ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

CNR ISMN
ISTITUTO PER LO STUDIO DEI MATERIALI NANOSTRUTTURATI

SUMMER SCHOOL on PHYSICAL SENSING & PROCESSING

Organic Optoelectronic Devices in a Smart-Integrated Miniaturized System for Optical Biosensing

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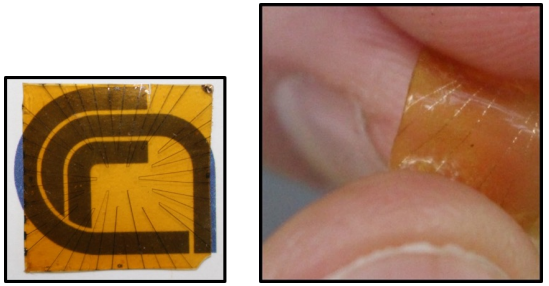
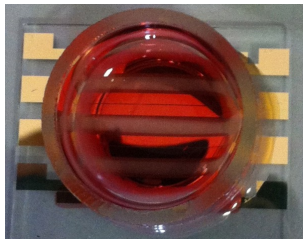
Organic/Hybrid Photonics @ CNR-ISMN

- Flexible organic light-emitting devices
- Organic photovoltaics
- Multifunctional organic transistors
- 2D materials: functionalization
- Organic bioelectronics
- Bioderived polymer for sensing
- Integrated systems for point-of-need



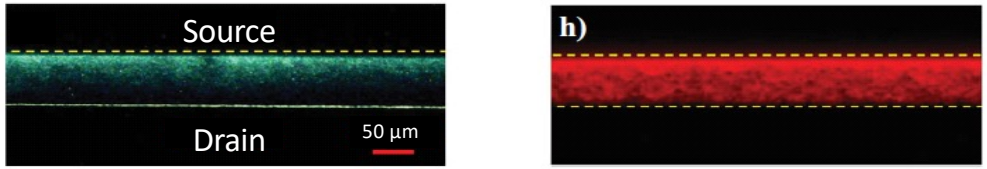
Free-standing keratin biosensor

Flexible transparent heterojunction OPV

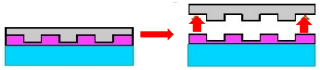


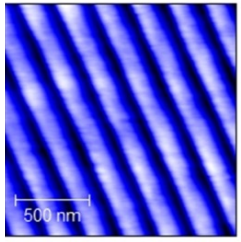
Integrated organic system for cell stimulation and recording

Top-emitting OLED on conformable metal substrate

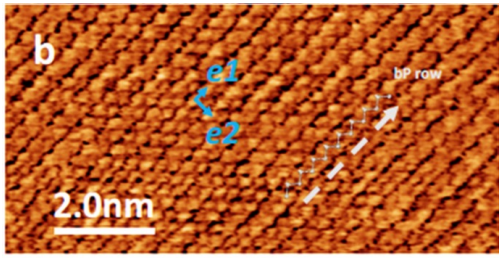


Multicolor Organic Light-emitting Transistors (OLETs)

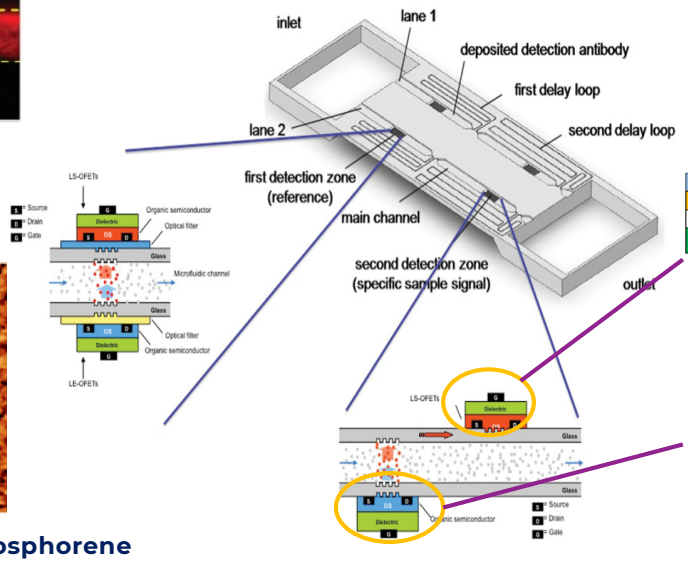


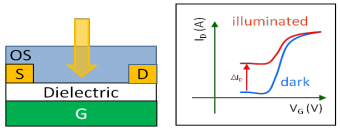


Integrable Organic-Hybrid Photonic Structure

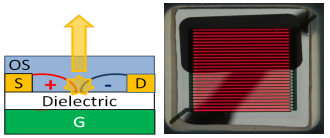


Epitaxial growth of organic moieties onto phosphorene





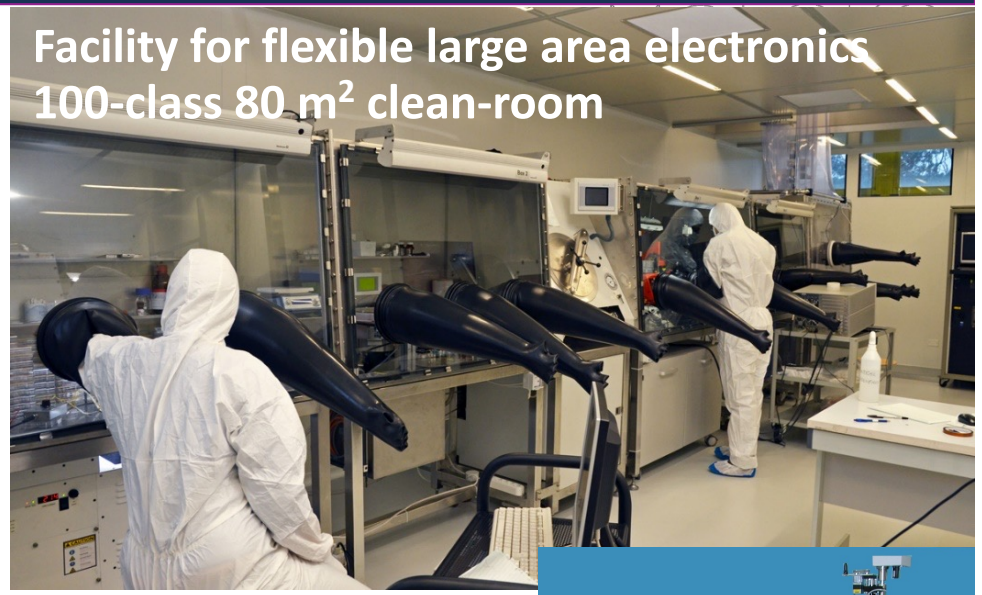
Light-sensing OFET



Light-emitting OFET

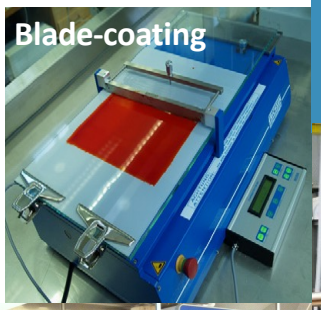
What/How?

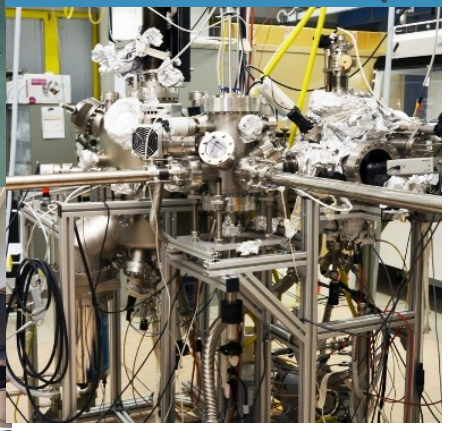
Definition of innovative device schemes integrating several functionalities (magnetic, electrical, photonic, biological) in organic-hybrid systems



Fabrication of organic-hybrid components and systems

- Physical techniques: *Vacuum sublimation, e-guns, pulsed plasma, …*
- Wet techniques: *Spin-coating, Doctor Blade, Slot dye,…*
- UV/e-beam lithography facility and nanoimprint system

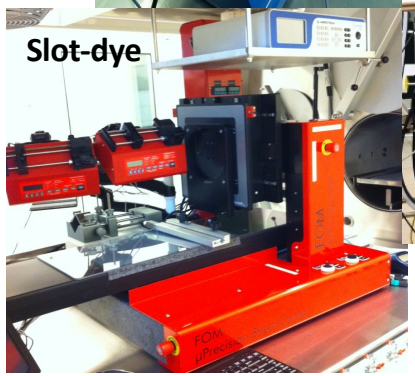




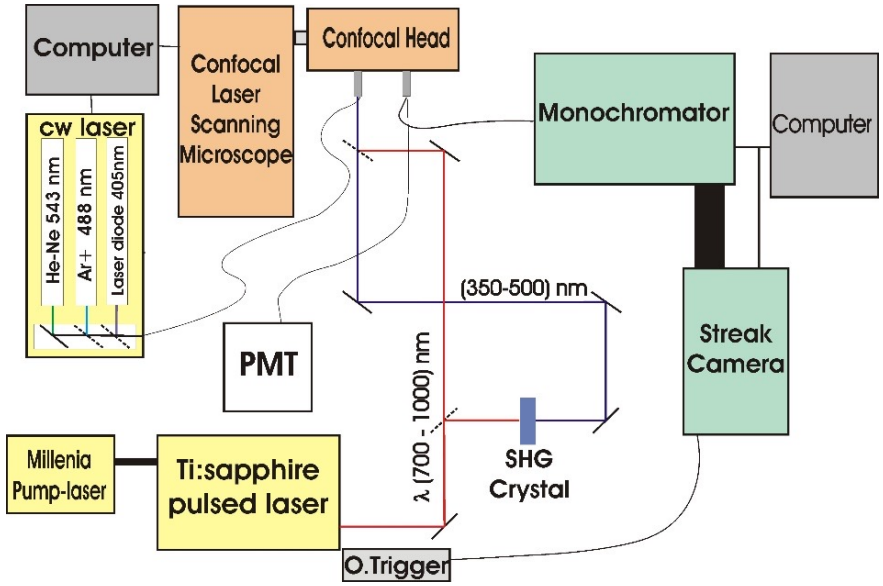
Pulsed plasma deposition

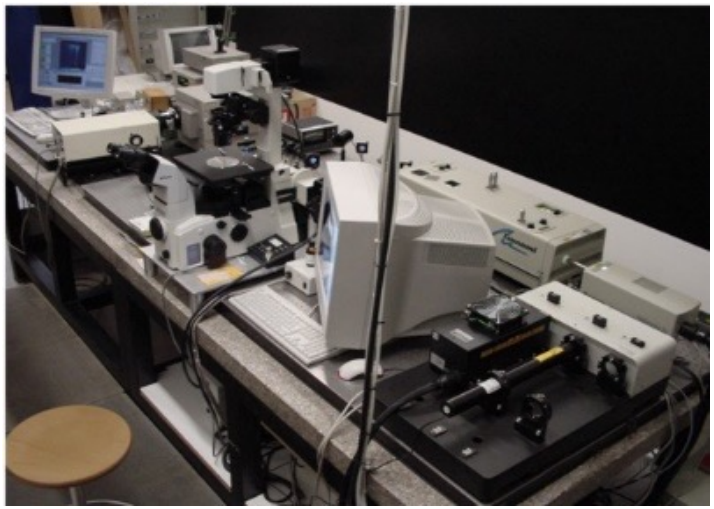
Multi-scale characterization for device engineering

- Photo-physical processes (*nm-scale*)
- Long-range morphology and structure (*µm-scale*)
- Working device optoelectronic simulation (*cm-scale*)

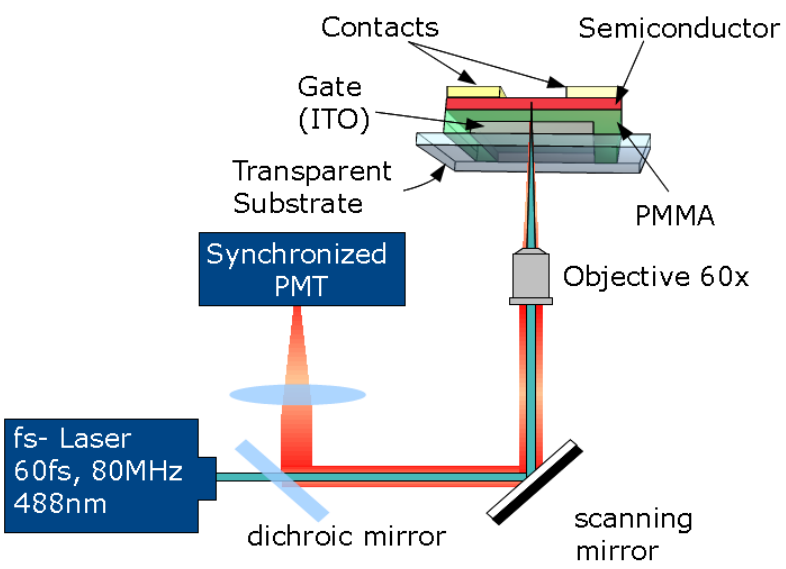


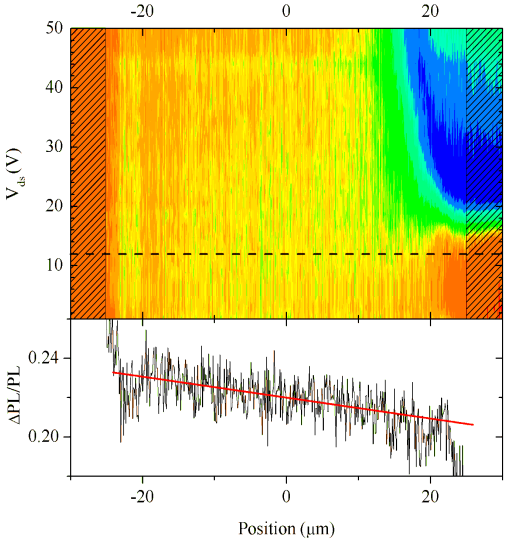
Advanced characterization in hybrid optoelectronics





Confocal photoluminescence electro-modulation microscopy on biased optoelectronic organic devices
with 300 nm lateral spatial resolution 2 ps time resolution and temperature control in the range 4-300 K



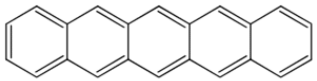


Mapping of charge density in organic thin-film transistor

W.A.W Koopman Nano Lett. 2014, 14, 1695−1700

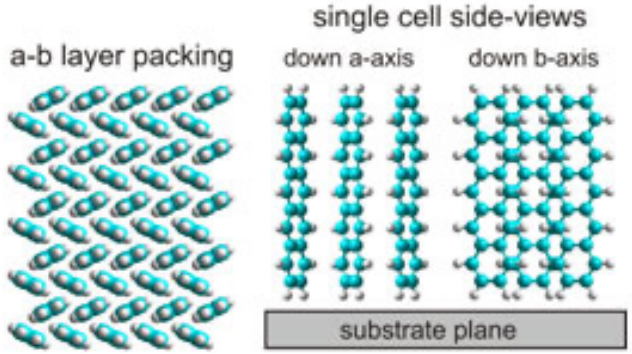
Molecular organization for multifunctionality in organics

Base unit: conjugated molecule

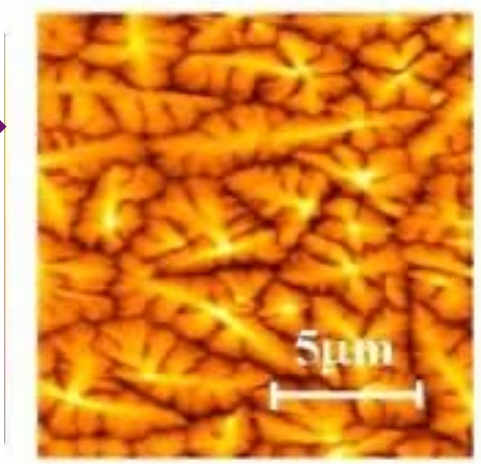


Packing force: weakly Van der Walls force

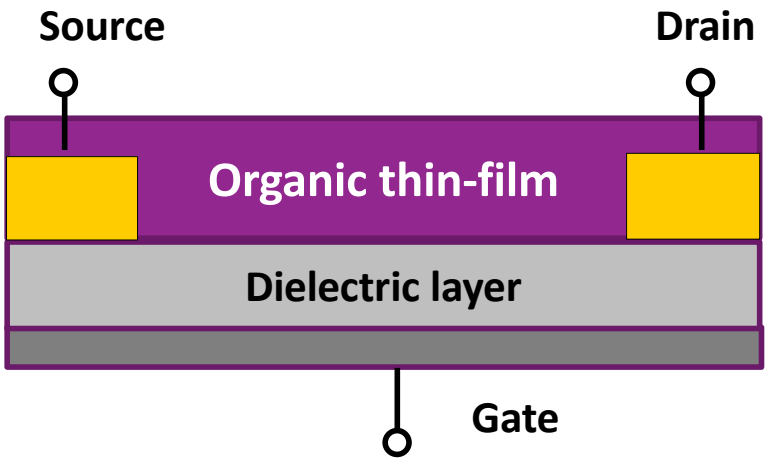
Semiconductor polycrystalline thin-film



Charge carriers transport/recombination

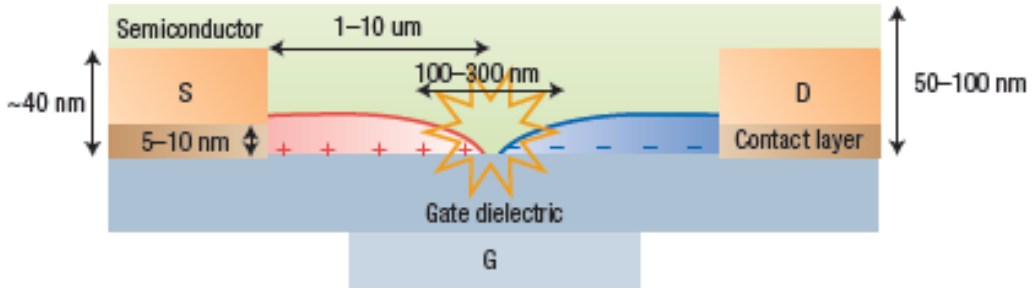


Locally-ordered molecular domains



Organic field-effect transistors as truly interface devices

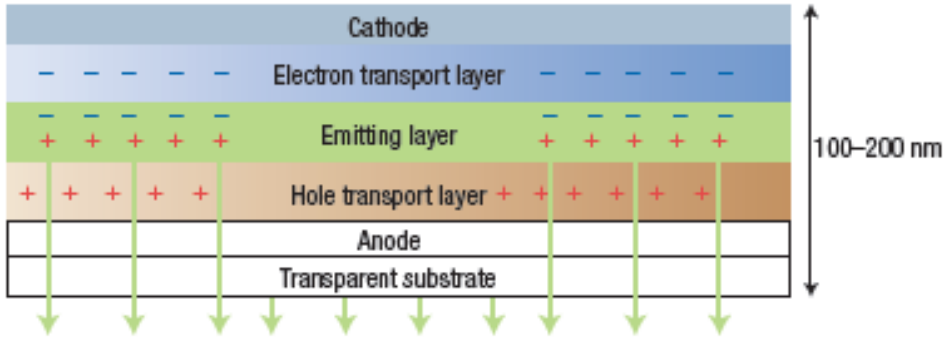
OLET vs OLED



$E_{field} \sim 10^4$ V/cm

HORIZONTAL TRANSPORT GEOMETRY

FIELD-EFFECT CHARGE TRANSPORT



$E_{field} \sim 10^6$ V/cm

VERTICAL TRANSPORT GEOMETRY

BULK CHARGE TRANSPORT

- Higher brightness
- Higher and balanced charge mobility (10^{-1} vs 10^{-4})
- Higher current densities (10 vs 10^{-3})
- Less manufacturing

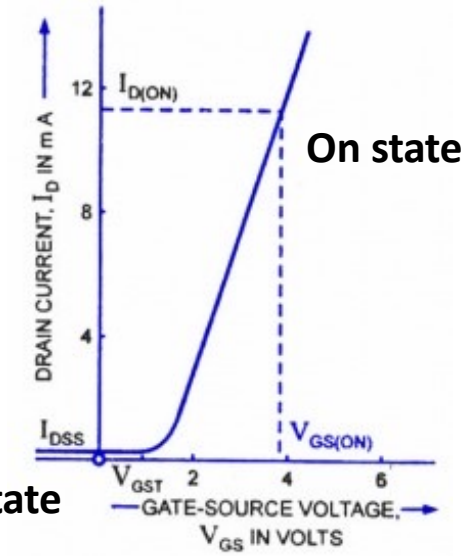
M. Muccini, *"A bright future for field-effect transitors"* , Nature Mat., 5, 605 (2006)

OLET as high-integration ICT component

Signal electrical switching as in field-effect transistor

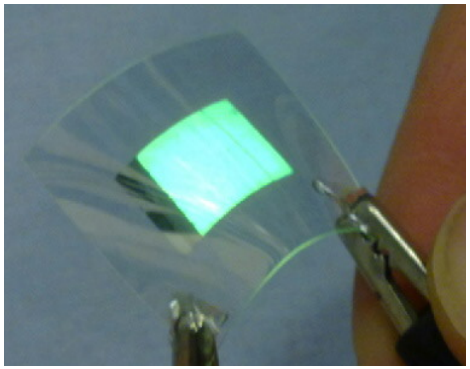
+

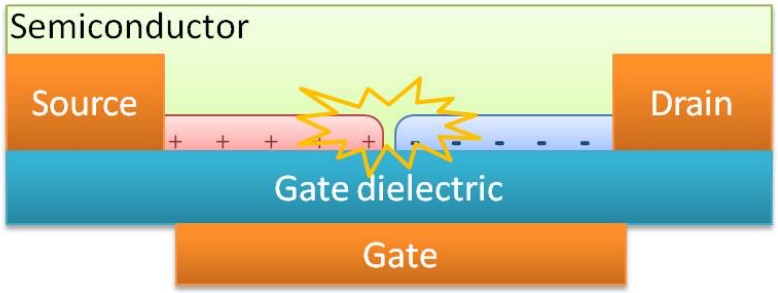
Light emission as in light-emitting diode



On state

Off state





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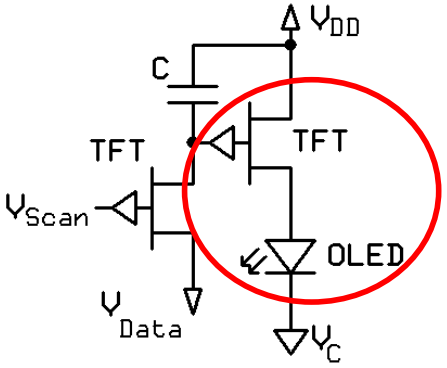


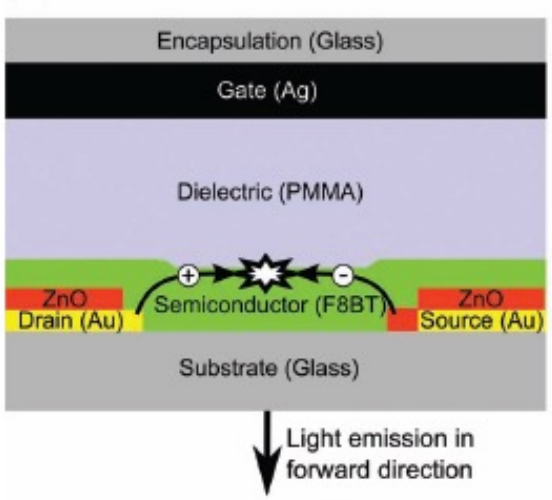
OLED pixel scheme

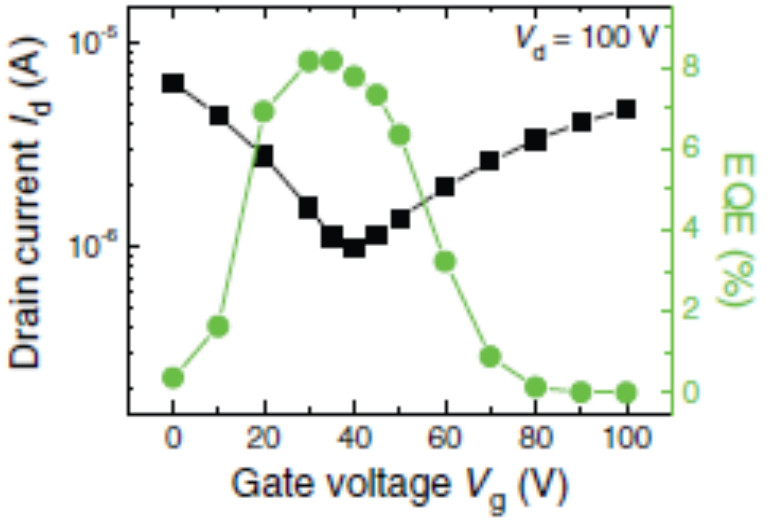
OLET figures of merit: state of the art

External quantum efficiency

$$\frac{\text{N° flowing charges}}{\text{N° emitted photons}}$$

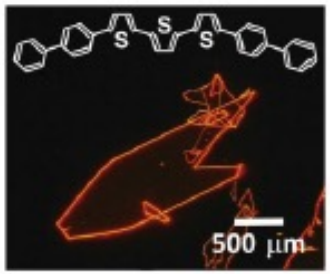
EQE > 8%

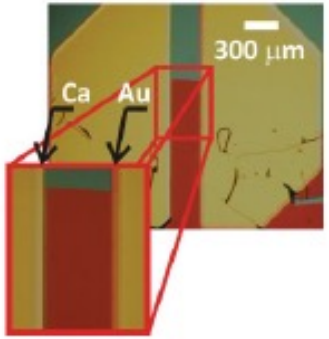




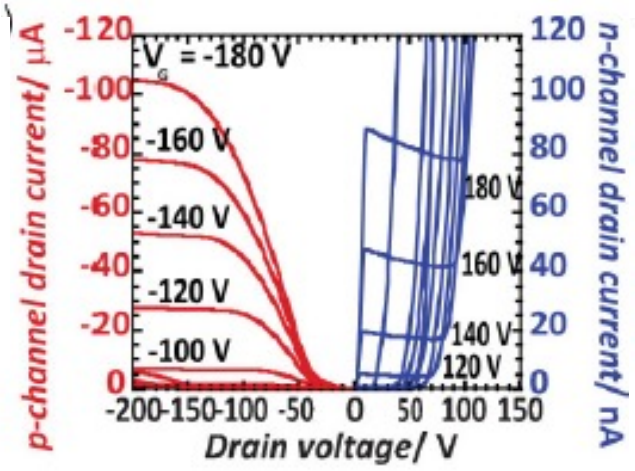
Adv. Mater. 2012, 24, 2728

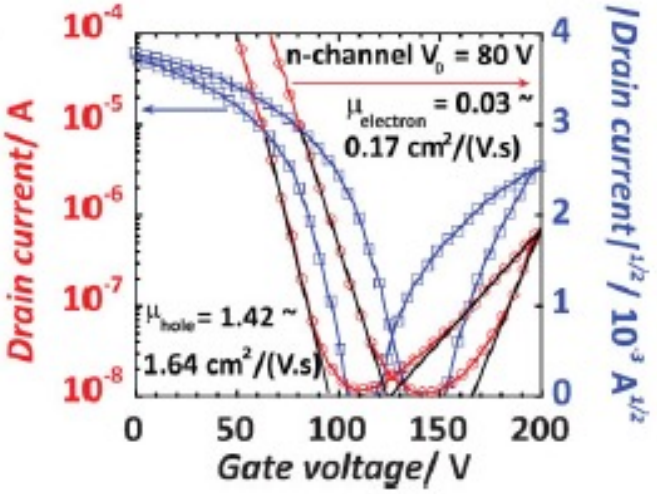
Ambipolarity





Single-crystal device

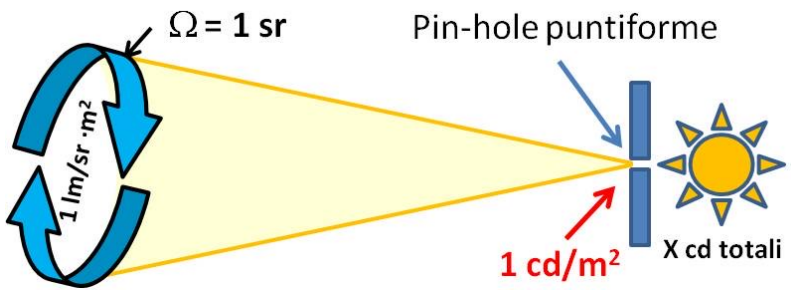


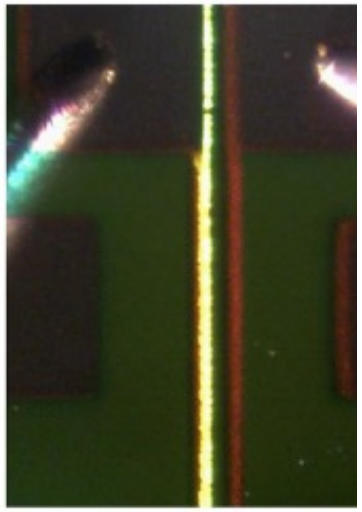


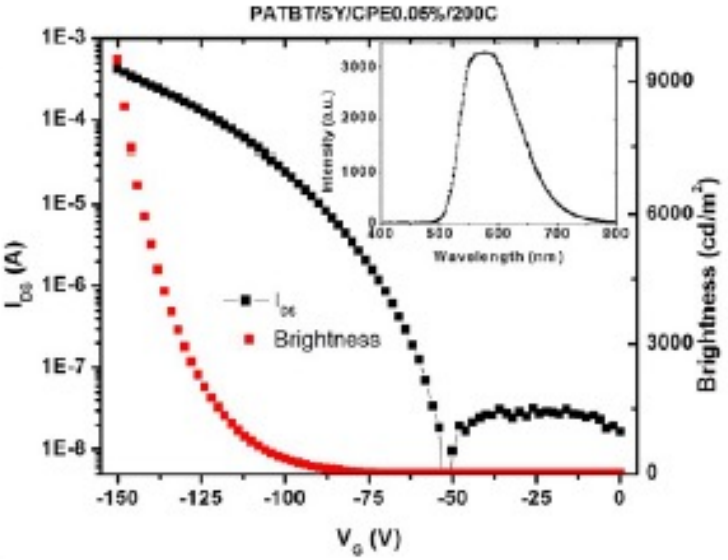
Adv. Funct. Mater. 2009, 19, 1728–1735

OLET figures of merit: state of the art

Brightness



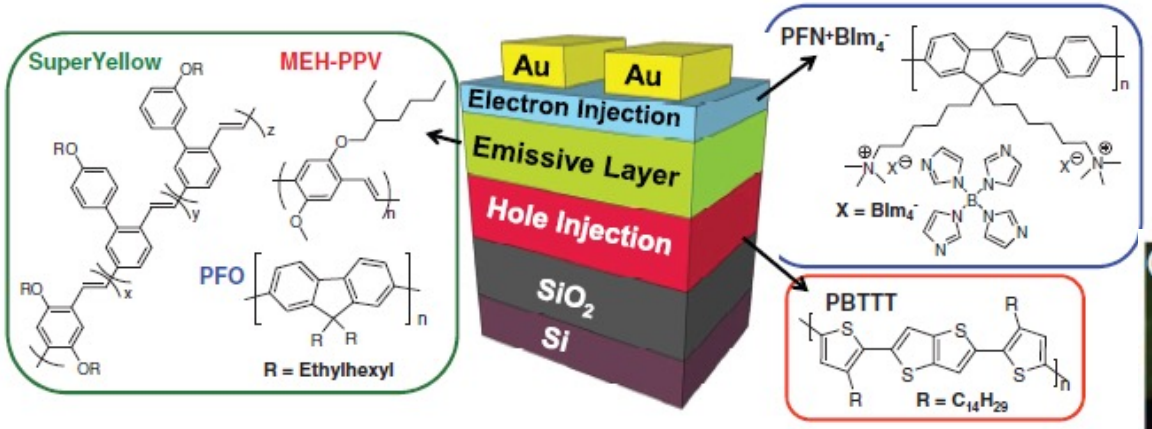


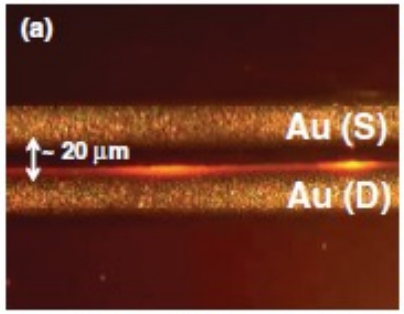


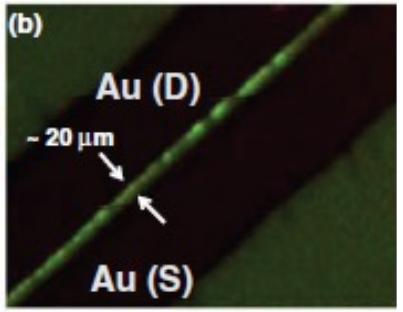
Form factor in OLETs!

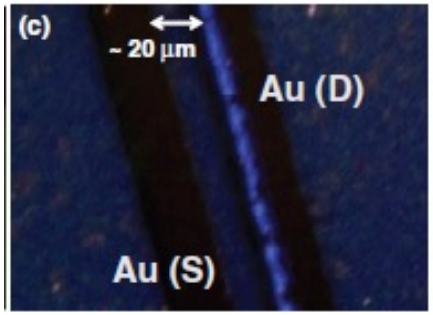
ACS Nano 7, 2344–2351, 2013

Color tunability



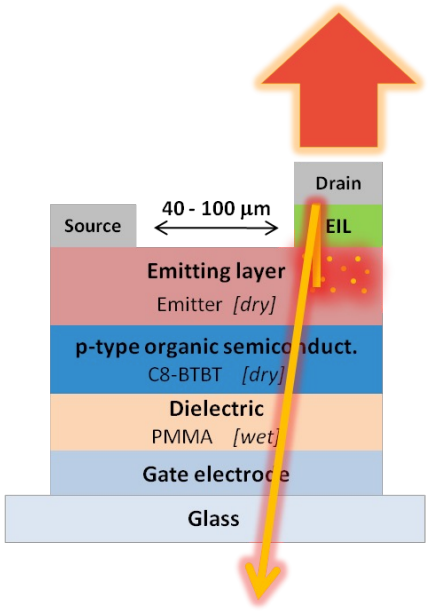






Adv. Funct. Mater. 2011, 21, 3667–3672

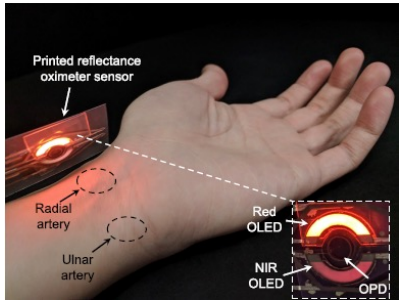
Colour palette and purity



Blue, green, red and red-near infrared (NIR) OLETs are typically produced at CNR-ISMN

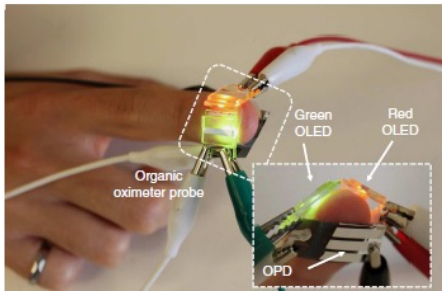
Emission	*Emissive materials*	*Emission peak [λ]*	*Full Width at Half Maximum*
Blue	DiPAXA	485 nm	≈ 35 nm
Green	TCTA:$Ir(ppy)_3$	520 nm	≈ 40 nm
Red	Alq_3:$Ir(piq)_3$	626 nm	≈ 50 nm
Red	Alq_3:PtOEP	650 nm	≈ 10 nm
Red-NIR	$Pt(pfrpz)_2$	740 nm	≈ 65 nm
Red-NIR	Alq_3:Pt(tpbp)	770 nm	≈ 20 nm

Organic optoelectronics in analytical monitoring

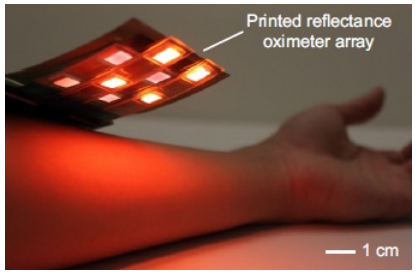


Khan et al, IEEE access 2019, 7,

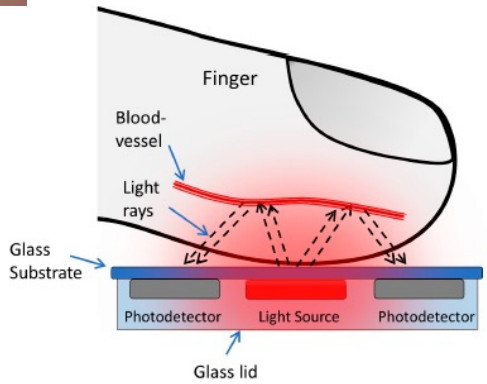
Kamada, et al. J. Soc. Inf. Display, 2019, 1.



Lochner et al, Nat .Comm. 2014, 5, 5745



Khan et al, PNAS 2018, 115, 11015.

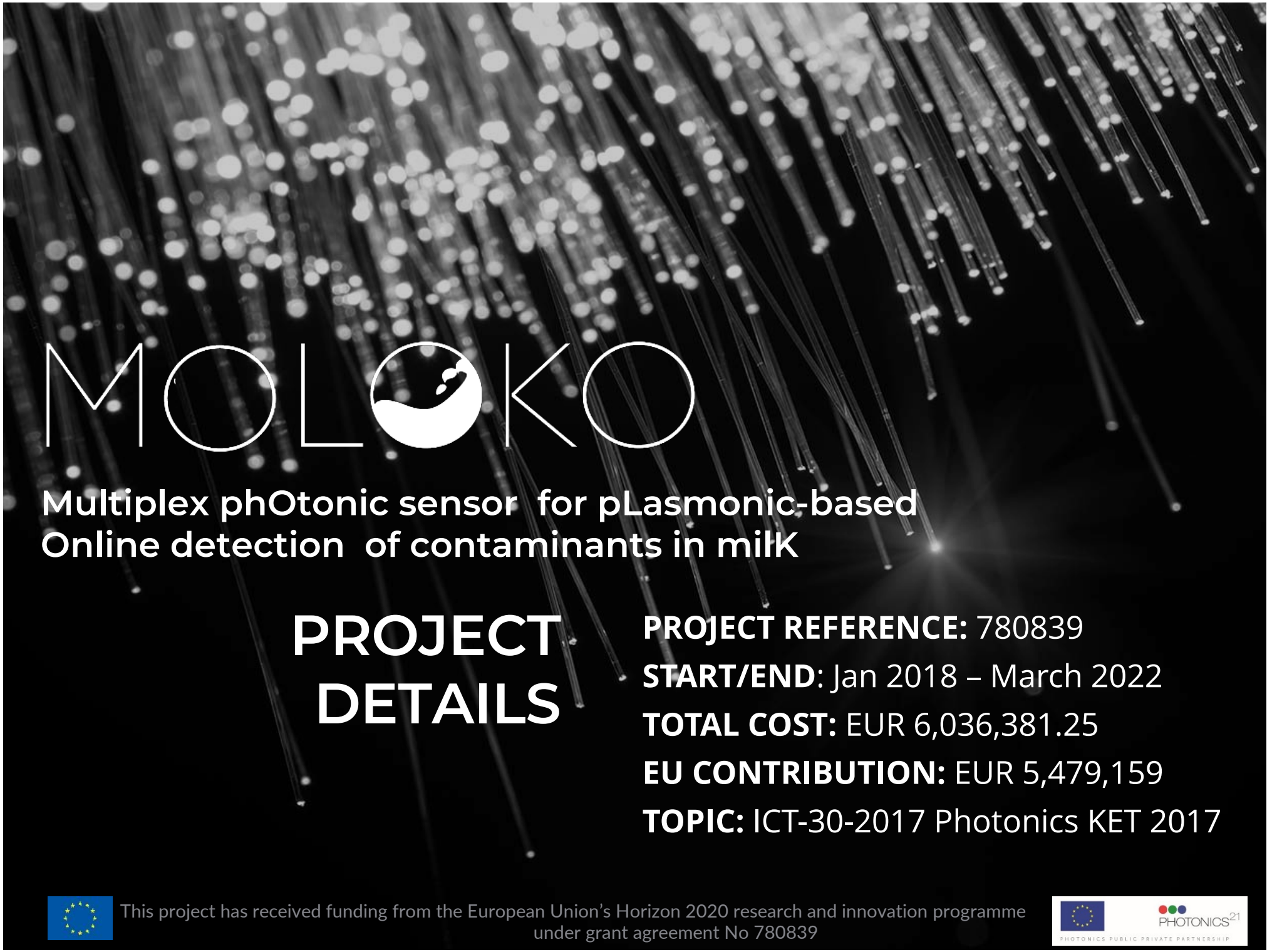


Organic optoelectronics

- Materials tunability & versatility
- Nanometer-thick films
- Large area
- Low cost
- Flexible and light-weight devices
- Integrability

Toffanin S. et al. Nanomaterials 2020, 10(3), 480; https://doi.org/10.3390/nano10030480

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 780839



Multiplex phOtonic sensor for pLasmonic-based Online detection of contaminants in milK

PROJECT DETAILS

PROJECT REFERENCE: 780839

START/END: Jan 2018 – March 2022

TOTAL COST: EUR 6,036,381.25

EU CONTRIBUTION: EUR 5,479,159

TOPIC: ICT-30-2017 Photonics KET 2017

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 780839

PHOTONICS 21
PHOTONICS PUBLIC PRIVATE PARTNERSHIP

Safety and competitiveness in the dairy chain

Contaminants in food

Consumer expectations

Regulatory requirements

Industrial competitiveness

Need of TOOLS for self-monitoring of food parameters along the supply chain

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 780839

PHOTONICS21
PHOTONICS PUBLIC PRIVATE PARTNERSHIP

MOLOKO

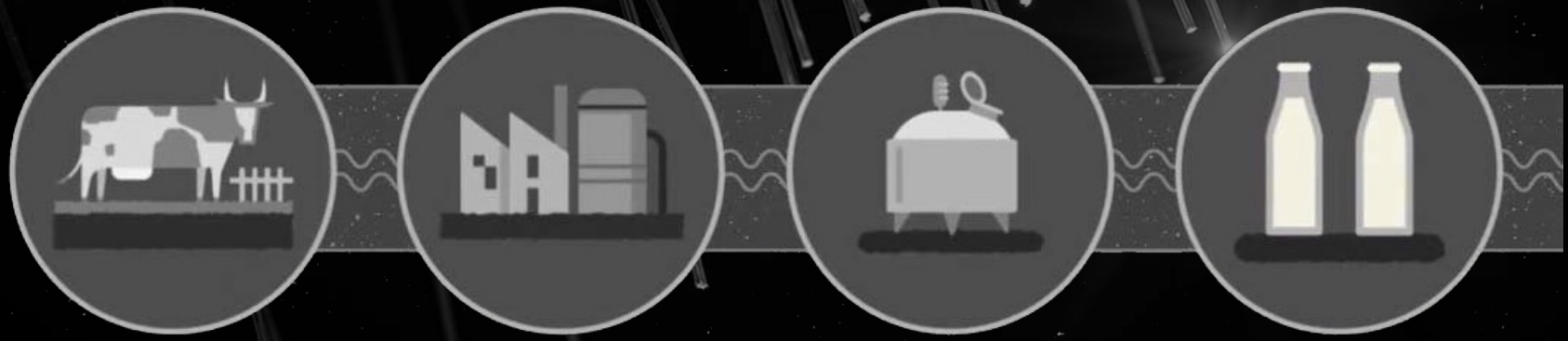
Why miniaturized integrated sensor?

Self-managing and automatic

Multiplex quantitative detection of food safety and quality parameters

Fast-response on-site monitoring

User-friendly reusable



Production ***Bulk milk handling*** ***Processing*** ***Distribution***

To be used in strategic checkpoints along the entire supply and value chain of milk

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 780839

PHOTONICS21
PHOTONICS PUBLIC PRIVATE PARTNERSHIP

Use cases: in-field validation

- To diagnose the level of contaminants at the earliest in the supply chain
- To implement modernized risk management framework
- Different checkpoints of the milk chain by a single analytical instrument

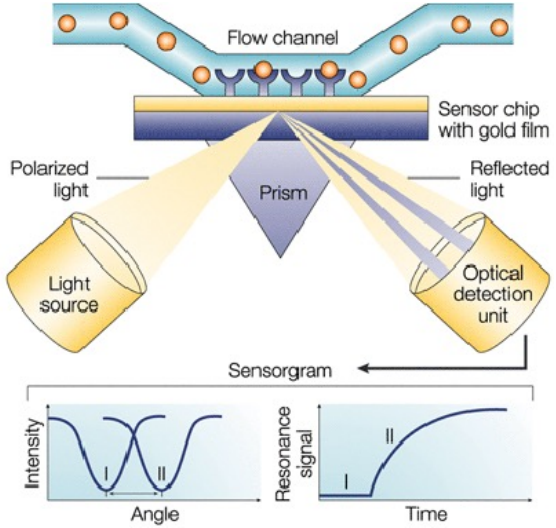
Primary producers (farmers)

Self-monitoring by food business operators

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 780839

Tech building-blocks

Continuous, autonomous, on-site, multiplexing analytical instrumentation

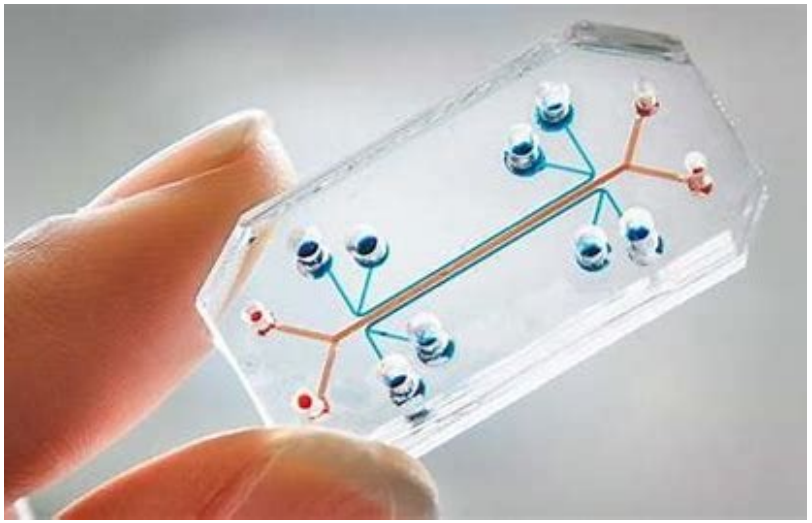


Surface Plasmonic Resonance (SPR) detection scheme based on immunoassays:

- routine and multiplexing method
- robust and quantitative results
- high specificity
- short time
- No labeling procedure

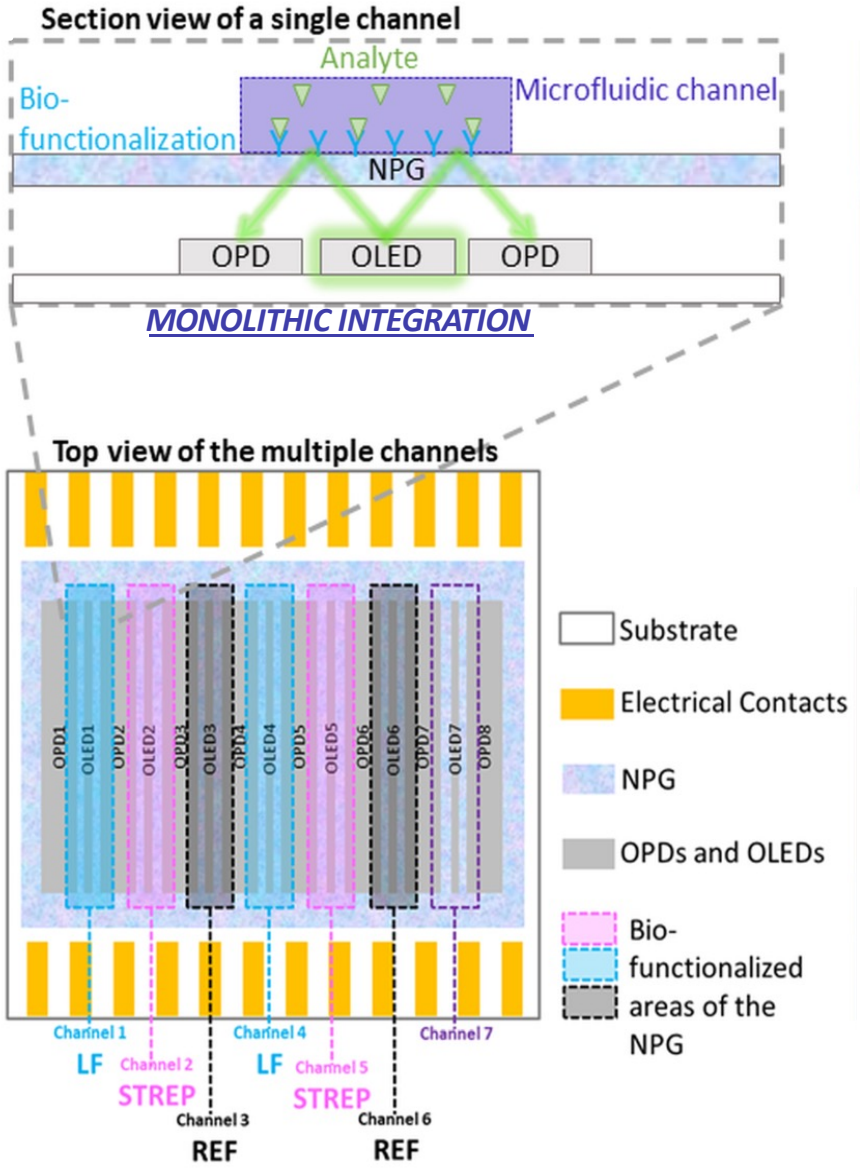
Microfluidic systems:

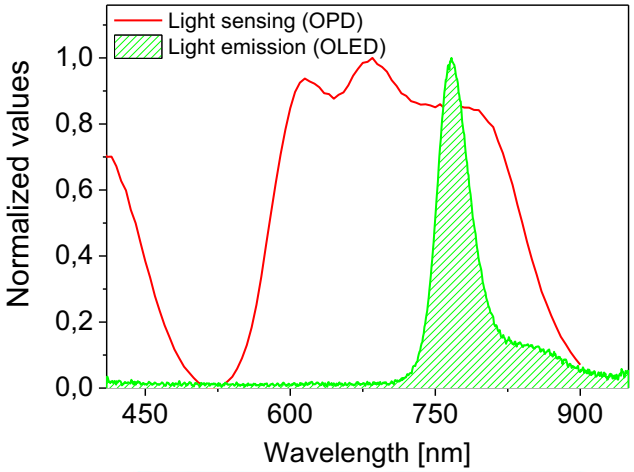
- field deployable
- using small samples and reagent volumes
- easier waste management
- simple to assemble

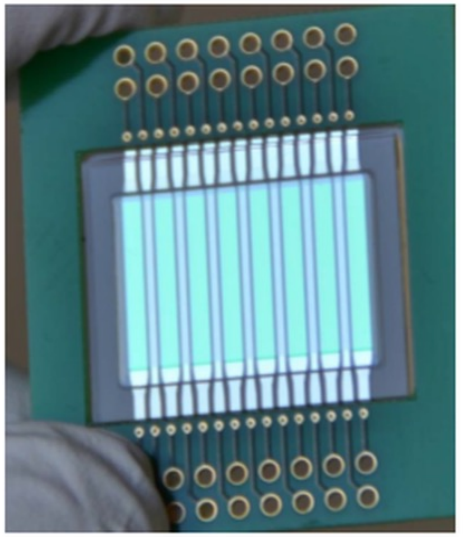


This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 780839

The organic optoelectronic devices



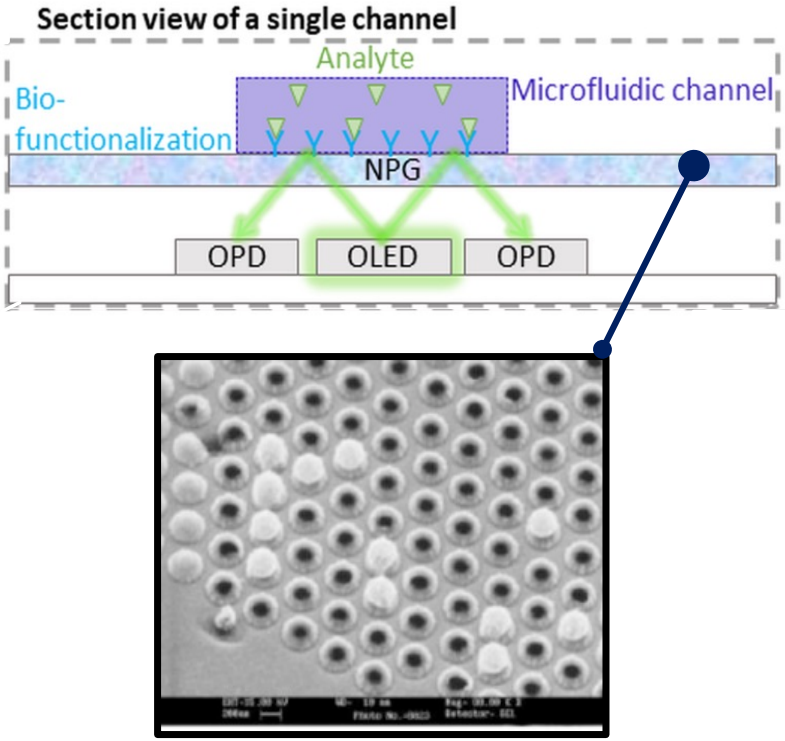


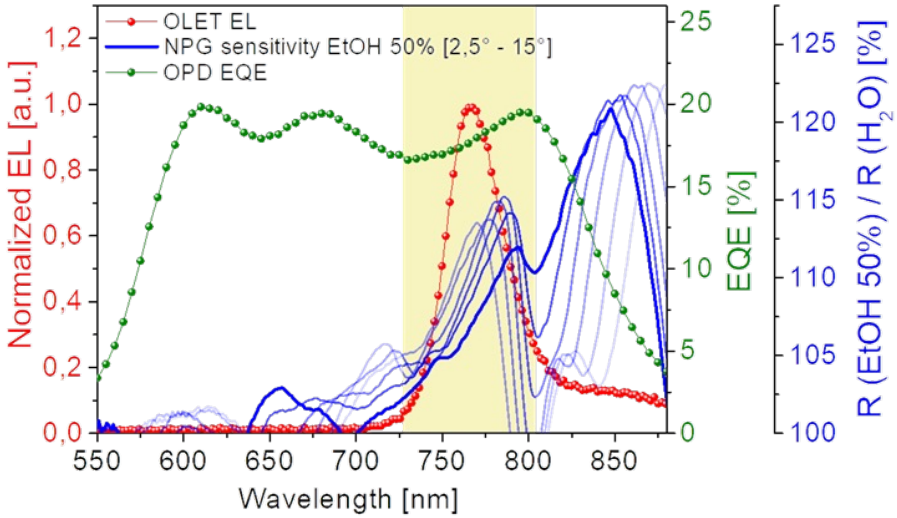


Bolognesi, M. ..., Toffanin S. Adv. Mater. 2023, 2208719

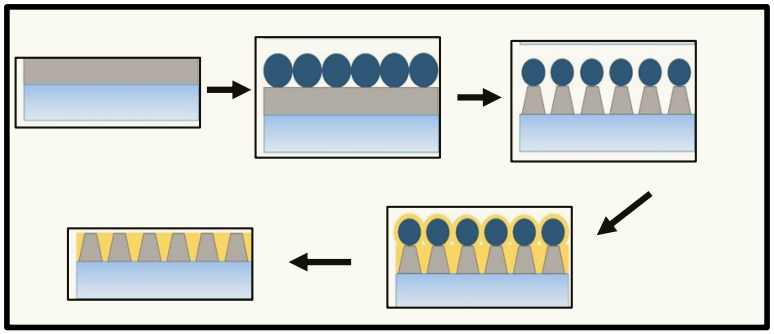
This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 780839

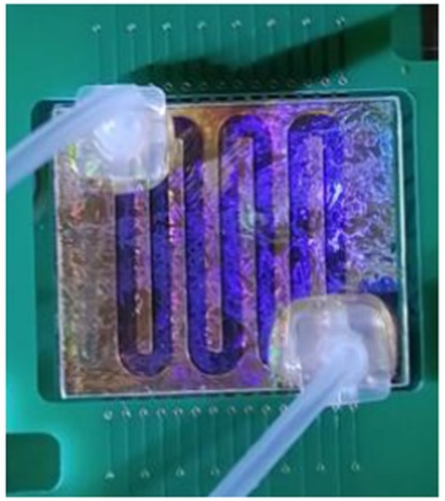
The plasmonic sensing surface





NANOLASMONIC GRATING (NPG)

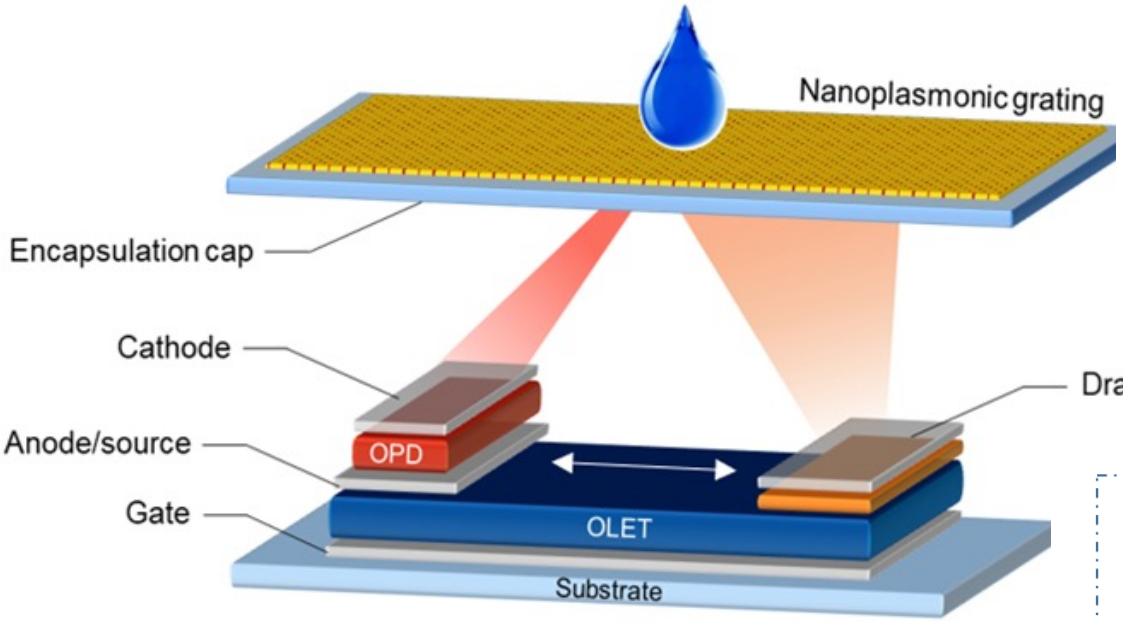




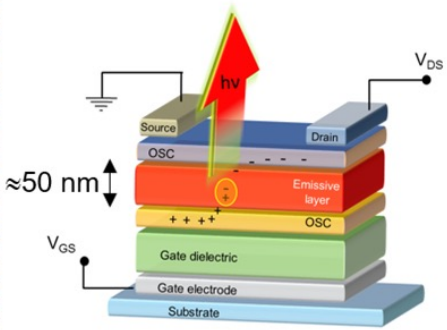
This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 780839

Smart-system integration

- ❑ Sensor size as low as 0.1 cm^3
- ❑ Inherent signal amplification
- ❑ Optics-less architecture



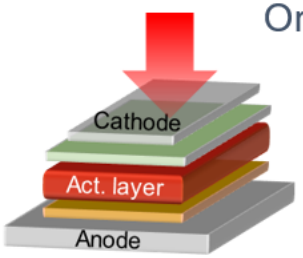
Organic Light-Emitting Transistor (**OLET**)



- ❑ Planar light emitter
- ❑ Electrical switcher
- ❑ Tunable light stripe

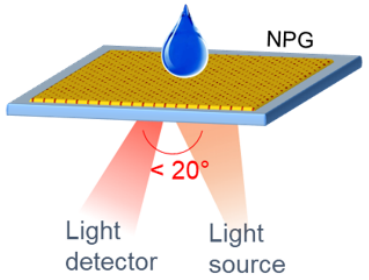
M. Prosa, et al, *J. Mater. Chem. C.* **2020**, *8*, 15048.

Organic photodiode (**OPD**)

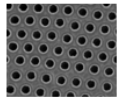


- ❑ Light detector
- ❑ Sharing the OLET electrode

Nanostructured grating (**NPG**)



Grid of polymeric pillars in a gold matrix



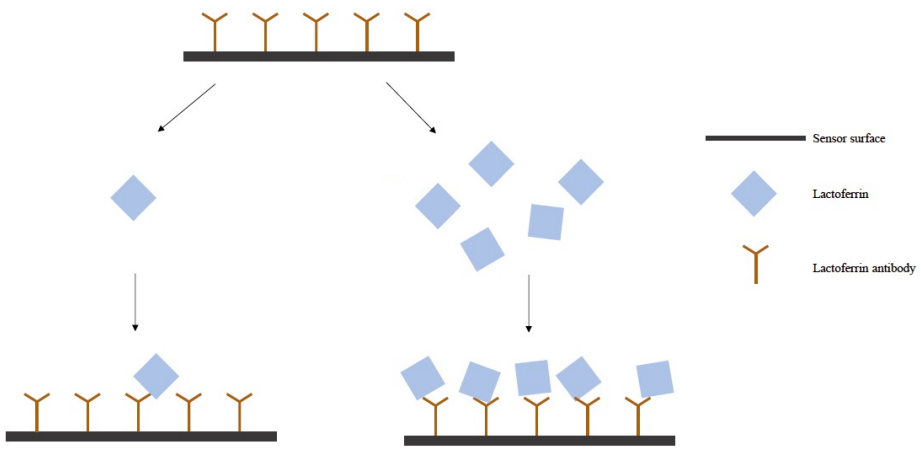
B. Bottazzi, et al, *J. Biomed. Opt.* **2014**, *19*, 017006.

Prosa, M., …, Toffanin, S. Adv. Funct. Mater. 2021, 31, 2104927

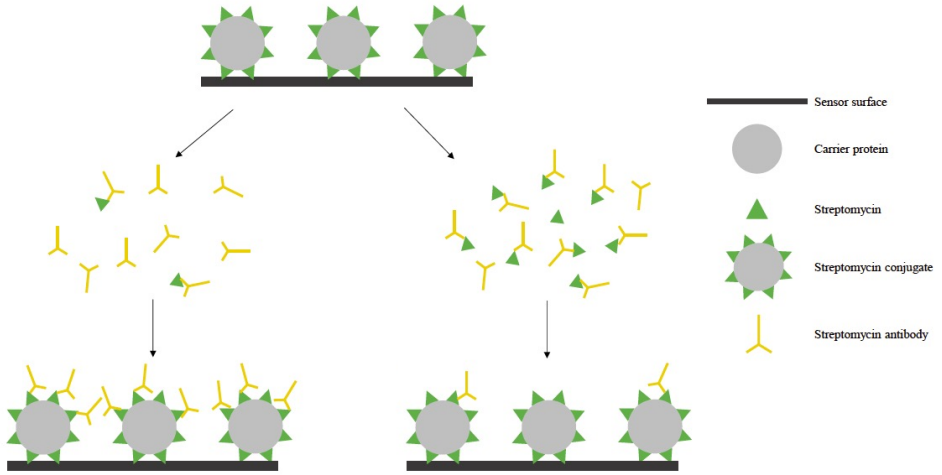
This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 780839

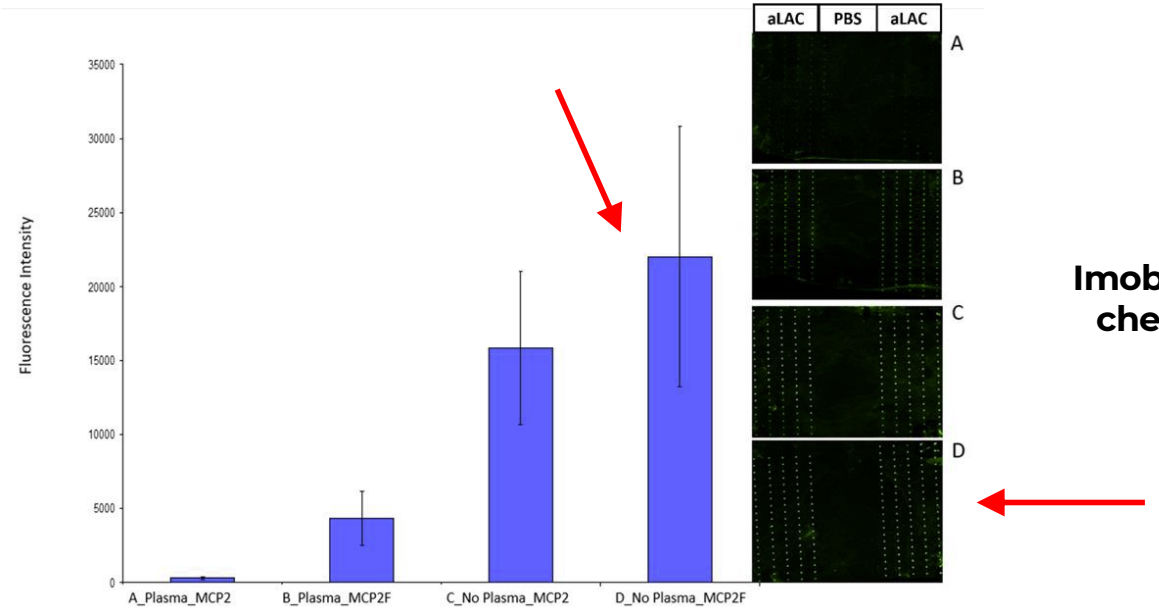
The Immunoassay Tech

Direct biosensor immunoassay
(lactoferrin detection)



Competitive biosensor immunoassay
(streptomycin detection)

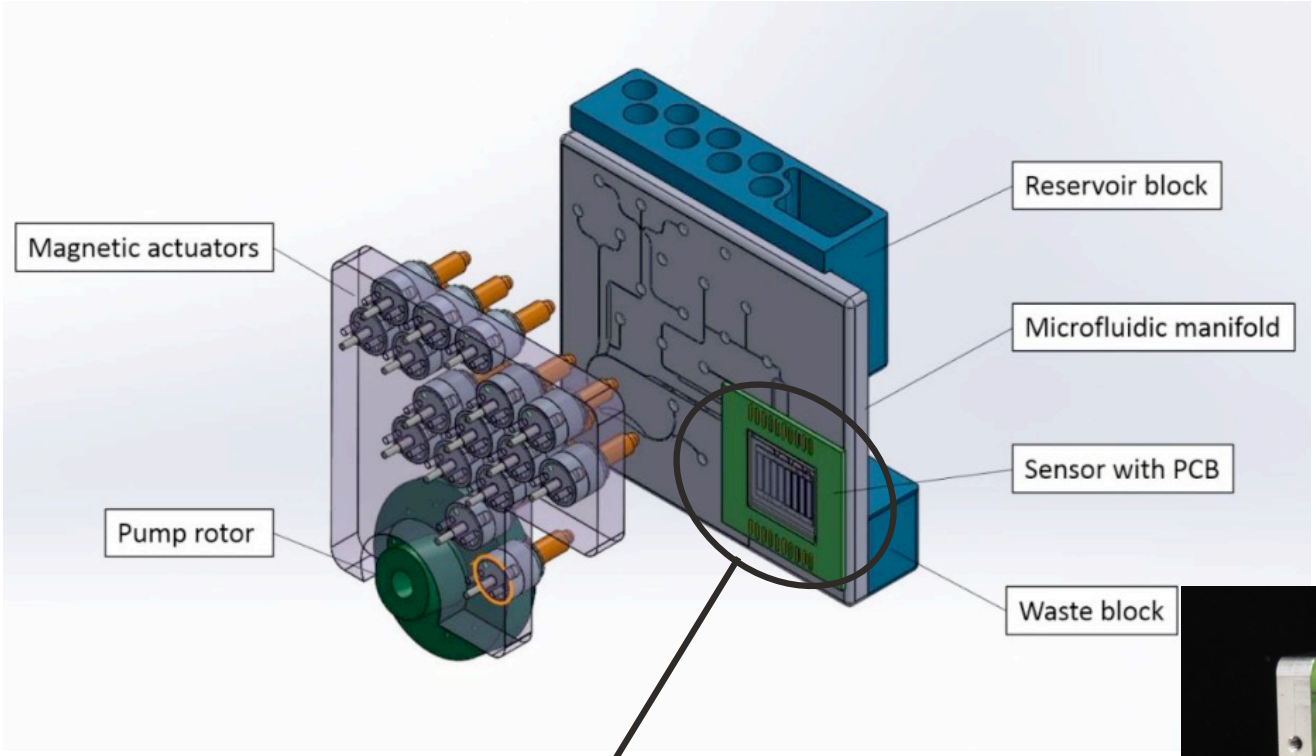


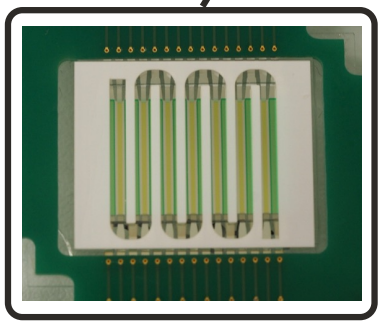


Imobilization of lactoferrin pAb on chemically functionalized NPGs

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 780839

The microfluidic module



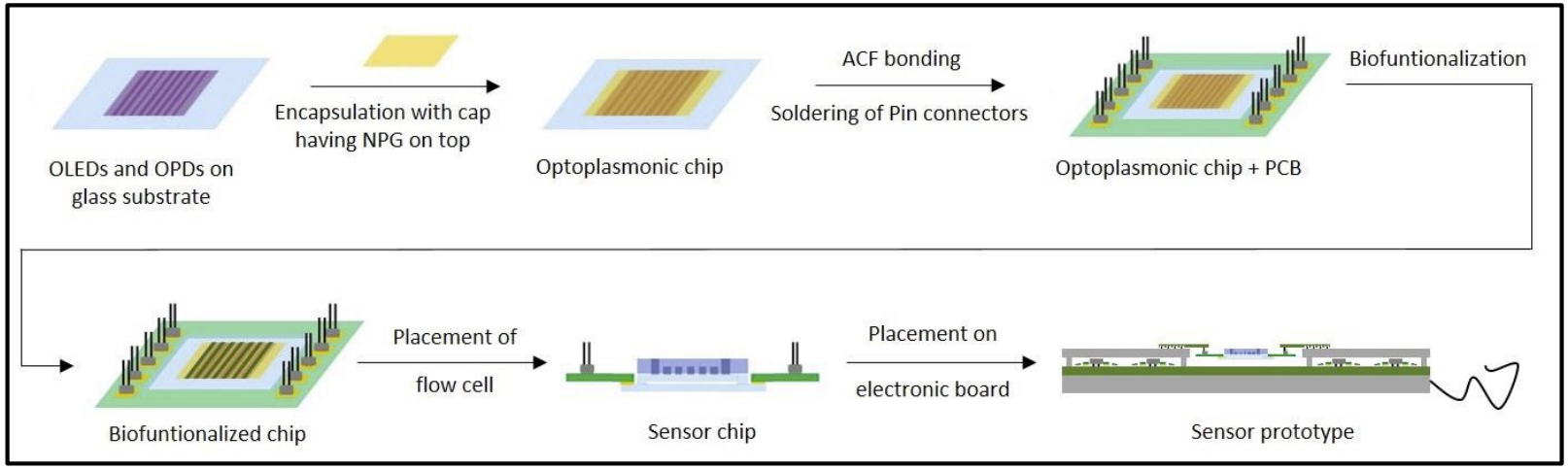


Flow channel pattern with respect to the sensor elements

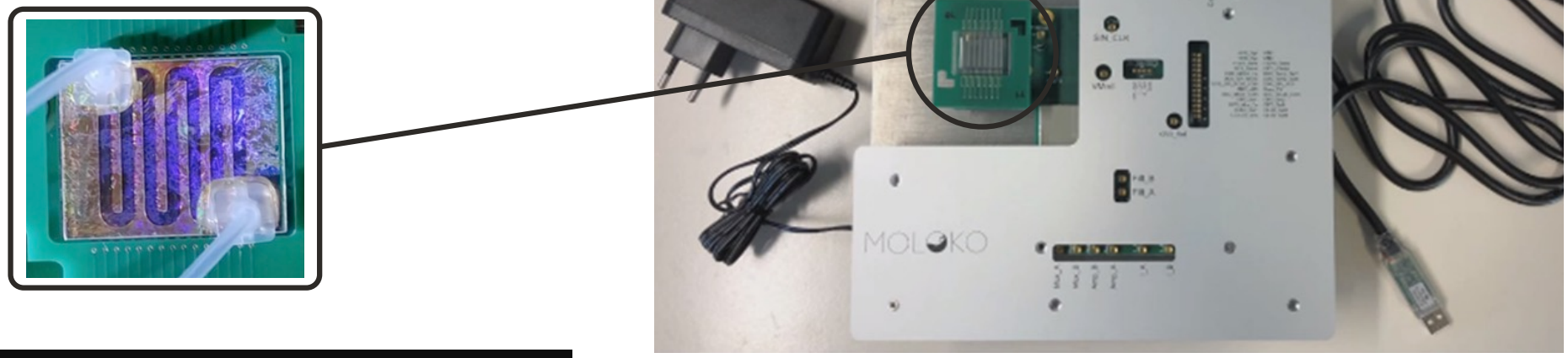
Enabling measure protocol in a miniaturized and automated approach

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 780839

Sensor prototyping



Assembly of the chip

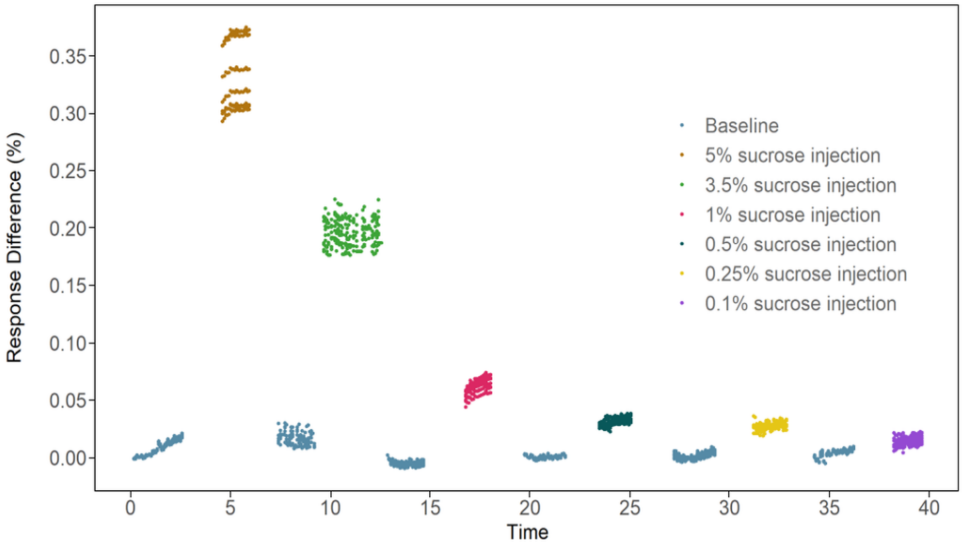


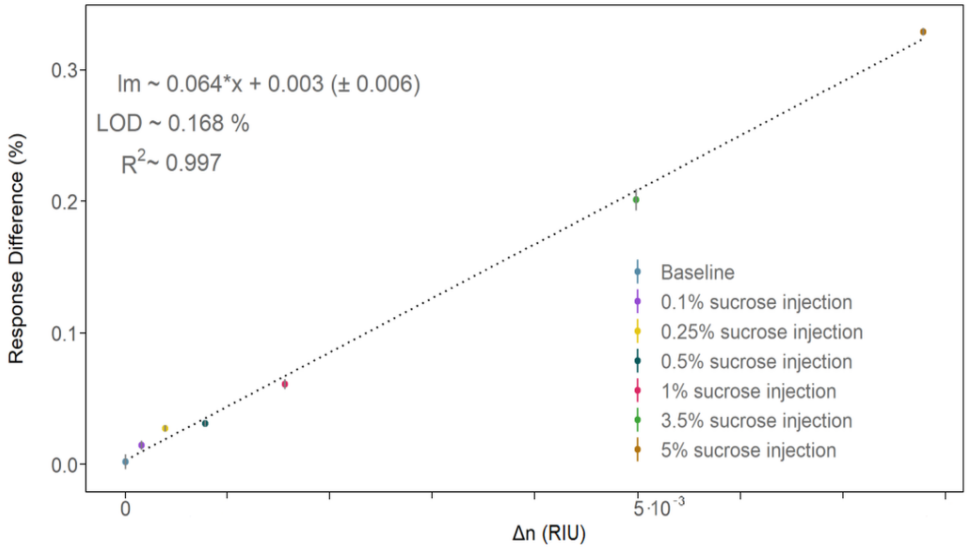
Automatic Sensor

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 780839

Self-testing and calibration

- **Linear dependence** of the measured signal with respect to different concentrations of reference solutions (ethanol, sucrose)
- Sensitivity limit down to the scale of **100 RU (10^{-4} RIU)**
- Channel-specific correction factor is extrapolated to be used for the **quantitative assay analysis**





This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 780839

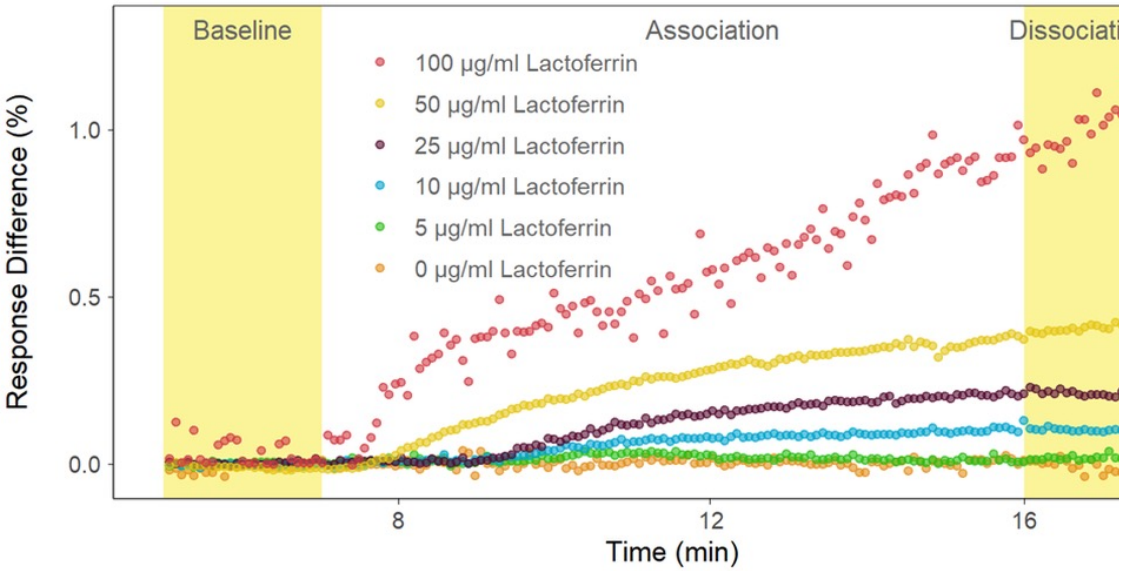
Analytical detection

Multiplex detection

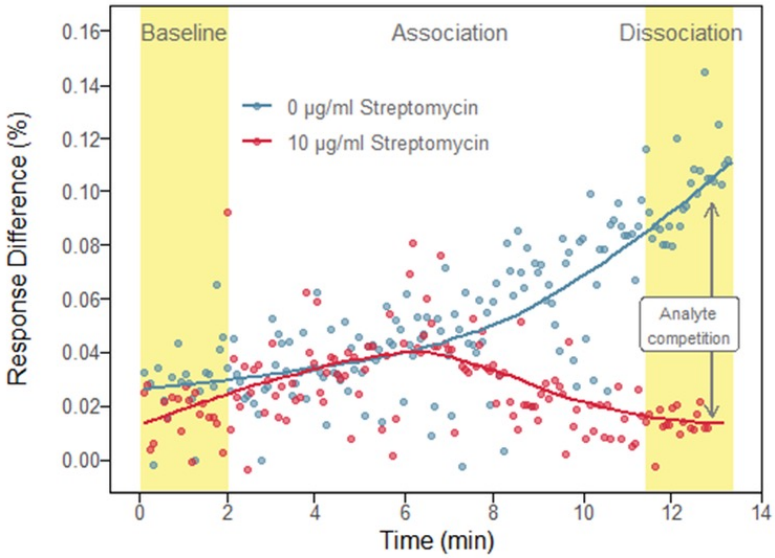
Multiplexing detection of lactoferrin (quality parameter), streptomycin and quinolone (safety parameters) in buffer medium simultaneously on the same chip:

Limit of Detection (LOD) of Lactoferrin comparable to golden lab instrumentation (Biacore) at around 9 µg/mL

Direct assay for Lactoferrin detection



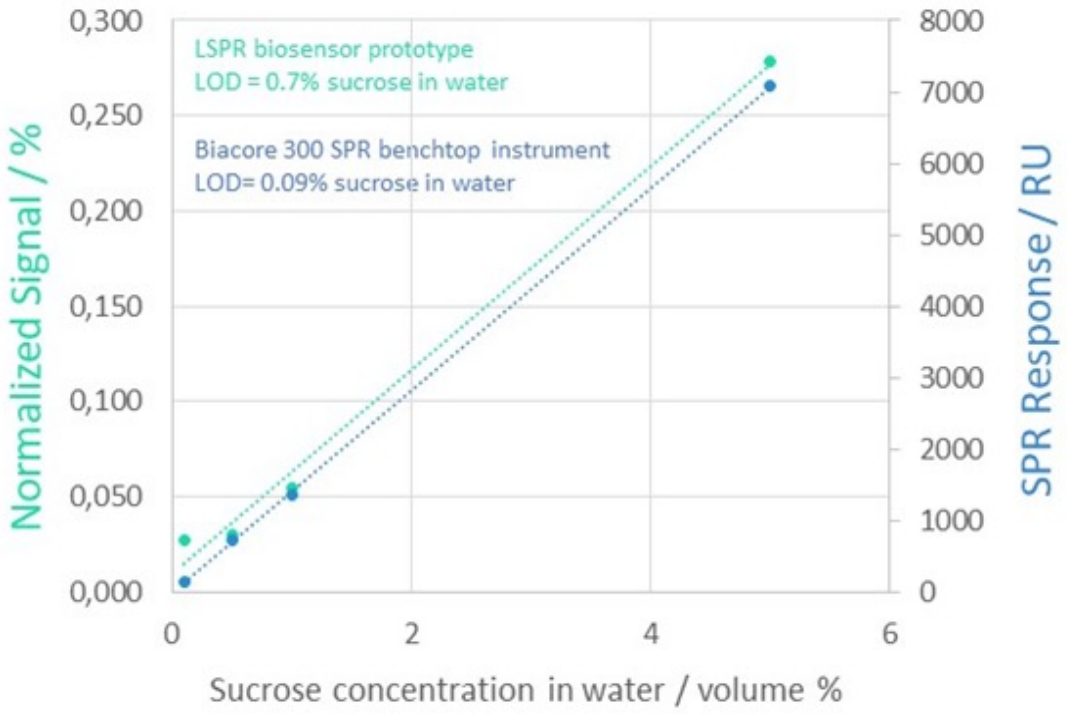
Competitive assay for Streptomycin detection

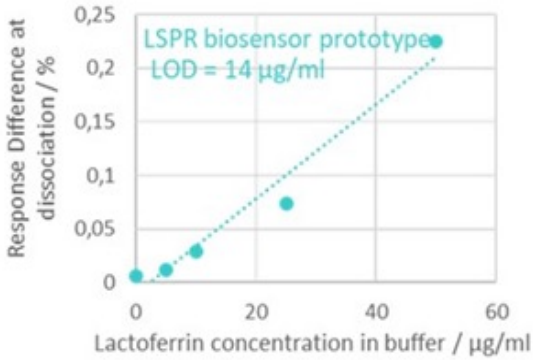


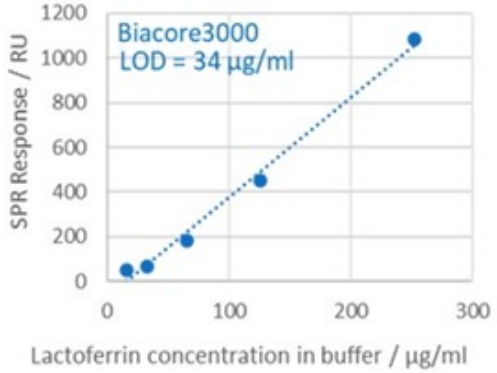
Data Analysis from KODE srl

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 780839

Comparison with standard SPR instrument







Quantitative linear response of biosensor prototype vs Biacore 3000:

- ❑ Sensitivity with reference sucrose solutions
- ❑ LOD for lactoferrin concentration in buffer

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 780839

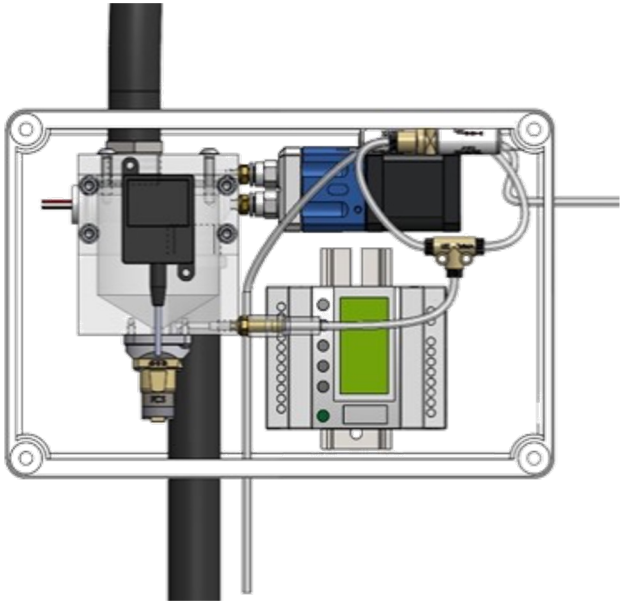
Competitors of MOLOKO sensor

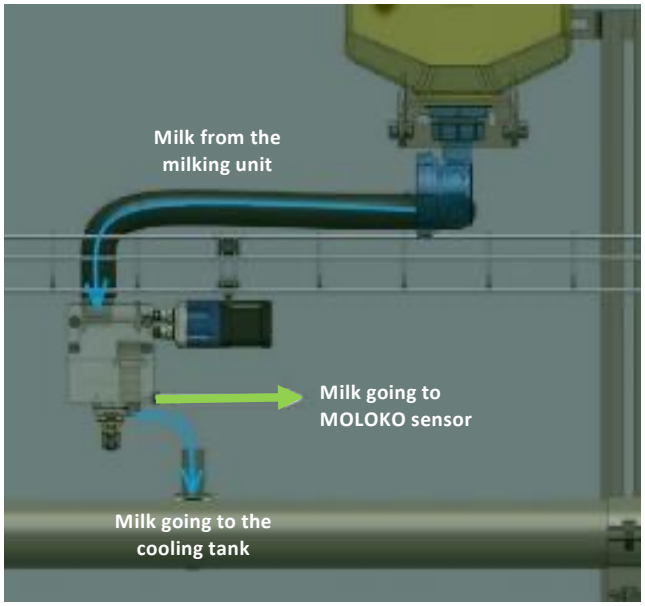
	Method	Principle	Time	Typical Cost per Test	Market Suitability	Comments
	**DELVO Test**	Colour spore test, during incubation spore grows altering pH	**3-3.5hr**	Varies on volume, guide **€2-4** Instrument cost **€300**	**Accepted industry standard** across all locations, screening against all most families of antibiotics.	Simple and easy test to be performed anywhere with incubator block.
	**Lateral Flow Immunoassay LFI**	Sample flows up immunoassay based paper-stick to a test line.	**5-10 min**	Guide **€1-10** depending on format.	Used by **>95% of dairies** as the milk tanker acceptance test. Many suppliers.	**More antibiotic families** can be detected using multi-format tests.
	**UniSensor EXTENSO**	Multiplex biochip suitable for **>120 analytes.**	**15 min**	**Unknown**, but depends on what customer tests for.	Could be a routine analysis tool but the **test time longer** than dairies' expectation	Details are not widely known.
	**NEOGEN Raptor**	A new system based on LFI to improve usability.	**5-10 min**	Varies on volume, guide **€2-4**	Successor to BetaStar test but **more expensive**	Includes incubation and reader along with barcode for test type.
	**MOLOKO**	Innovative SPR based system	**15 min**	**€5**	Yet to be determined	Additional benefits with **multiplexing**, automated testing, **quality parameters** and **reusability**

In-field demonstration of MOLOKO sensor

Integration in milking parlours

Automated composite sampler for analyser system developed and installed in a milking parlour (farm) and demonstrated on-line operation including cleaning in place (PIC)





This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 780839

Conclusions

- Realization and demonstration of an innovative miniaturized optical biosensor for PON based on:
  - **Monolithically integration** of organic light source and detector
  - Biofunctionalized transducing surface for **SPR label-free detection**

- Detection of a **high-molecular-weight analyte** (i.e., lactoferrin) by direct assay, and of a **low-molecular weight analyte** (i.e., streptomycin) by competitive assay

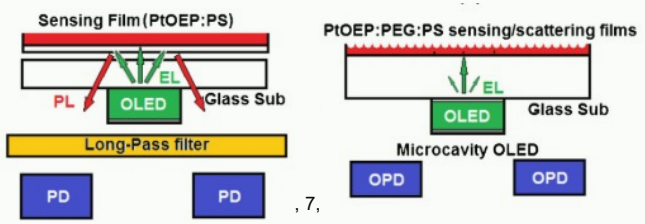
- **Quantitative linear response** when exposed to a refractive-index change of the surrounding bulk medium:
  - **LOD of 10^{-4} RIU** *(only 1 ord order of magnitude lower than the reference benchtop SPR instrument Biacore)*

- **Key-performance indicators**:
  - Competitive sensitivity
  - Cost per test
  - Speed of analysis *(15 min-long measurement protocol)*
  - Multiplex capabilities
  - Portability *(multiple end-user scenarios)*

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 780839

Multimode detection in miniaturized systems

Back-scattering mode



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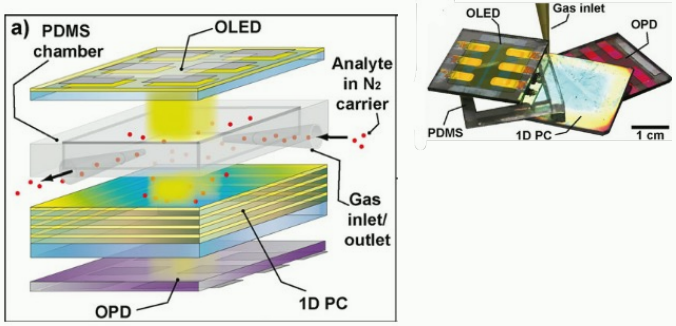
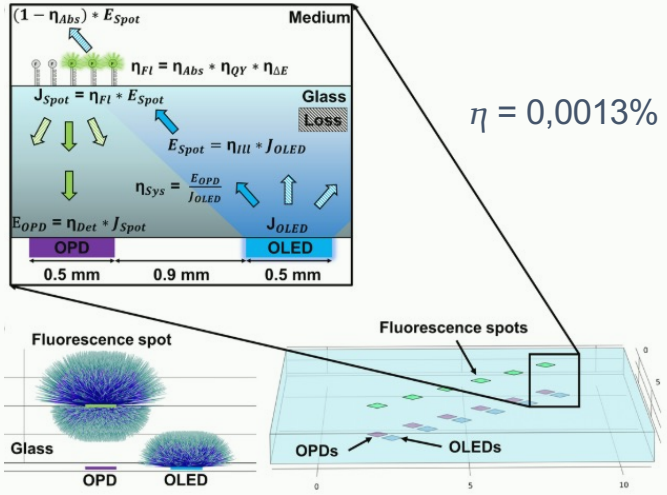
Liu et al, Anal. Chim. Acta, 2013, 778, 70

Transmission mode



Exner et al. Laser Photon. Rev., 2014, 8, 726

Back-scattering side-by-side mode

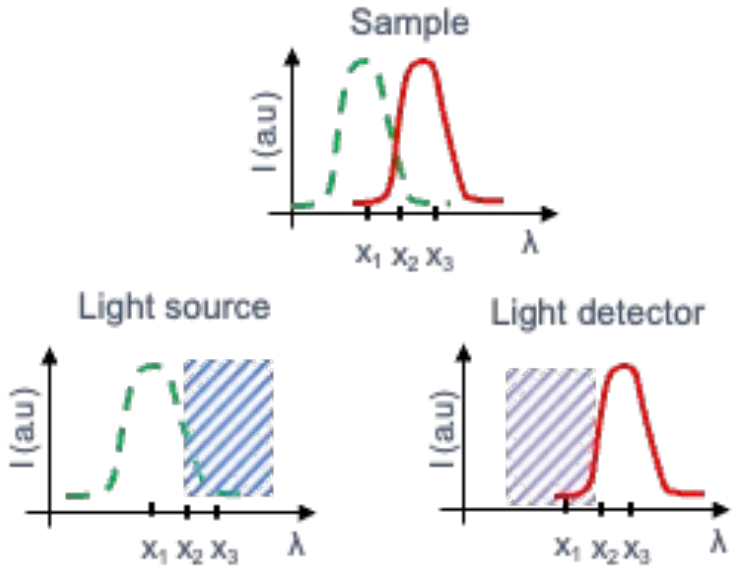


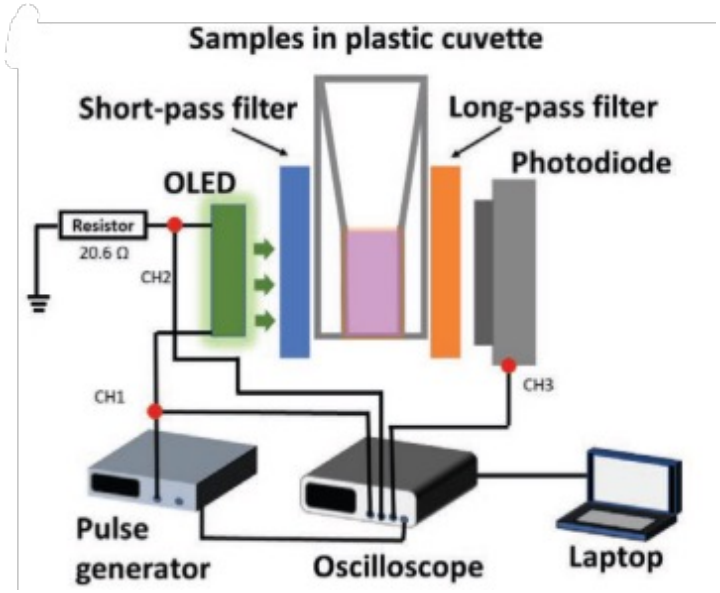
Tito et al, Biomedical Opt. Expr. 2022, 12, 6300.

Multimode detection in miniaturized systems

Optical observables:

- Absorption
- Reflectivity (i.e. plasmonic resonance)
- Photoluminescence





PROJECT DETAILS

PROJECT TITLE: photonic system for Adaptable muLtiple-analyse Monitoring of fOod quality

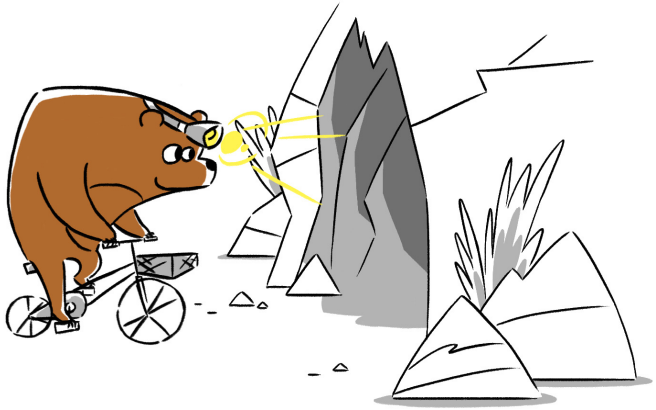
ACRONYM: h-ALO

START DATE: 01/01/2021

DURATION: 36 Months

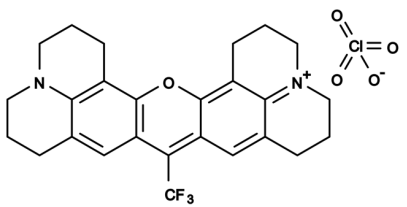
TOPIC: ICT-37-2020 | Advancing photonics technologies and application driven photonics components and the innovation ecosystem

EU CONTRIBUTION: 4,239,432 Euro

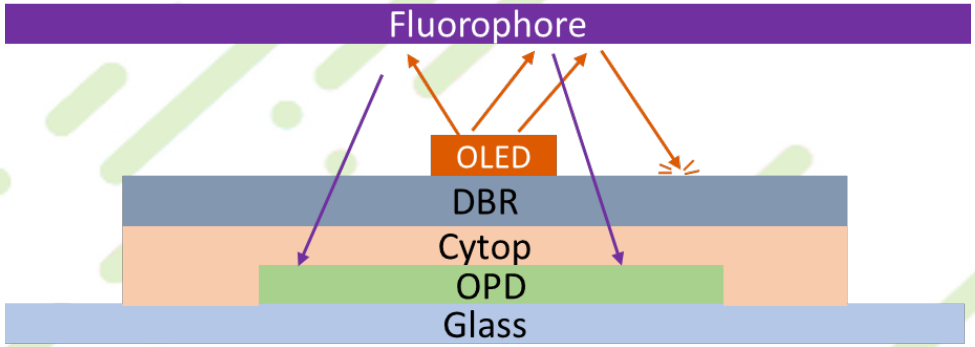


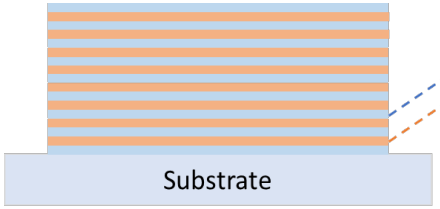
"This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101016706".

On-chip all-organic fluorescence sensor



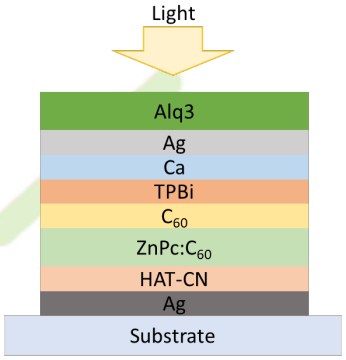
BiologicaL fluorophore
(Rodhamine 700)



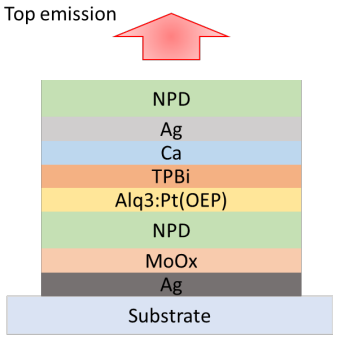


Distributed Bragg Reflector filter (DBR)

The OPD photocurrent arises only/mainly from the fluorophore emission



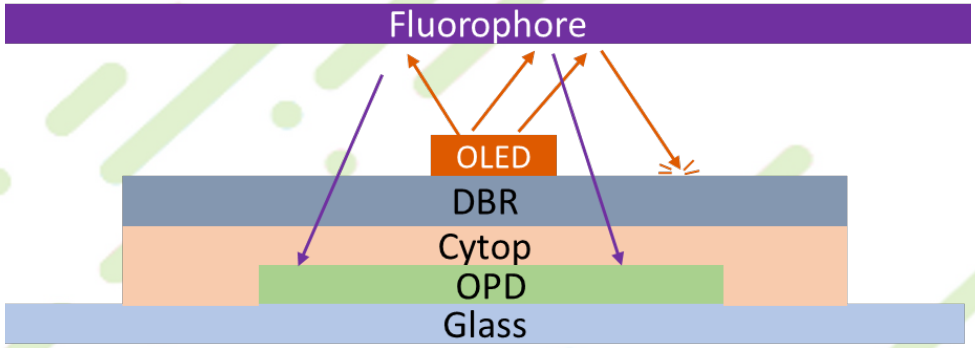
OPD



OLED

"This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101016706".

Development of single components



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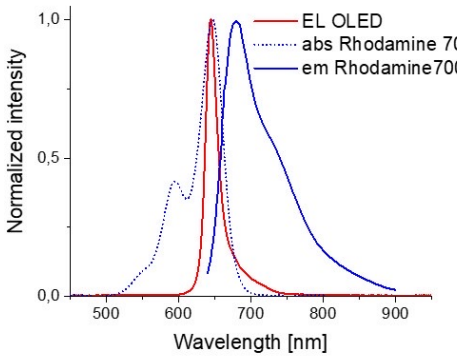

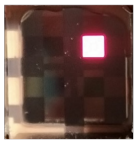

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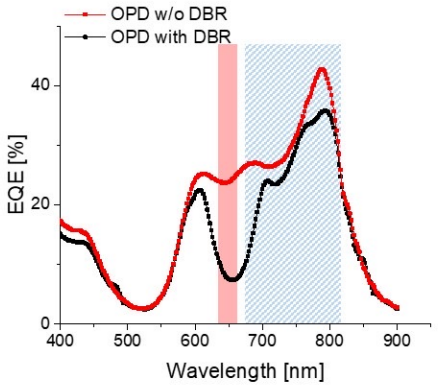
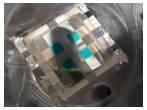
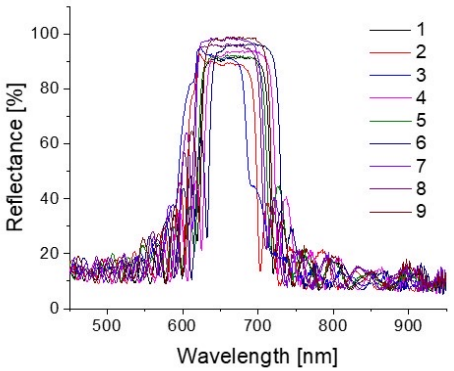
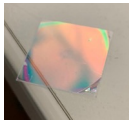




DBR





- Good spectral overlap
- Dependence of the DBR on the x and y directions
- Need of an accurate design of the system (not collimated light)

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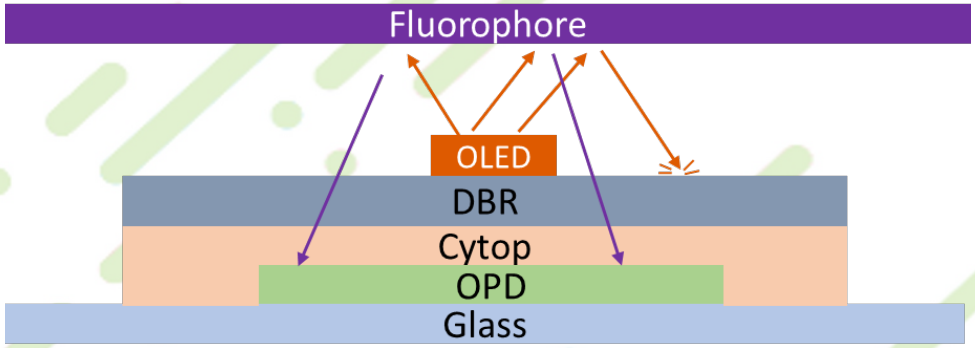
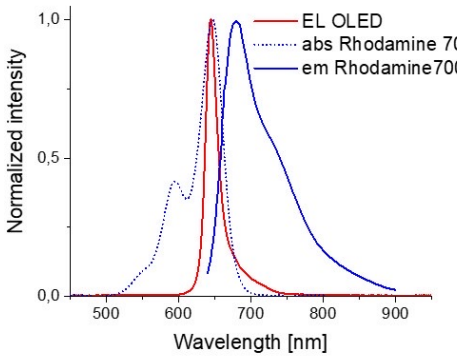
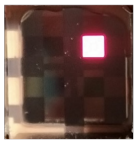
Development of single components

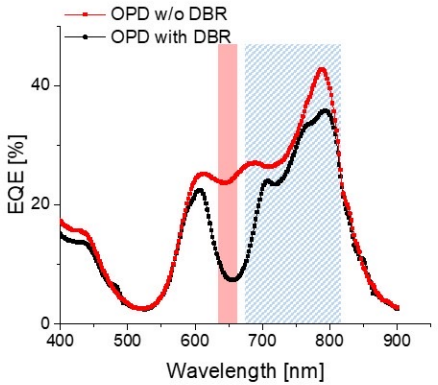


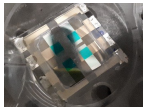
OLED



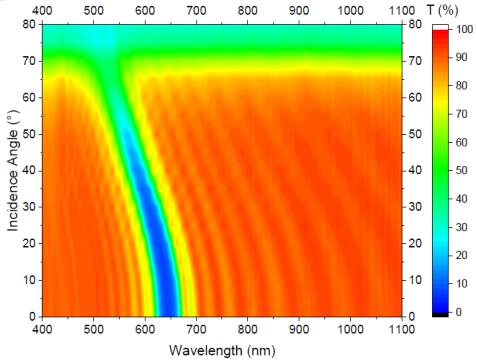


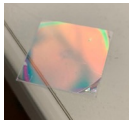
OPD





DBR





- Good spectral overlap
- Dependence of the DBR on the x and y directions
- Need of an accurate design of the system (not collimated light)

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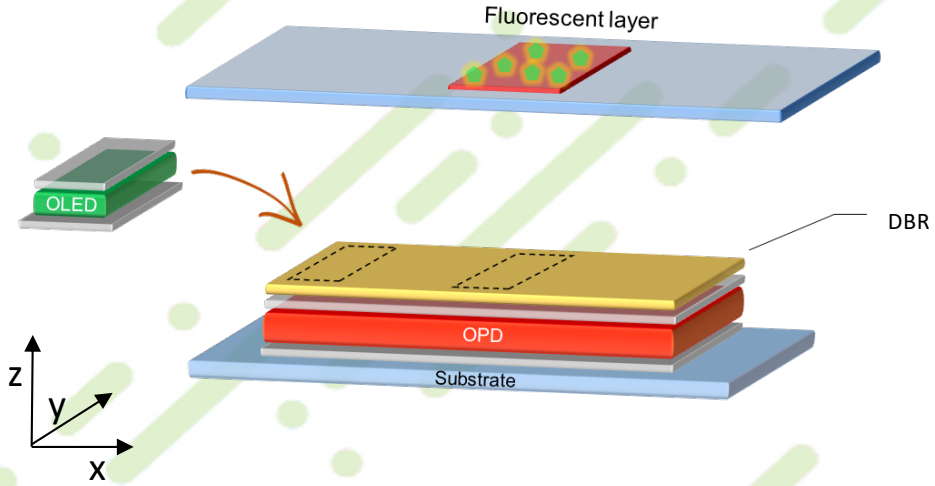
Design of the system



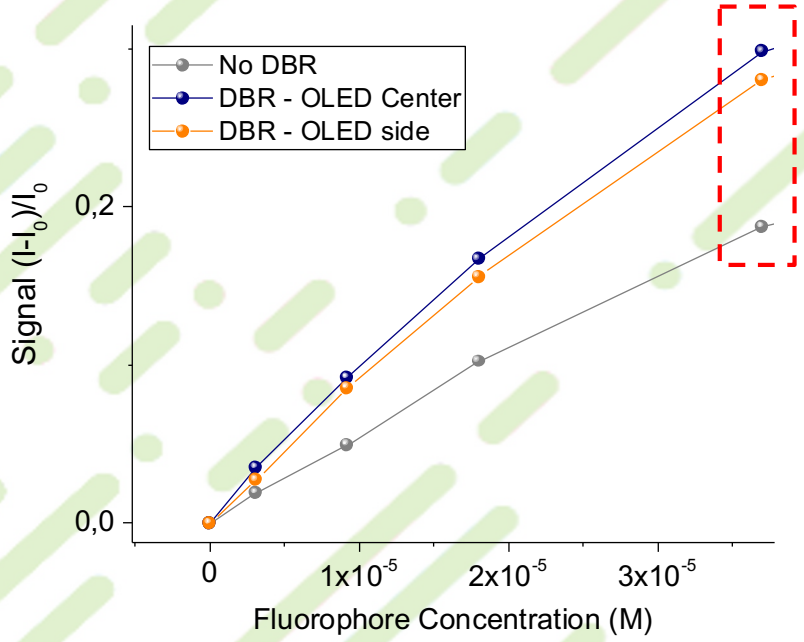
Optical simulation

Experimental data as input for a ray-tracing of the system

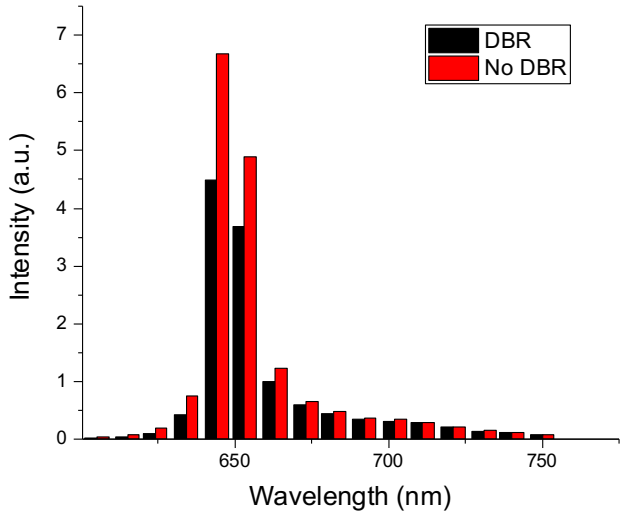
? Most sensitive area

? Device dimensions

? Relative positioning in the xyz space



η = 0,13%



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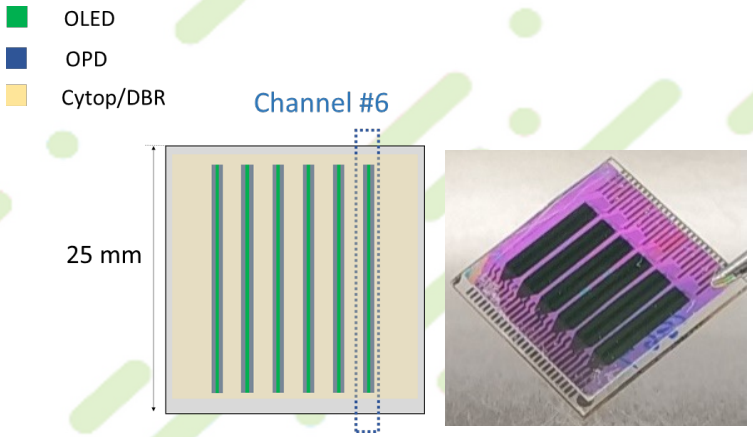
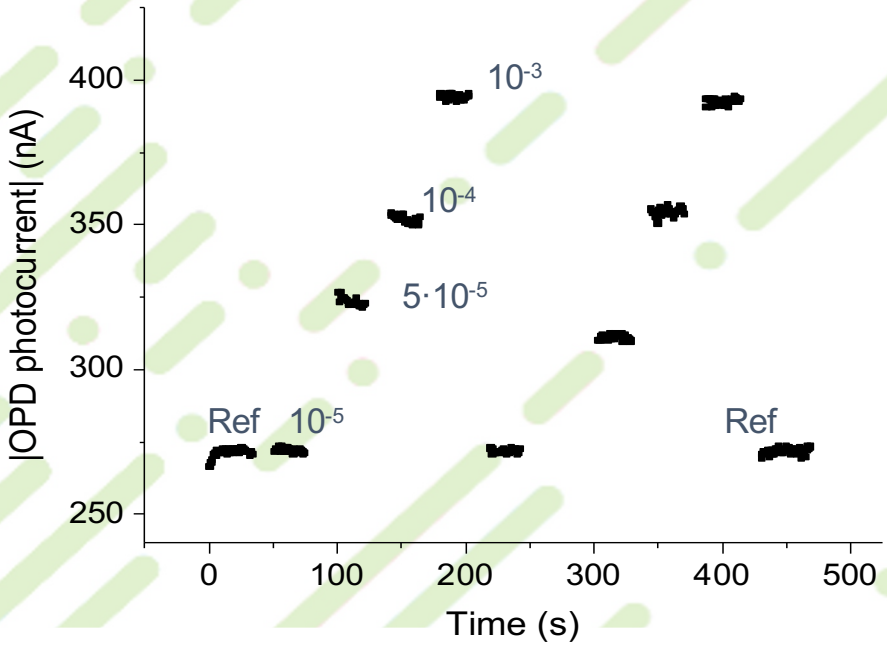
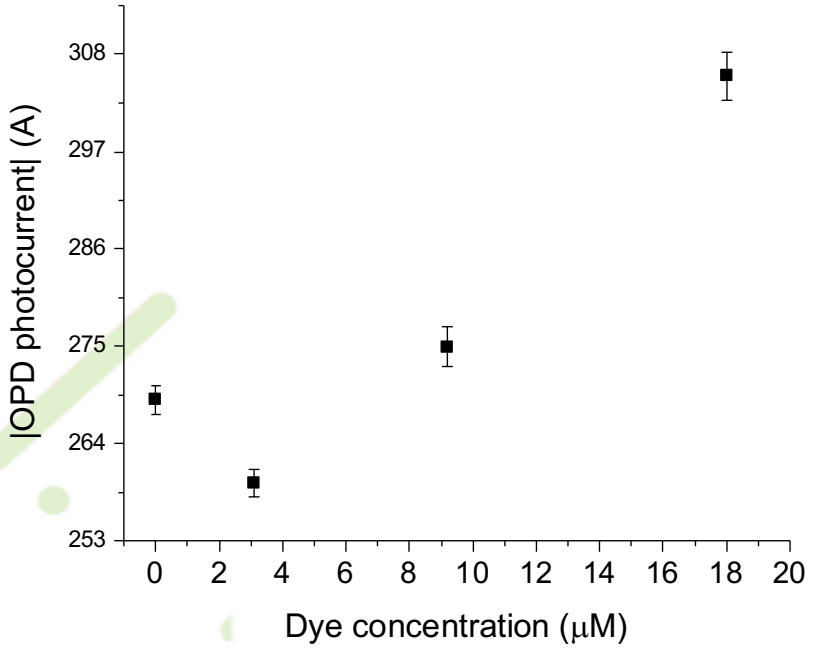
Output signal



- 6 Active channels
- 1 OLED is placed symmetrically with respect to the OPD of each channel
- The OPD photocurrent is monitored over time while the OLED is driven at constant J = 31mA/cm^2);
- Fluidic volume = 350ul, optical path = 1 mm





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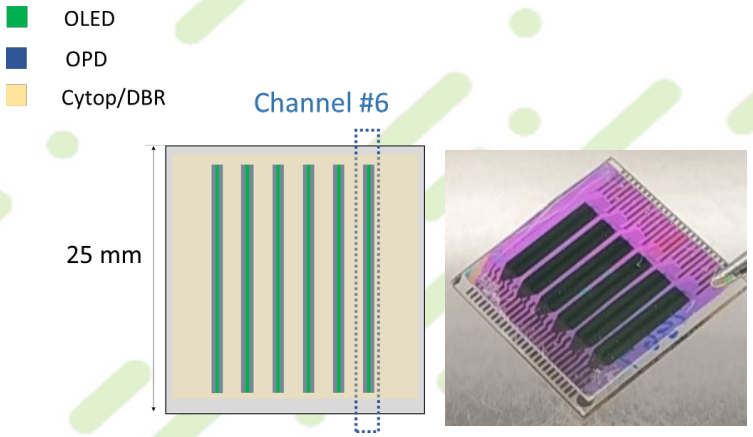
Limit of detection



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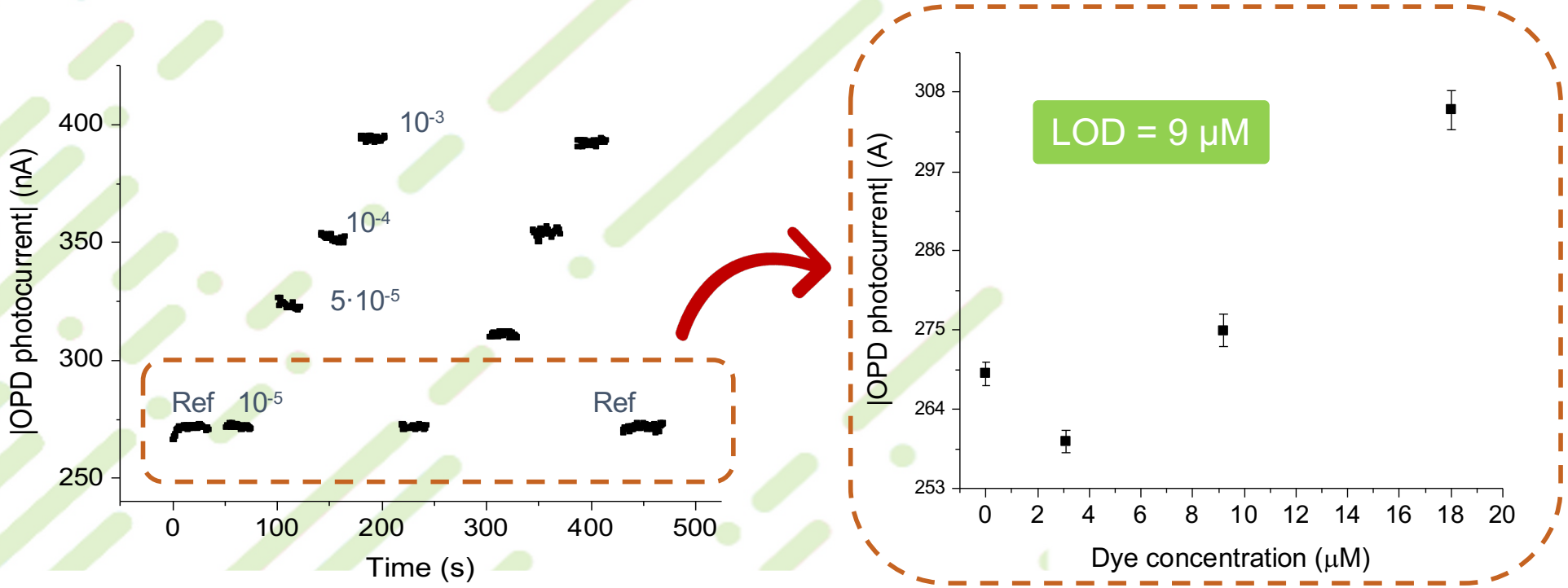

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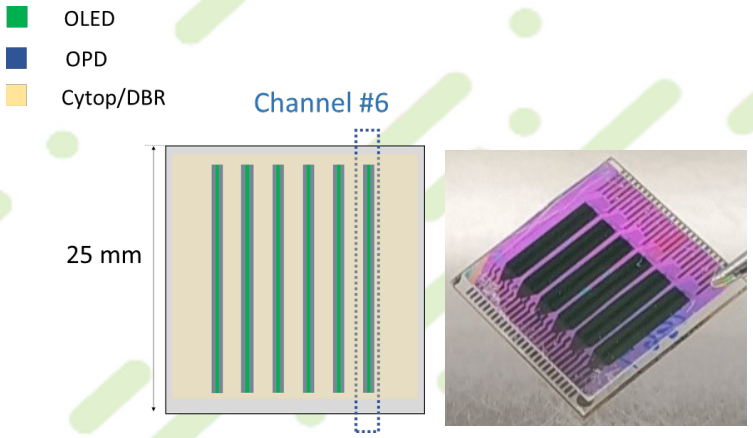
Limit of detection



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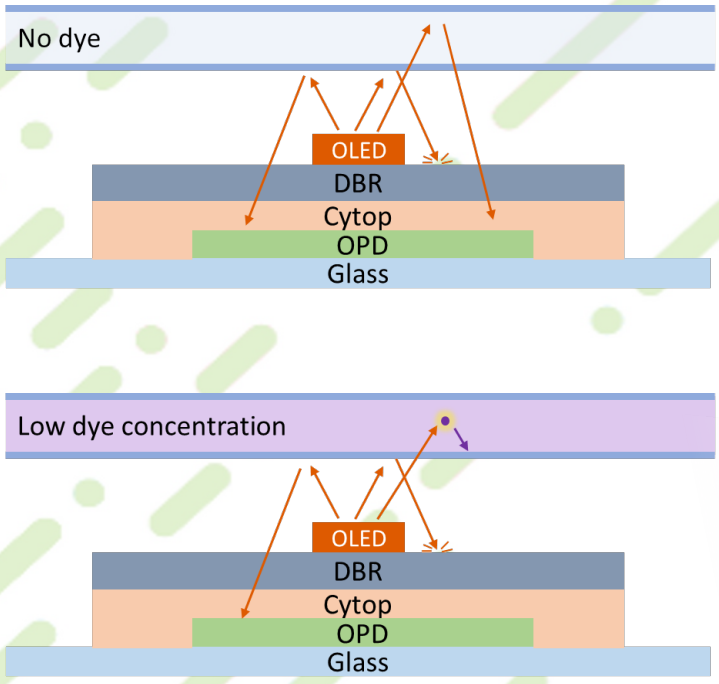

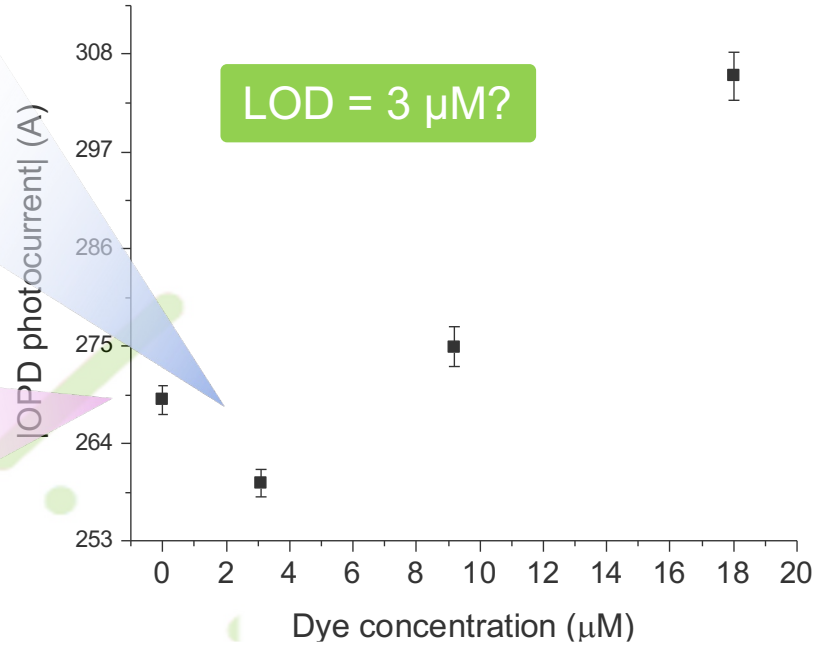

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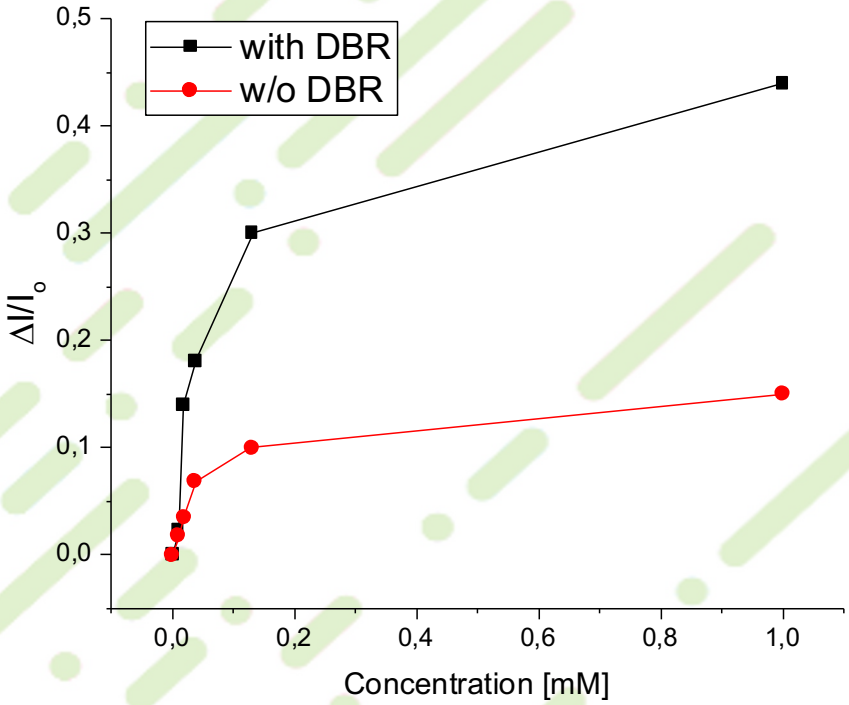
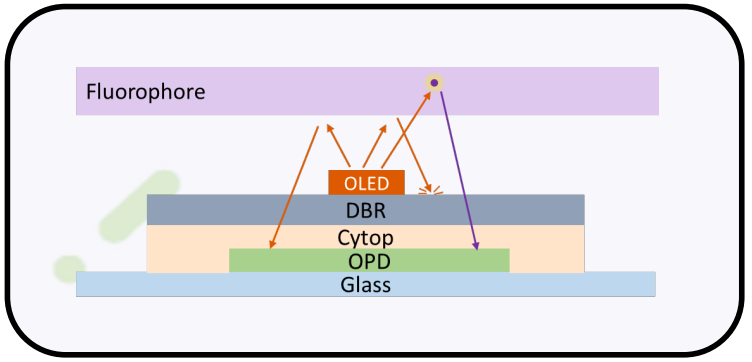
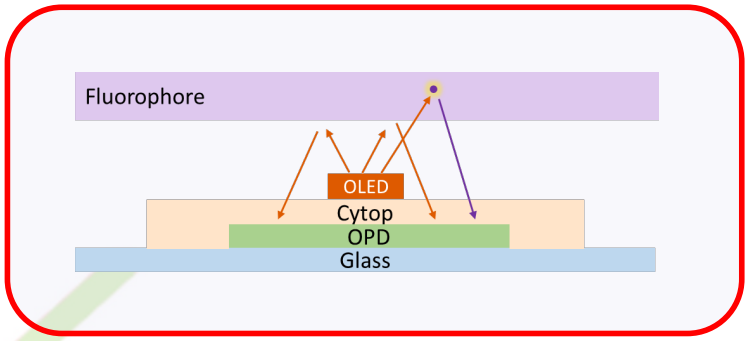
Emission optical filter

$(I - I_0) / I_0$

Fluorescence signal variation normalized to the chip response to ethanol (S/N ratio)







The use of a DBR filter reduces the noise arising from back-scattered OLED light

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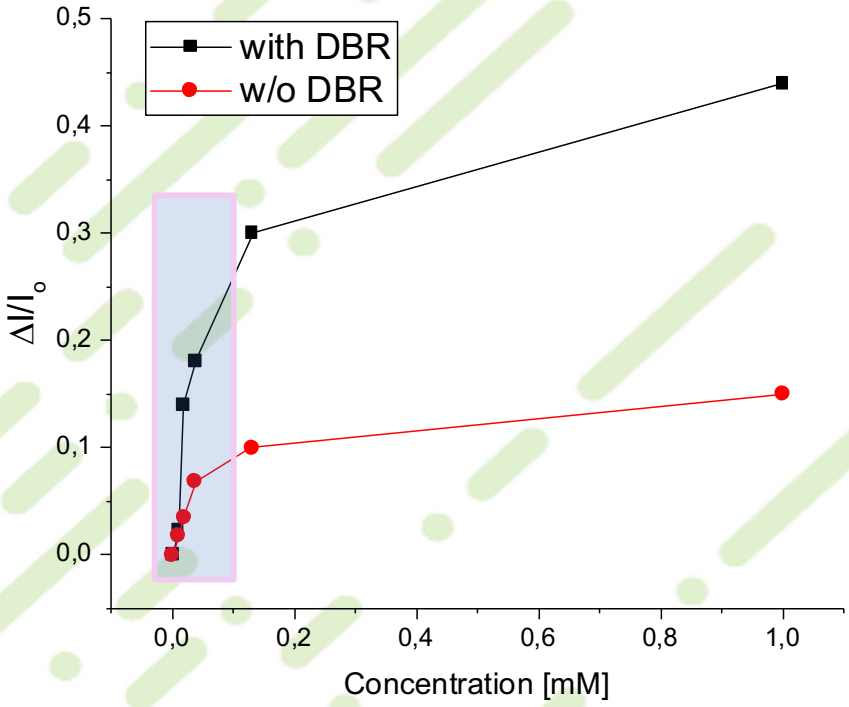
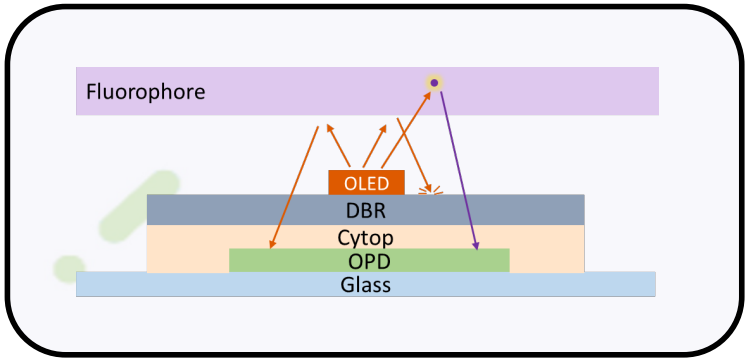
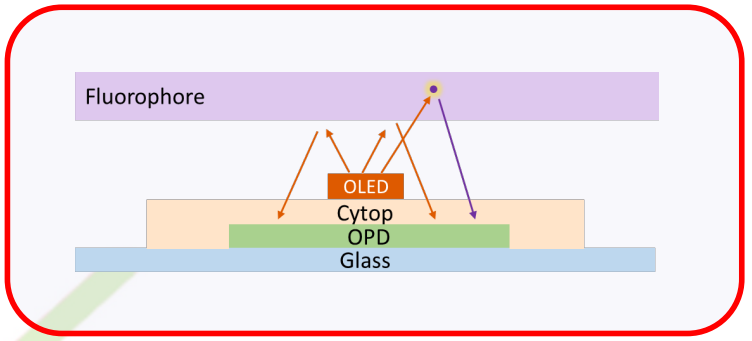
Linearity in dose-response curve

$(I - I_0) / I_0$

Fluorescence signal variation normalized to the chip response to ethanol (S/N ratio)







Deviation from Lambert-Beer's law

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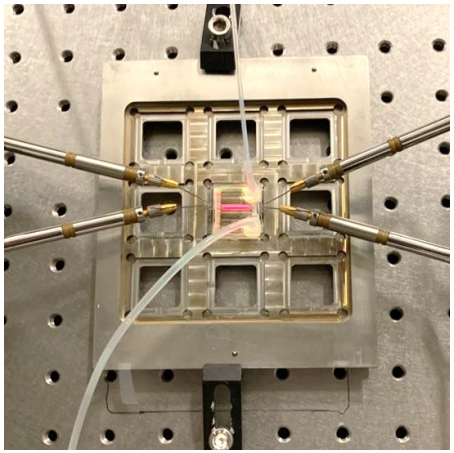
Conclusions

- On-chip all-organic fluorescence sensor comprising optical component
- Optimized design to increase the system efficiency
- Detection of biological dyes up to micromolar concentrations
- Prone to DNA detection (fluorescent nucleic acid stain conc. = 5 mM)



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Photonic system for adaptable multiple-analyte monitoring of food quality
Grant agreement No 101016706

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