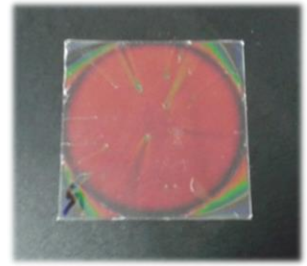


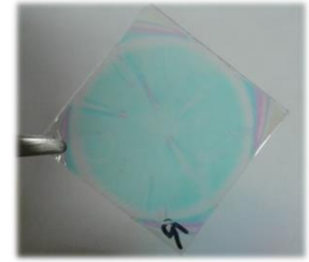
G. Galli - PISA

SPIN CAST 1D POLYMER PHOTONIC CRYSTALS

- 1D polymer PhC







Multilayers = Distributed Bragg Reflectors (DBR).

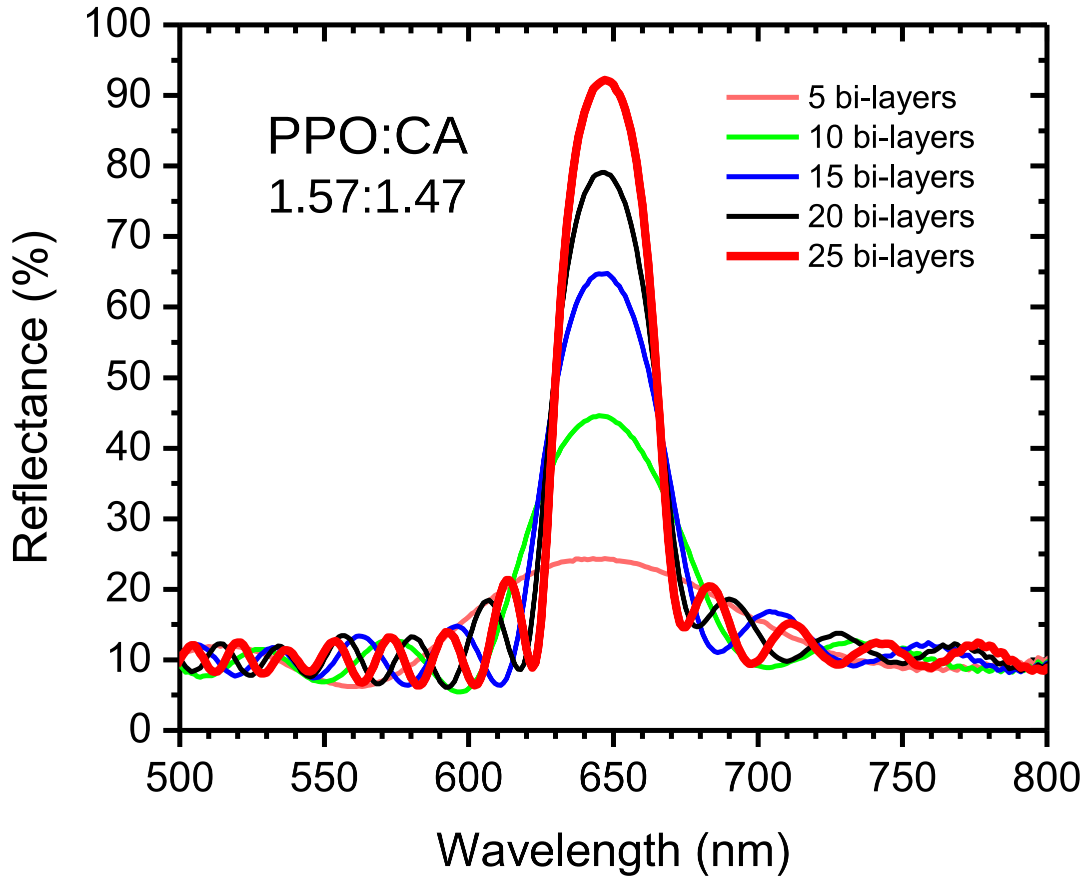
- Increased dielectric contrast provides wider band gap and more intense reflection peak.

For λ/4 condition

$$d_1 = \frac{\lambda}{4n_1} = d_2 = \frac{\lambda}{4n_2}$$

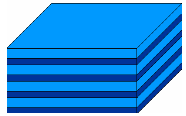
$$\Delta E = \frac{4}{\pi} E \frac{|n_1 - n_2|}{n_1 + n_2}$$

$$R = 1 - 4\left(\frac{n_1}{n_2}\right)^{2N}$$



SPIN CAST 1D POLYMER PHOTONIC CRYSTALS

- 1D polymer PhC



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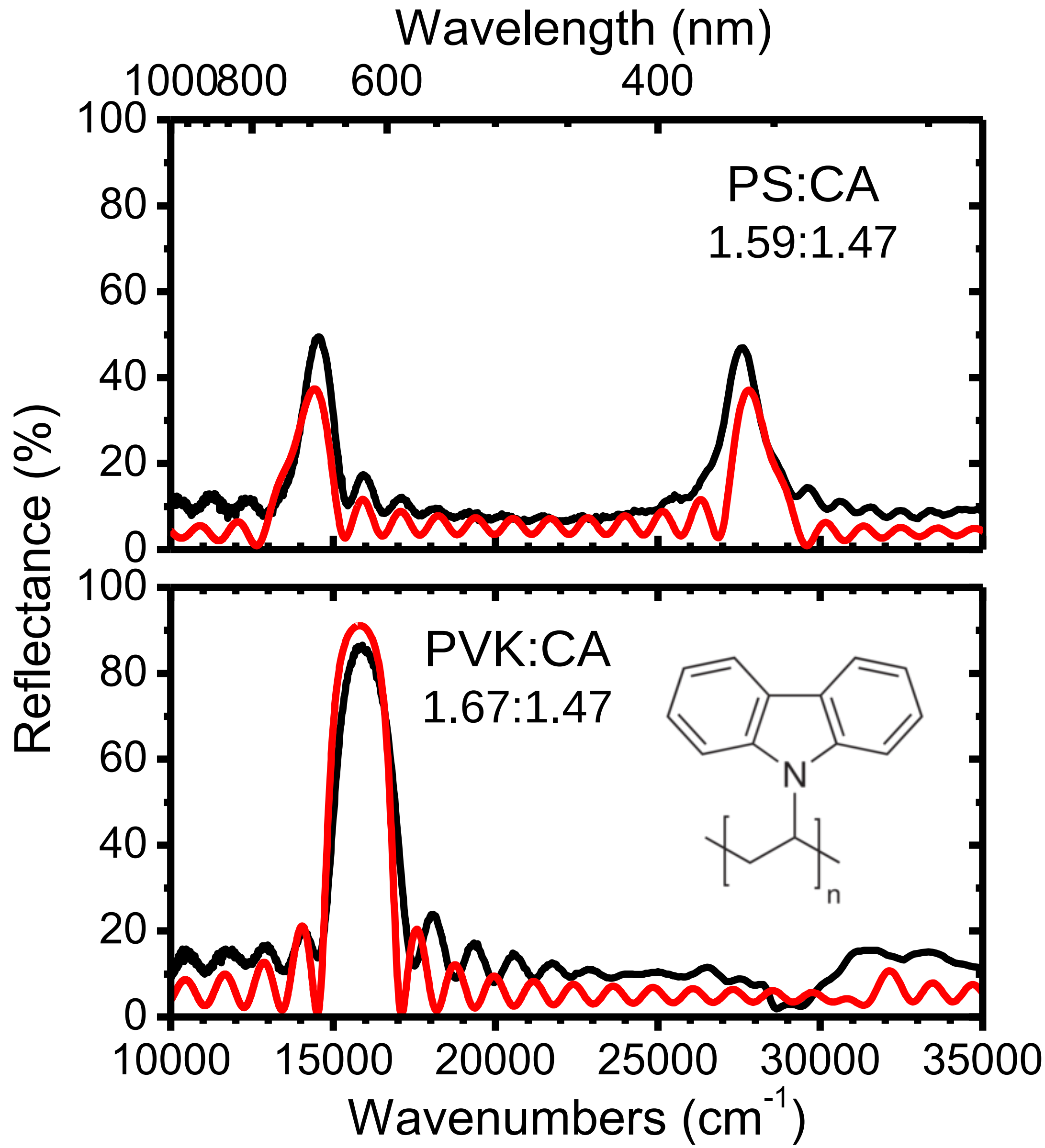
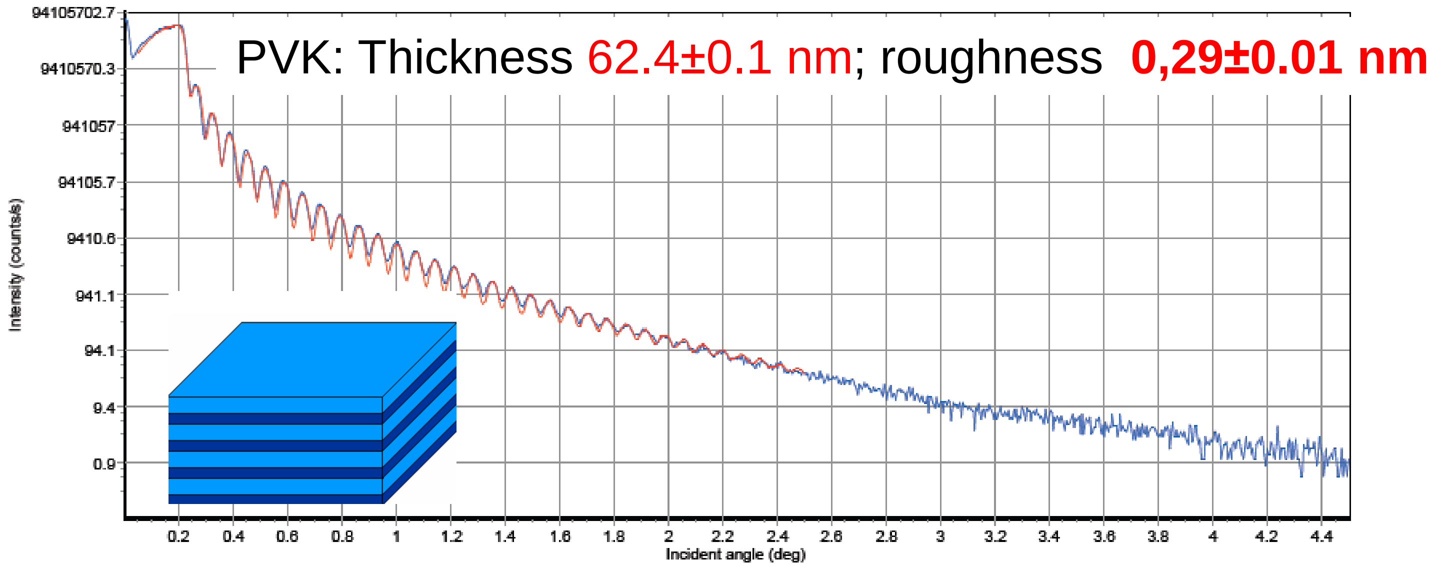
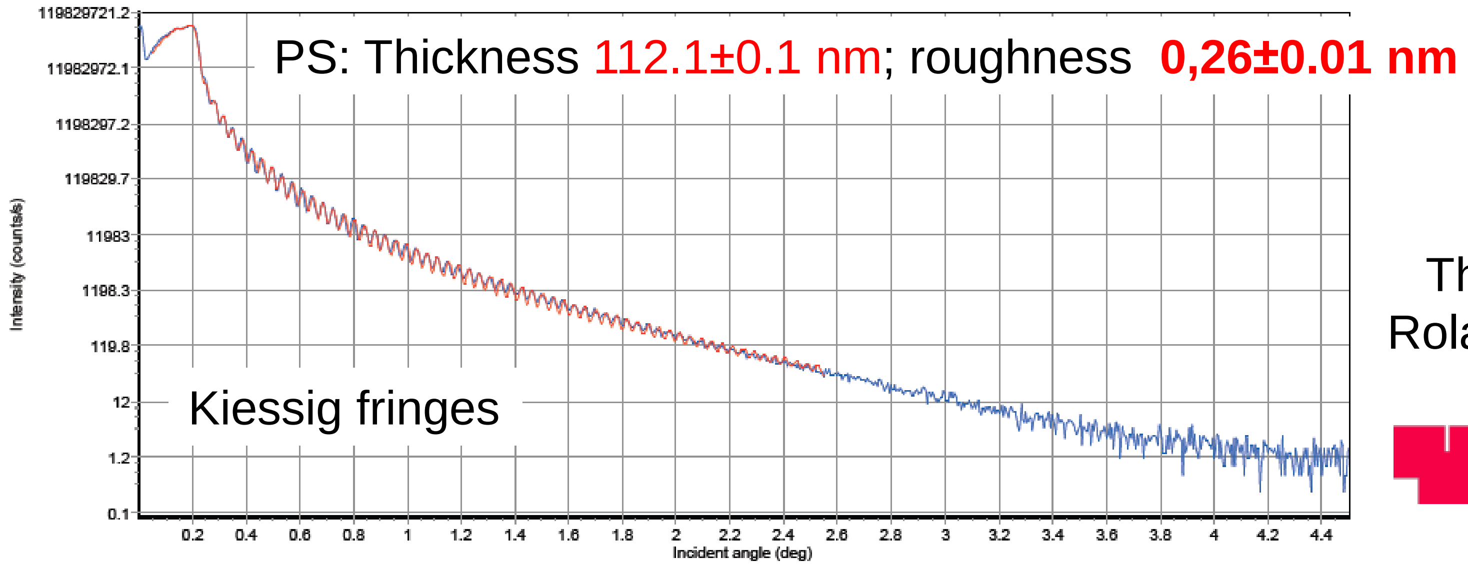


DBR: X-RAY REFLECTANCE SPECTROSCOPY





Thanks to Roland Resel

TU Graz

TALK OUTLINE

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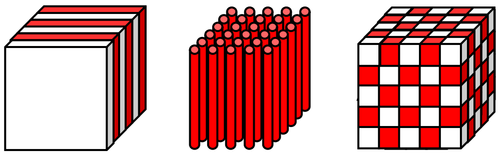

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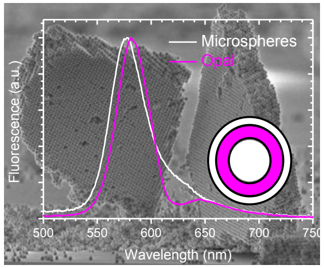

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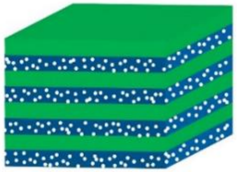

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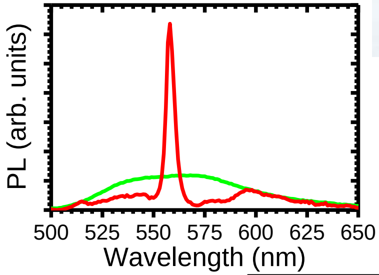

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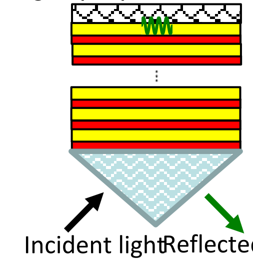
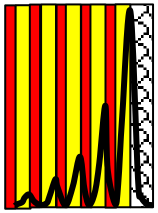
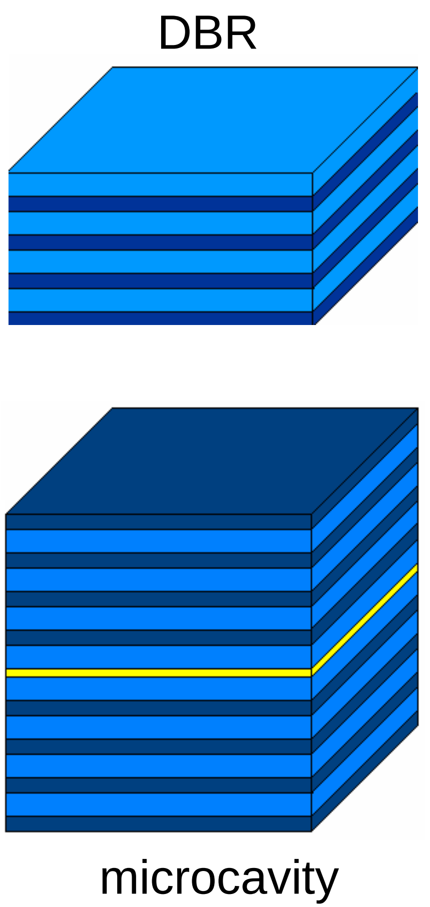
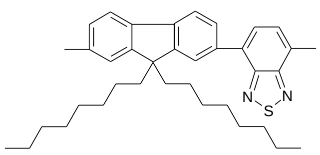




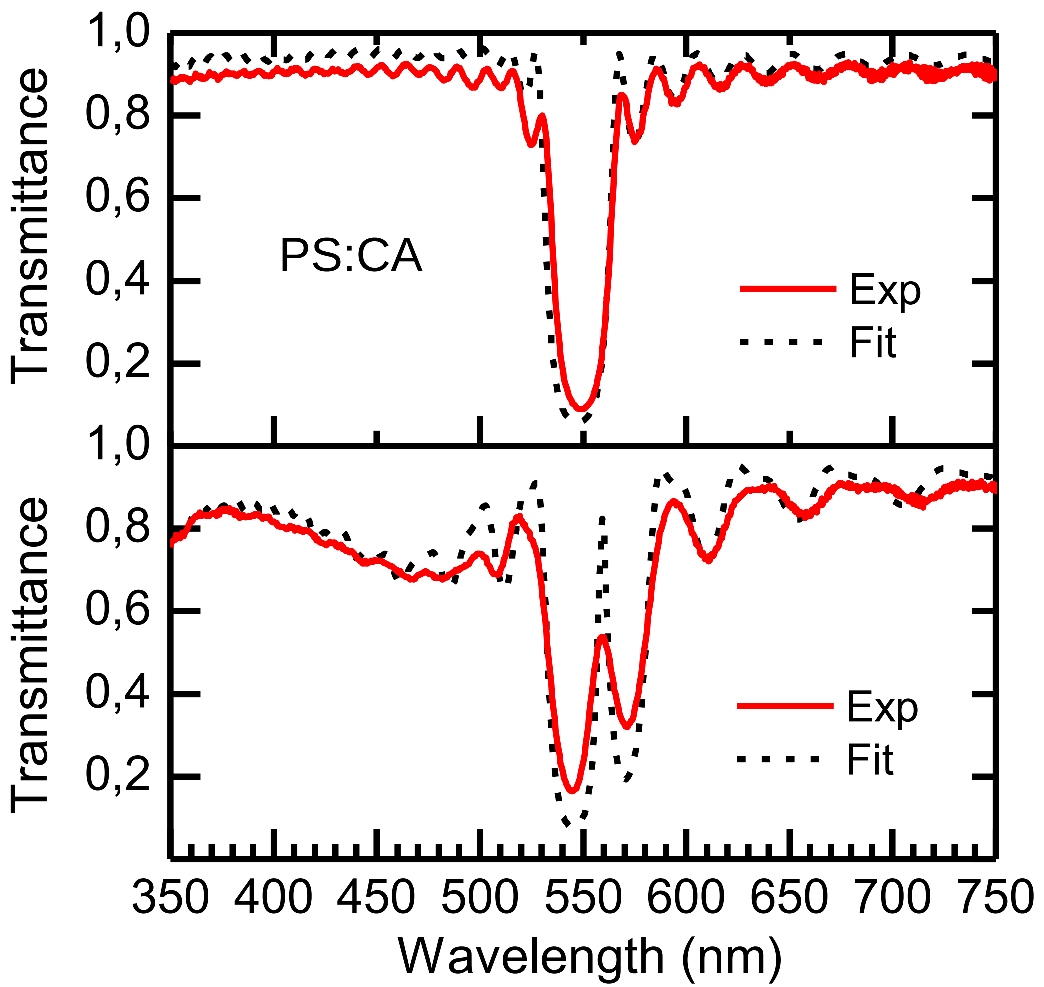
- Bloch Surface Waves: Polaritons & Light Localization

POLYMER MULTILAYERS & MICROCAVITIES



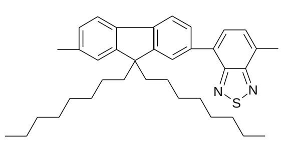


F8BT
10-150 nm

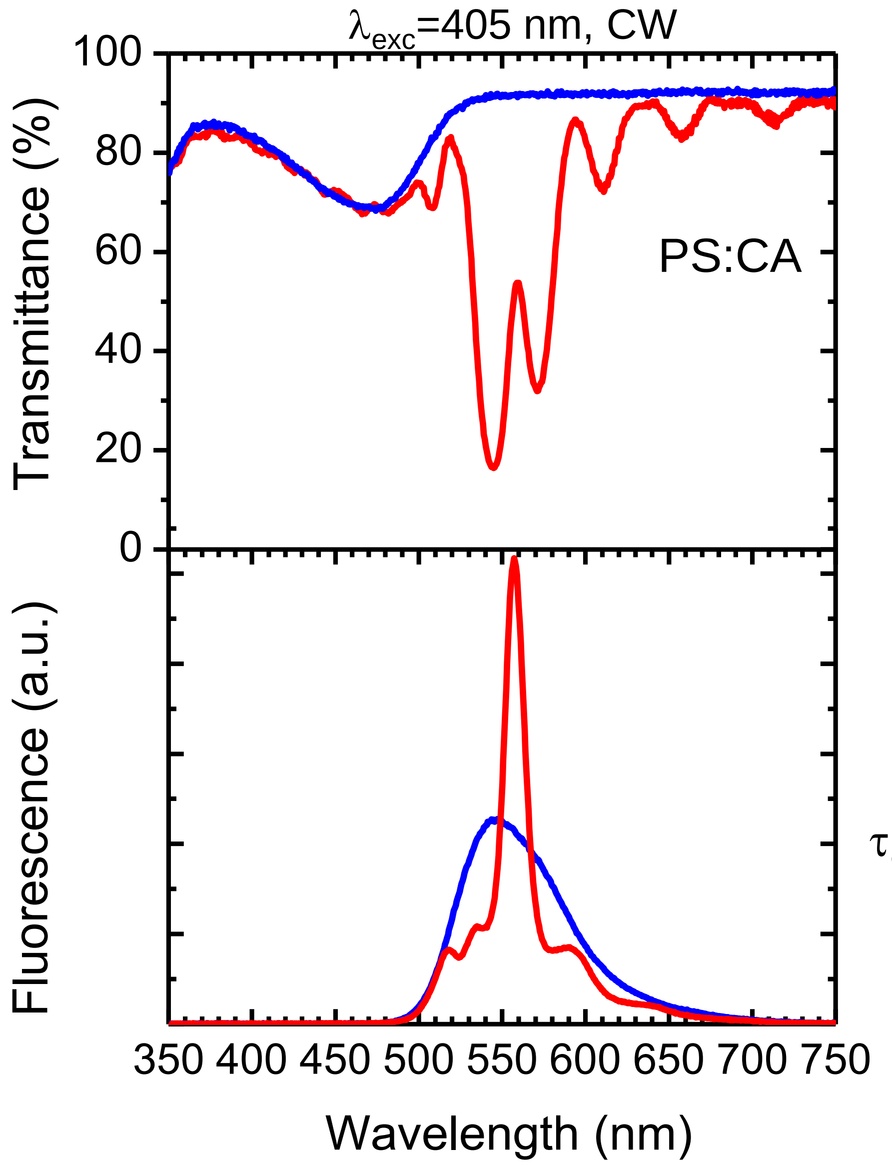


L. Frezza et al., J. Phys. Chem. C115, 19939 (11)
G. Canazza et al. Laser Physics Lett. 11, 035804 (14).

FLUORESCENCE OF MICROCAVITIES



F8BT



Microcavity Quality Factor (Q)

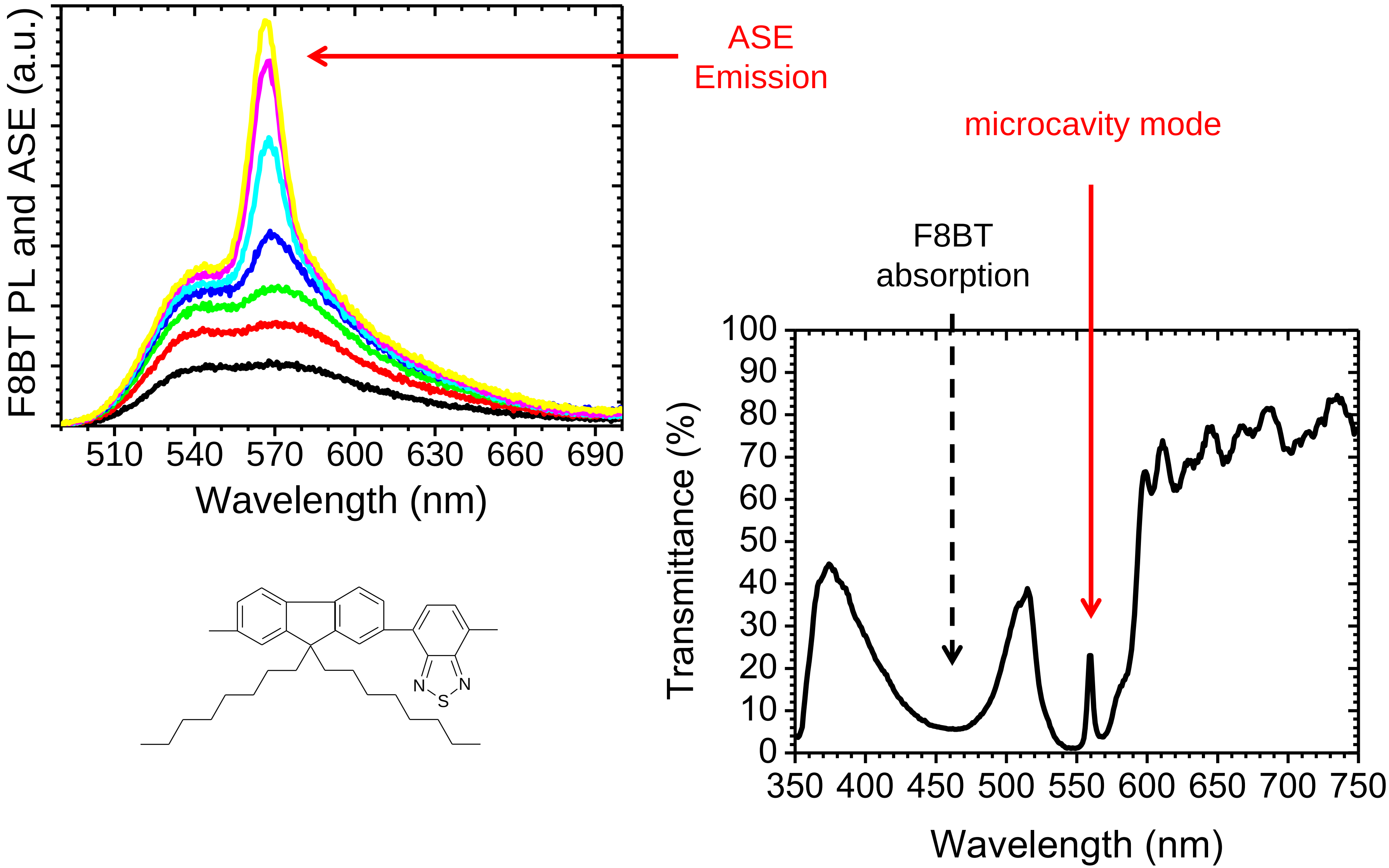
$$\mathbf{Q} = \frac{\boldsymbol{E}}{\boldsymbol{\Delta E}} = 2\pi\nu\tau_c$$

E=hν, emission energy

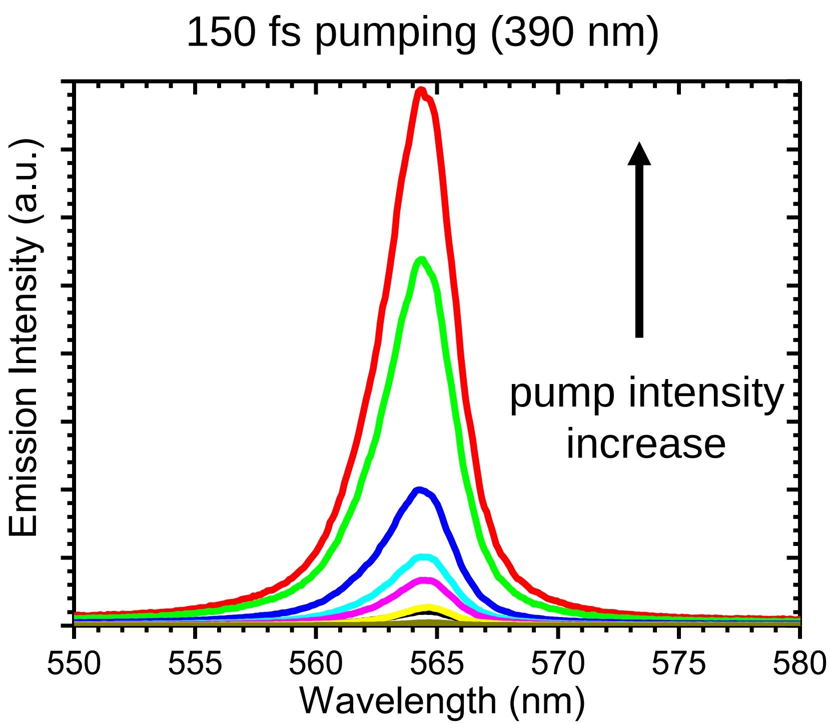
ΔE, FWHM (~16 nm)

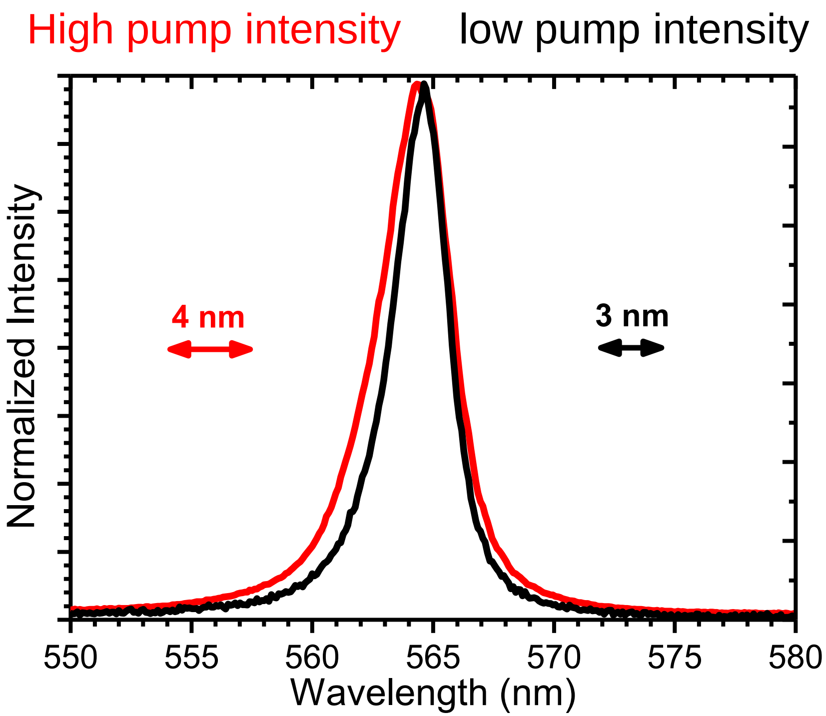
τ_c, photon lifetime in the cavity

MICROCAVITY TUNED ON ASE



MICROCAVITY LASING?





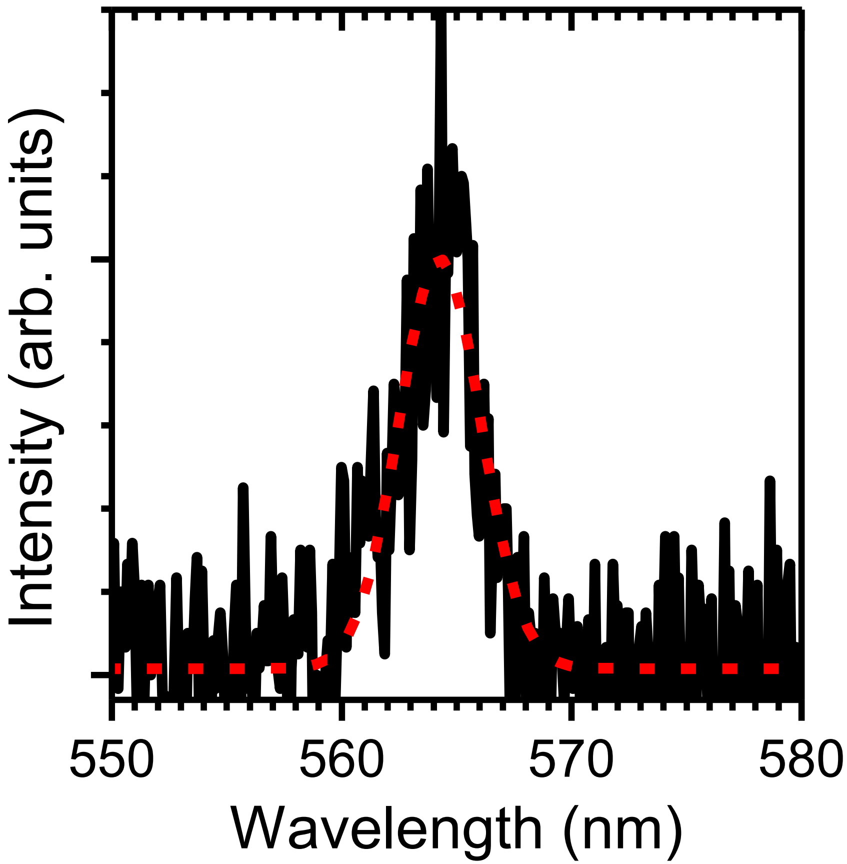
- For very low pumping intensity, the linewidth is very small, indicating an high optical quality of all-polymer microcavities.
- No apparent evidence of line sharpening is observed for strong pumping.

MICROCAVITY EMISSION: PEAK ASIMMETRY

150 fs pumping (390 nm)

SINGLE GAUSSIAN

FWHM=4.2 nm

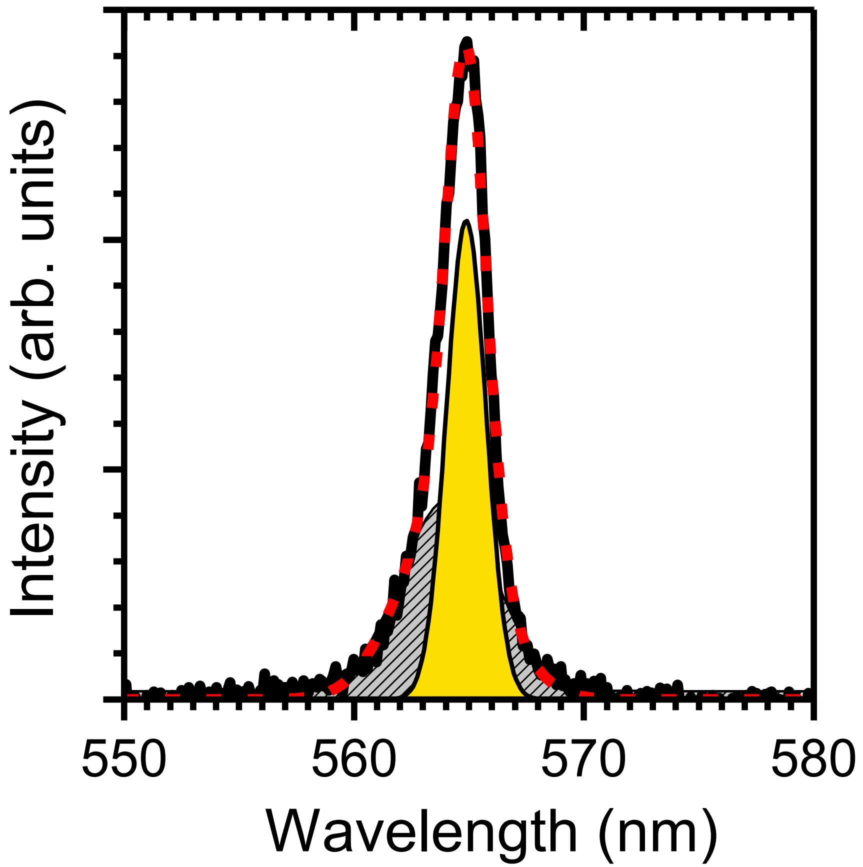


Low pump 1,2 nJ/cm²
(< threshold)

TWO GAUSSIANS

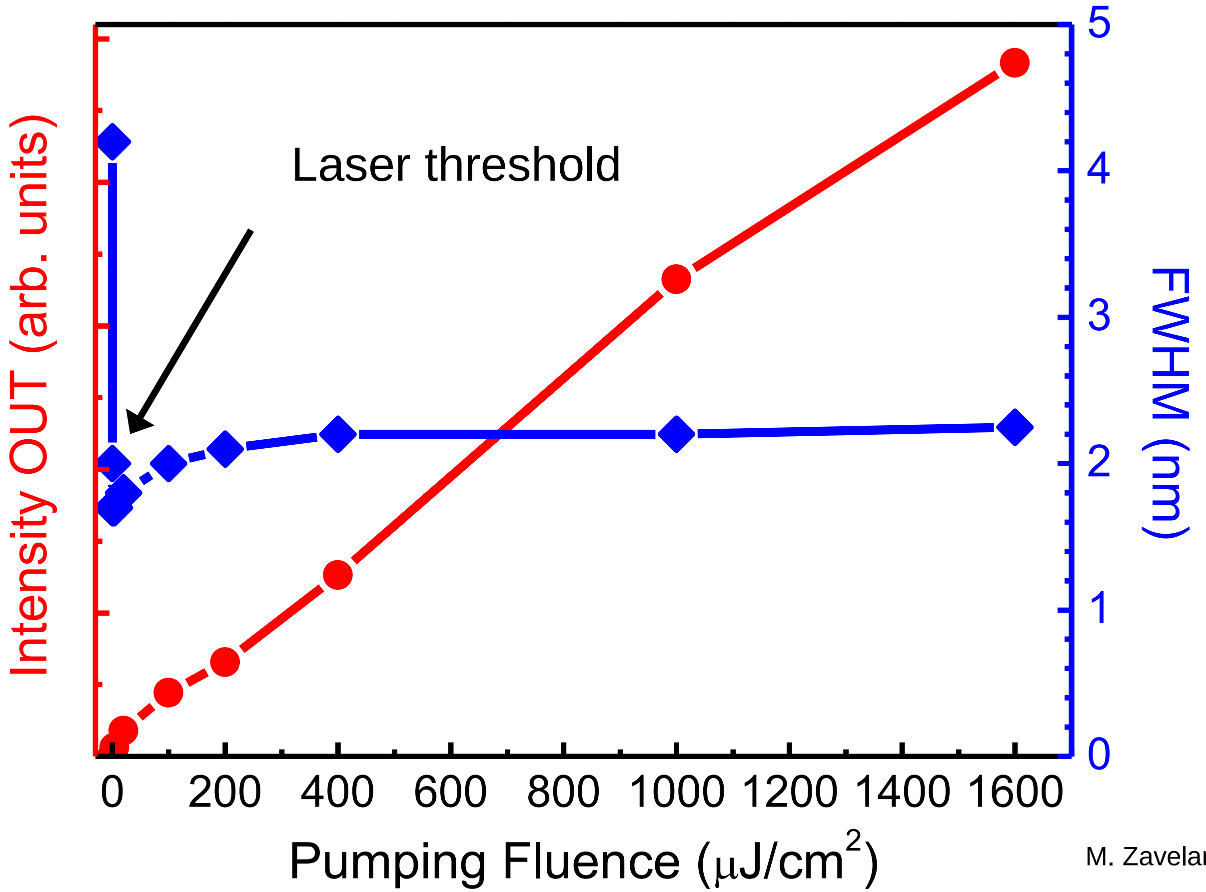
FWHM ~ 4.4 nm

FWHM ~ 1.8 nm



High pump 20 μJ/cm²
(~ threshold)

LASING FROM ALL POLYMER MICROCAVITIES



M. Zavelani-Rossi et al. IIT@POLIMI

- Very low threshold (<20 μJ/cm²).
- Gain switching regime above threshold: avalanche excited state decay makes faster and faster the emission thus broadening it.

CONCLUSIONS

- I reported an overview of the work on organic & hybrid photonic crystals we are performing in Genoa.

- Opals, microsphere monolayer arrays and polymer multilayers are simple and cheap playgrounds useful to address different photonic topics like lasing, fluorescence enhancement, hybrid photonic-plasmonic or photonic-excitonic excitations, switching and sensing.

- **I hope this talk could foster your curiosity and stimulate the study of novel phenomena or technological applications by using functional polymer/hybrid photonic/plasmonic materials.**

ACKNOWLEDGMENTS

Special Thanks to:
Serena Gazzo
Giovanni Manfredi
Robert J. Knarr
Francesco Campanella
Filippo La Rosa
Marina Alloisio
Rosa Silvia Raggio
Giancarlo Canazza
Simone Congiu
Paola Lova
Luca Occhi
Valentina Robbiano
Marco Pisano
Emanuele Bozzoni

PRIN MIUR

Materiali Polimerici Nanostrutturati con strutture molecolari e cristalline mirate, per tecnologie avanzate e per l'ambiente (2010XLLNM3)

Plasmonic Nanostructures @ Opals
F. Buatier de Mongeot & Co.
Dipartimento di Fisica Università di Genova

Opals & Engineered Colloids
M. Laus, K. Sparnacci & Co.
Università del Piemonte Orientale (AL)

Azo-type Photochromic polymer synthesis
G. Galli et Co.
Università di Pisa

SEM Photonic crystals
L. Boarino & Co.
INRIM - Torino

Advanced Optics & Theory
M. Patrini, M. Liscidini, F. Marabelli, L.C. Andreani
Dipartimento di Fisica "A. Volta", Università di Pavia

Lasing action in all-polymer microcavities
F. Scotognella, M. Zavelani-Rossi, G. Lanzani
IIT@Polimi

Conjugated Polymers @ Opals
F. Cacialli, F. Di Stasio, V. Robbiano
UCL (UK)

Hybrid Photonic Crystals
C. Soci, P. Lova
NTU - Singapore

X-Ray Reflectance
R. Resel
TU – Graz (A)

Clathrating Polymers for Photonics
G. Guerra & Co.
Università di Salerno

Nano Crystals @ Polymer Microcavities
F. Di Stasio, R. Krahne
IIT@Genova

ADVERTISING

EOSAM 2014

Location: Berlin Adlershof, Germany
Duration: 15 - 19 September 2014

TOM 7 – ENERGY HARVESTING AND ORGANIC PHOTONICS

Chair: Guglielmo Lanzani, Istituto Italiano di Tecnologia, (IT)
Co-chairs: David Lidzey, University of Sheffield (GB)
Davide Comoretto, University of Genova (IT)

INVITED SPEAKERS

Jeremy Baumberg, Cambridge University (GB) - **PLENARY**
Christoph J. Brabec, Friedrich-Alexander University, Erlangen-Nürnberg (DE)
Francesco Buatier de Mongeot, University of Genova (ITA)
Franco Cacialli, University College London (GB)
Fredrik Krebs, Technical University of Denmark (DK)
Gianluca Farinola, University of Bari (IT)
Graham Turnbull, University of St. Andrews (GB)
Jérôme Cornil, Université de Mons (BE)
Jochen Feldmann, Ludwig-Maximilians University Munchen (DE)
Jordi Martorell, Institut de Ciències Fotòniques (ES)
Olle Inganäs, Linköping University (SE)
Roland Resel, Graz University of Technology (AT)
Stephan Kena Cohen, Imperial College (GB)