



Organic Field-Effect Devices for clinical applications

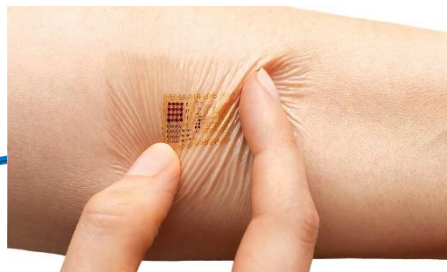
Corso di Tecnologie e Dispositivi
Elettronici Avanzati

Corrado Napoli
corrado.napoli@diee.unica.it

Outline

- Introduction: motivation, definition, classification
- Surface functionalization
- OTFT-based biosensors
- Transduction mechanisms
- Suitable structures for bio-related sensing applications

Biosensors



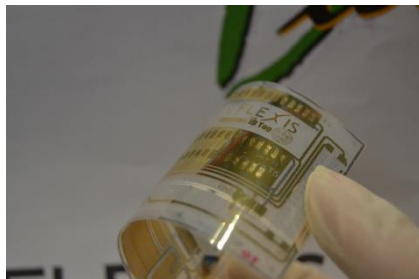
E-paper



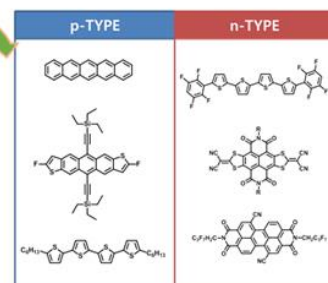
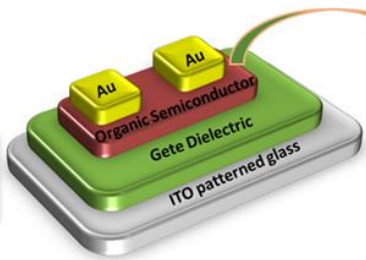
Bio Technology

E-paper Technology

RFID Tag

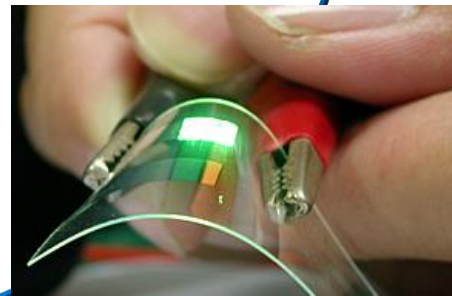
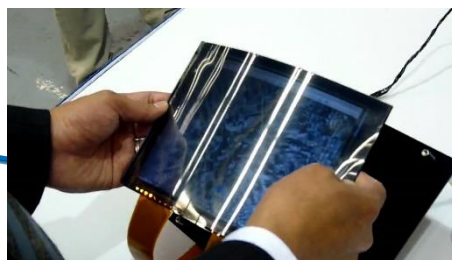


IC Technology

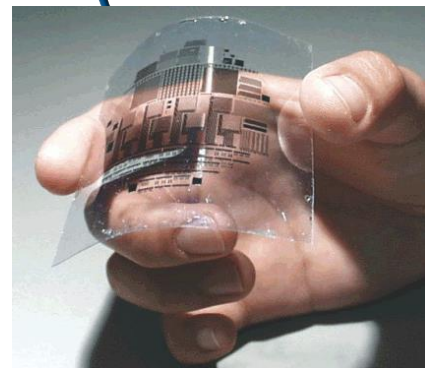


Optical Technology

LCD

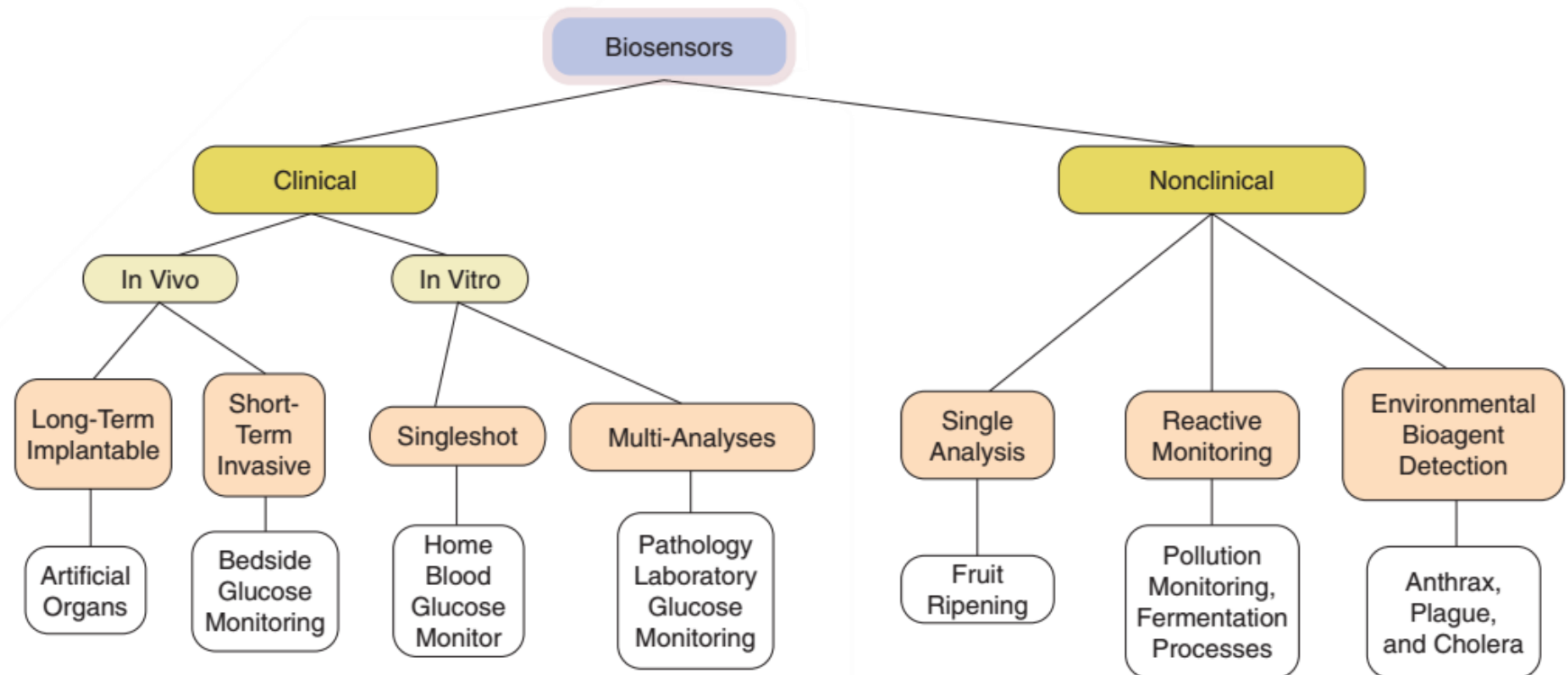


OLED

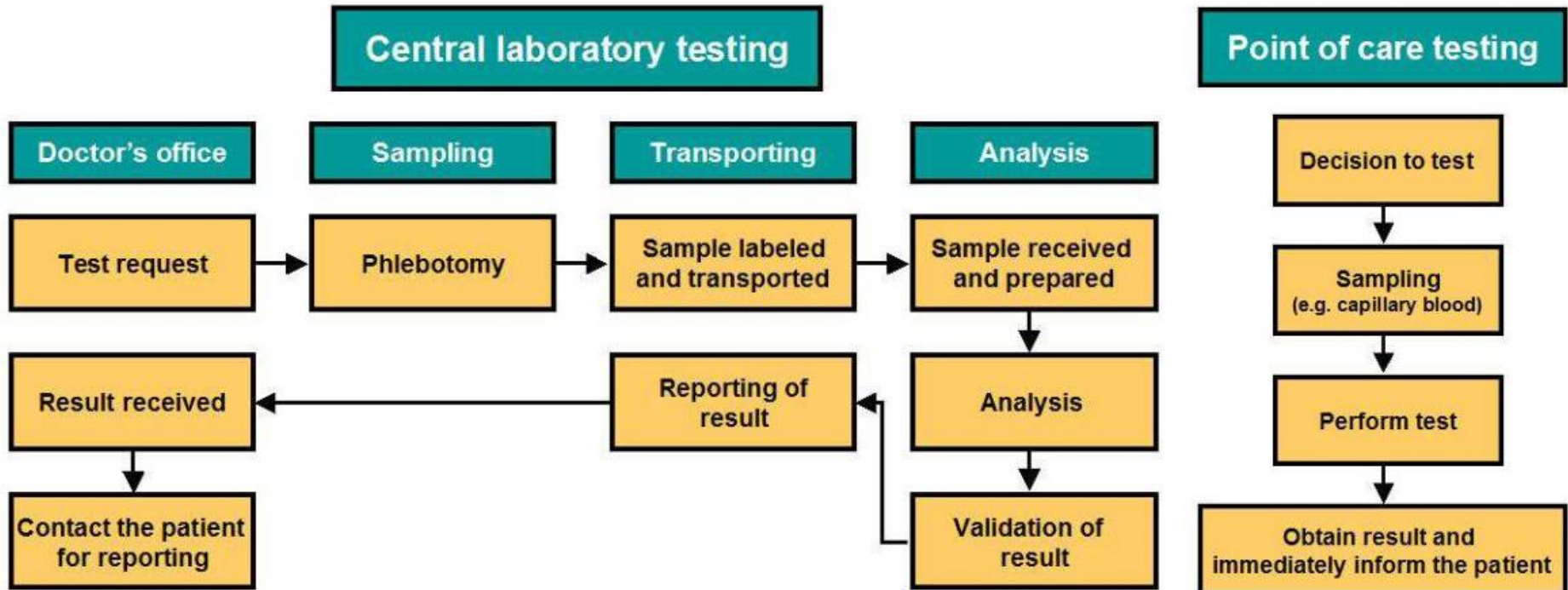


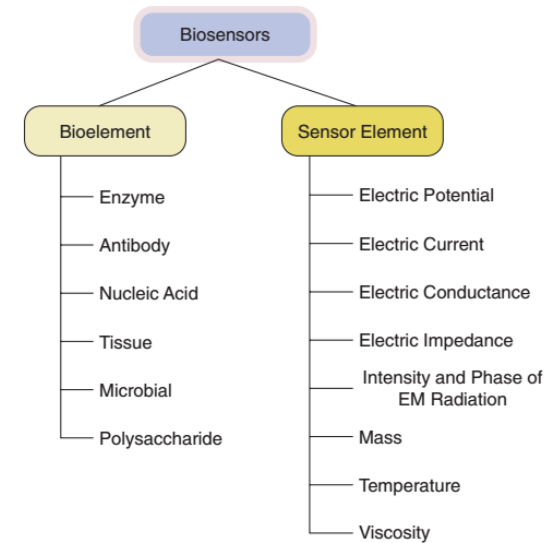
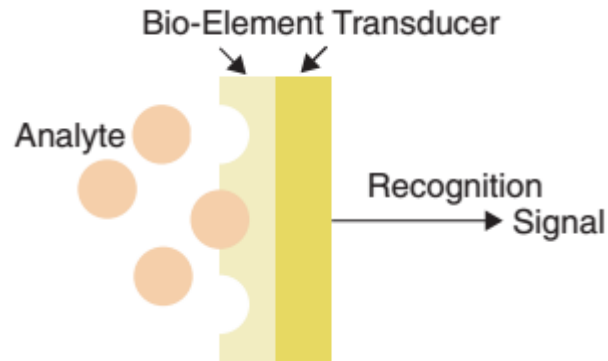
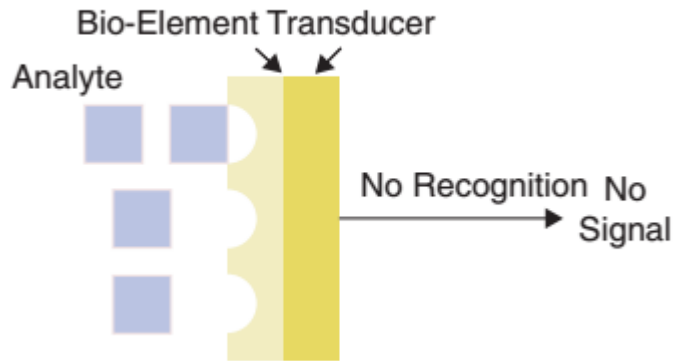
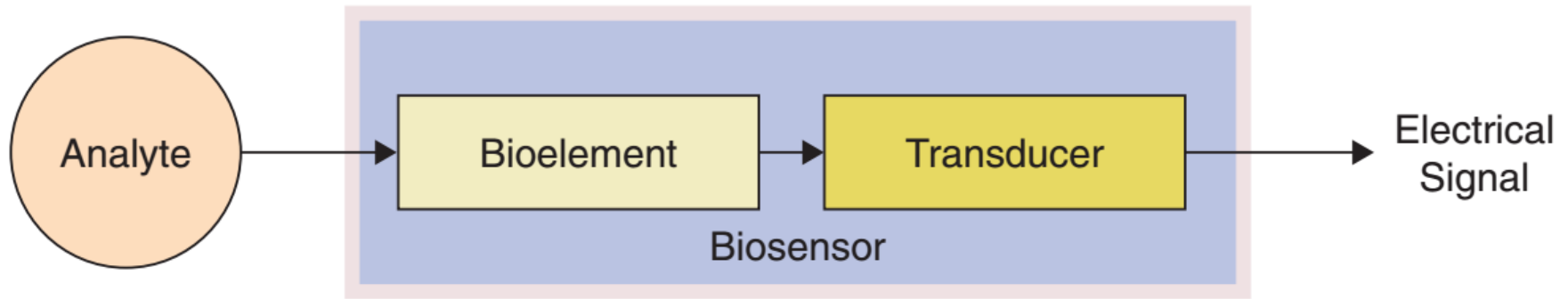
Circuits

Introduction



Motivation



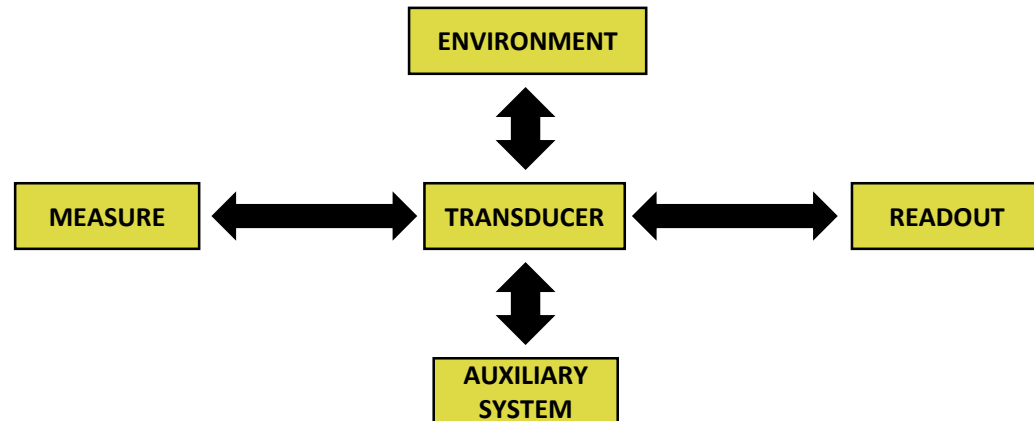


Def: A device that uses specific biochemical reactions mediated by isolated enzymes, immunosystems, tissues, organelles or whole cells to detect chemical compounds usually by electrical, thermal or optical signals. (IUPAC)

Analytical figures of merit

- Selectivity
- Sensitivity
- Reversibility, hysteresis
- Long-term reliability and stability
- Fast response
- Dynamic and calibration range
- Linearity, precision and accuracy
- Recovery time
- SNR
- Limit of Detection (LOD)
- Limit of Quantitation (LOQ)

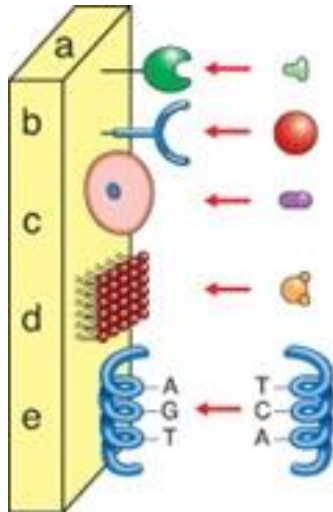
- Materials
- Physical/Chemical properties
- Measurement system
- Measurement environment



Selectivity

Def: **Selectivity** of a method refers to the extent to which it can determine particular analytes under given conditions in mixtures or matrices, simple or complex, without interferences from other components. (IUPAC)

Def: **Specificity** is the ultimate of Selectivity (IUPAC)



Binding selectivity
Chemoselectivity

LBF, Langmuir-Blodgett Film

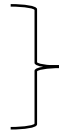
SAM, Self-Assembled Monolayer

Electrochemical

Surface functionalization

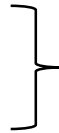
Deposition methods:

- Spin coating
- Vapour deposition



Multilayer

- Atomic layer deposition
- Self-assembly



Monolayer

Film's relevant properties:

- Wettability
- Uniformity and pinholes
- Chemical reactivity
- Electronic interactions
- Thermal stability

Surface functionalization

Deposition methods:

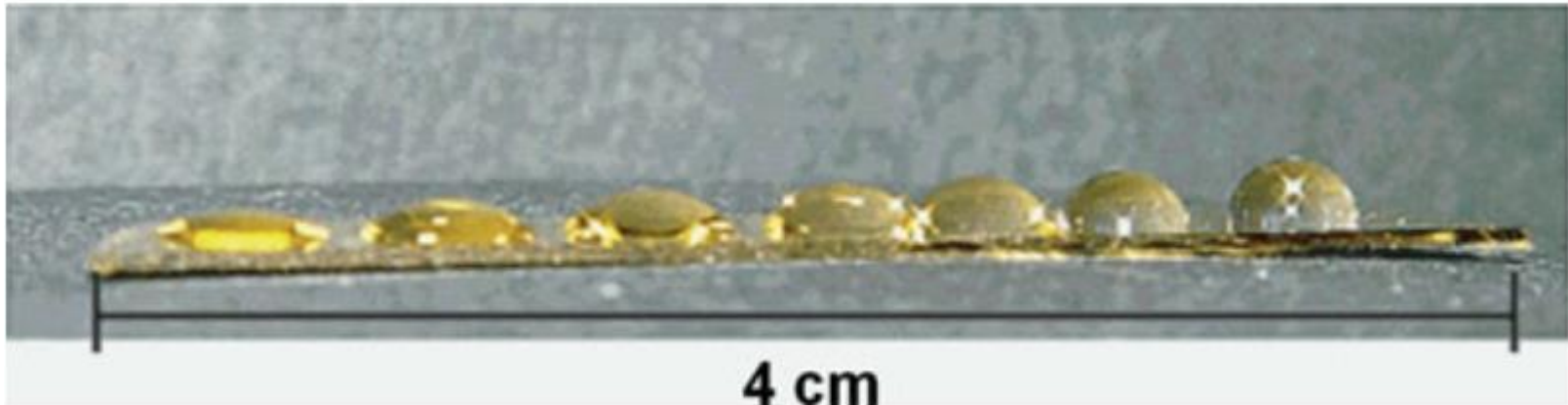
- Spin coating
- Vapour deposition
- Atomic layer deposition
- Self-assembly

Multilayer

Monolayer

Film's relevant properties:

- **Wettability**
- Uniformity and pinholes
- Chemical reactivity
- Electronic interactions
- Bond strength



Surface functionalization

Deposition methods:

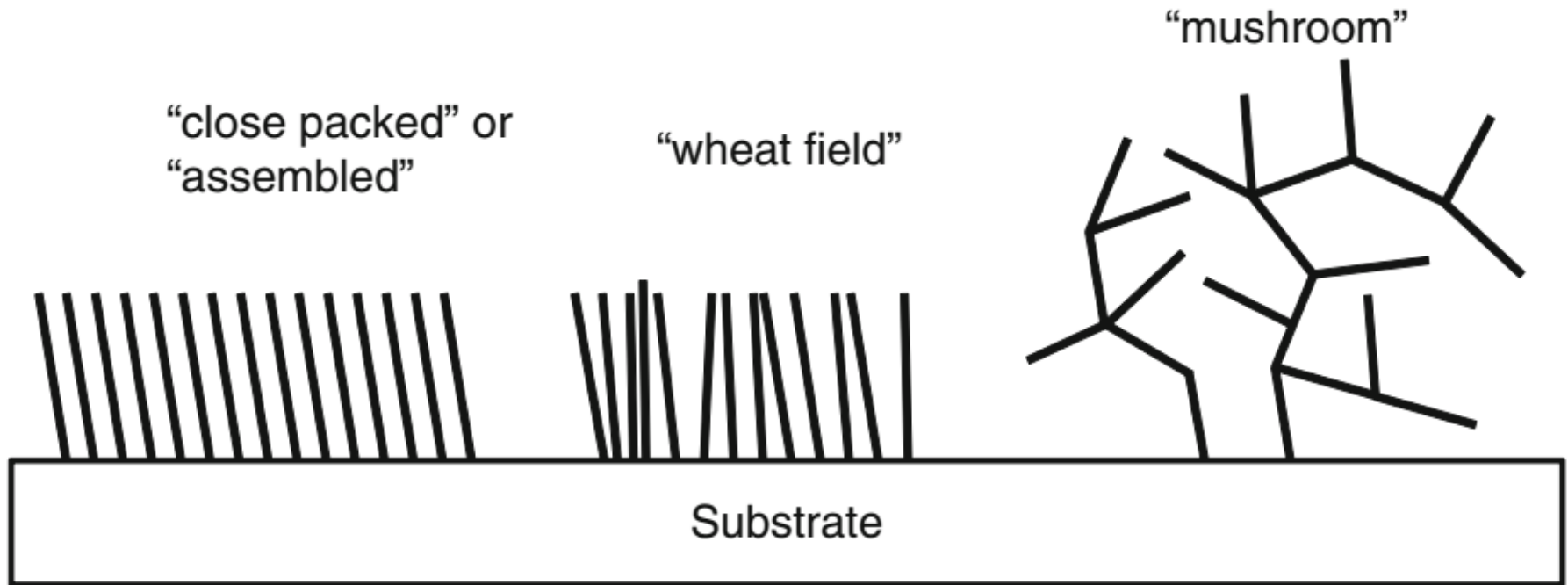
- Spin coating
- Vapour deposition
- Atomic layer deposition
- Self-assembly

Multilayer

Monolayer

Film's relevant properties:

- Wettability
- **Uniformity and pinholes**
- Chemical reactivity
- Electronic interactions
- Bond strength



Surface functionalization

Deposition methods:

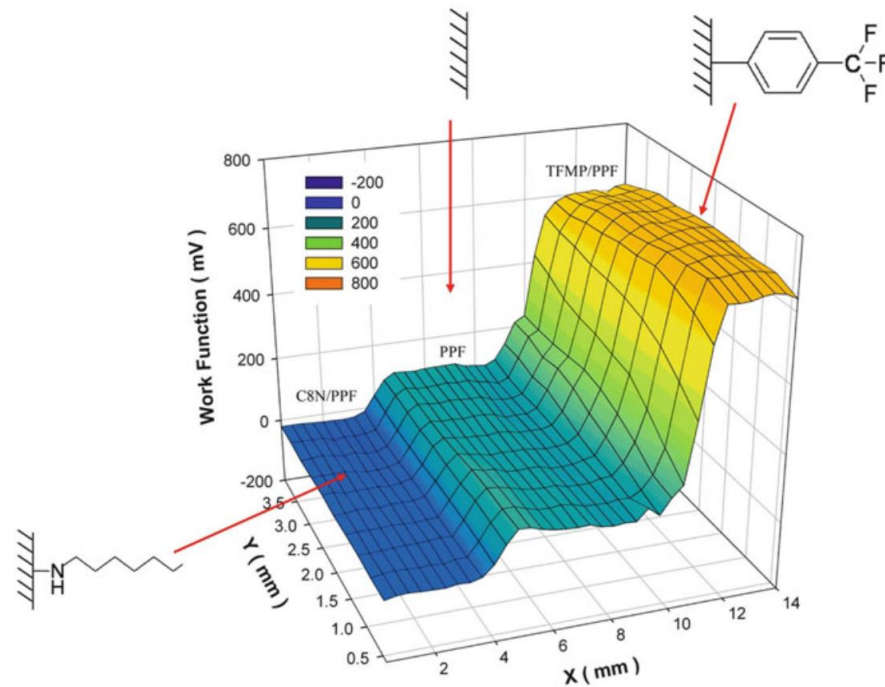
- Spin coating
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Multilayer

Monolayer

Film's relevant properties:

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- **Electronic interactions**
- Bond strength



Surface functionalization

Deposition methods:

- Spin coating
- Vapour deposition
- Atomic layer deposition
- Self-assembly

Multilayer

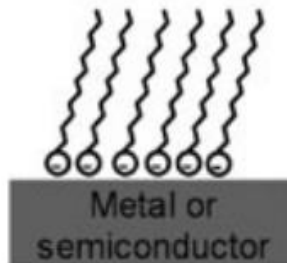
Monolayer

Film's relevant properties:

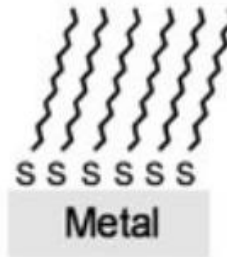
- Wettability
- Uniformity and pinholes
- Chemical reactivity
- Electronic interactions
- **Bond strength**

Layer Type

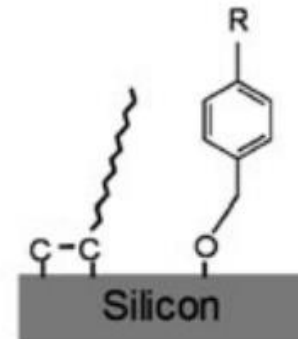
Langmuir-Blodgett



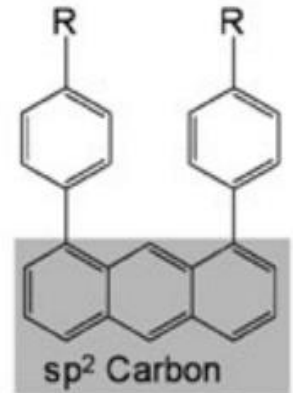
Self-Assembled Monolayer



Si-C and Si-O



Carbon-Carbon



Surface

<0.5 eV

~1.9 eV

3.5-4 eV

3.5-4 eV

Bond Energy

Organic, transistor-based, biosensors

A solid orange horizontal bar at the bottom of the slide.

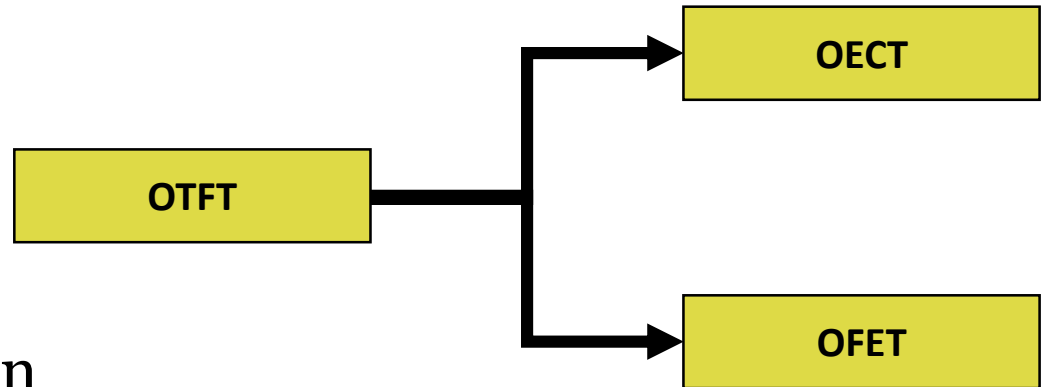
Why OTFT?

- Transistors:

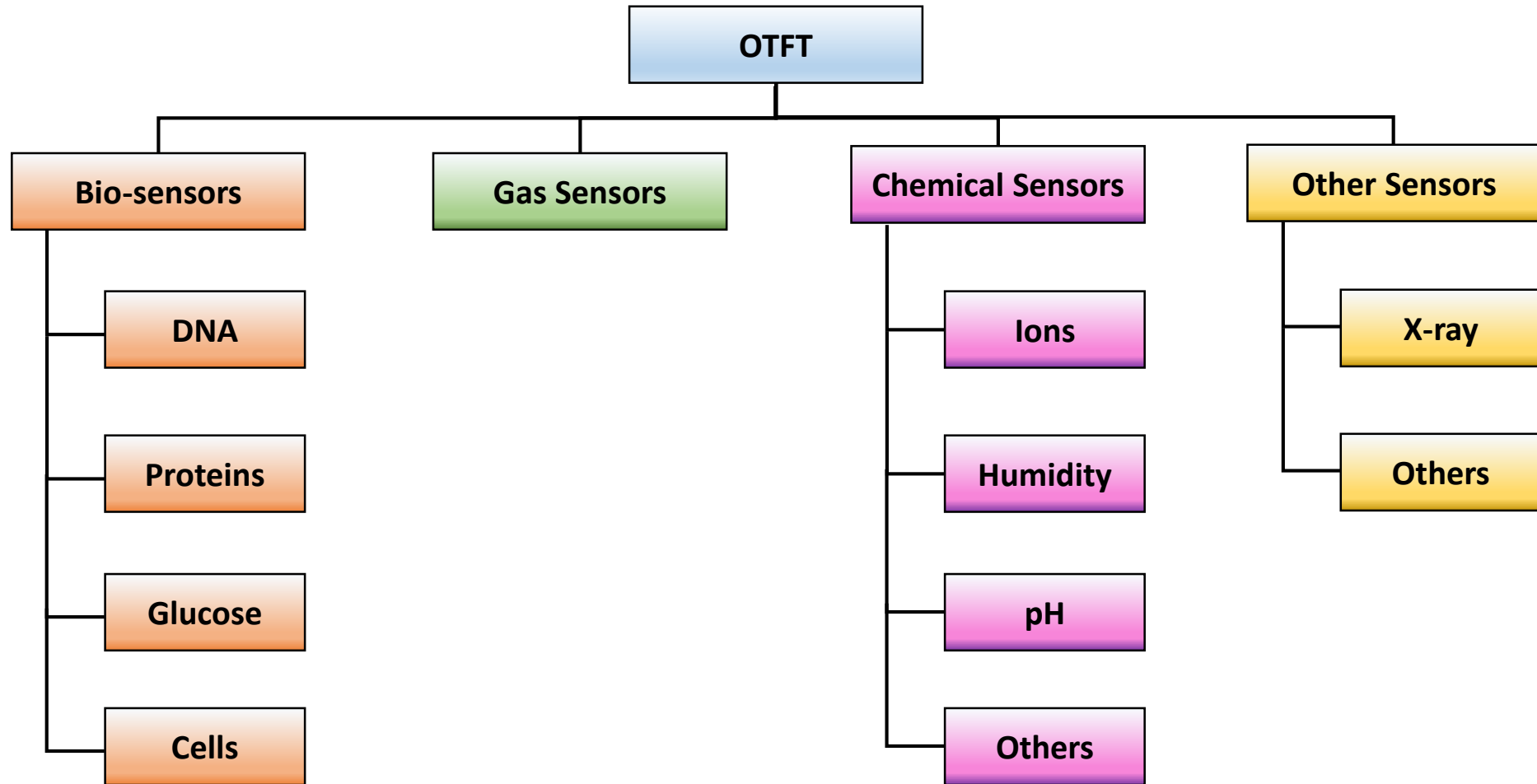
- Amplification
- Label free

- Materials:

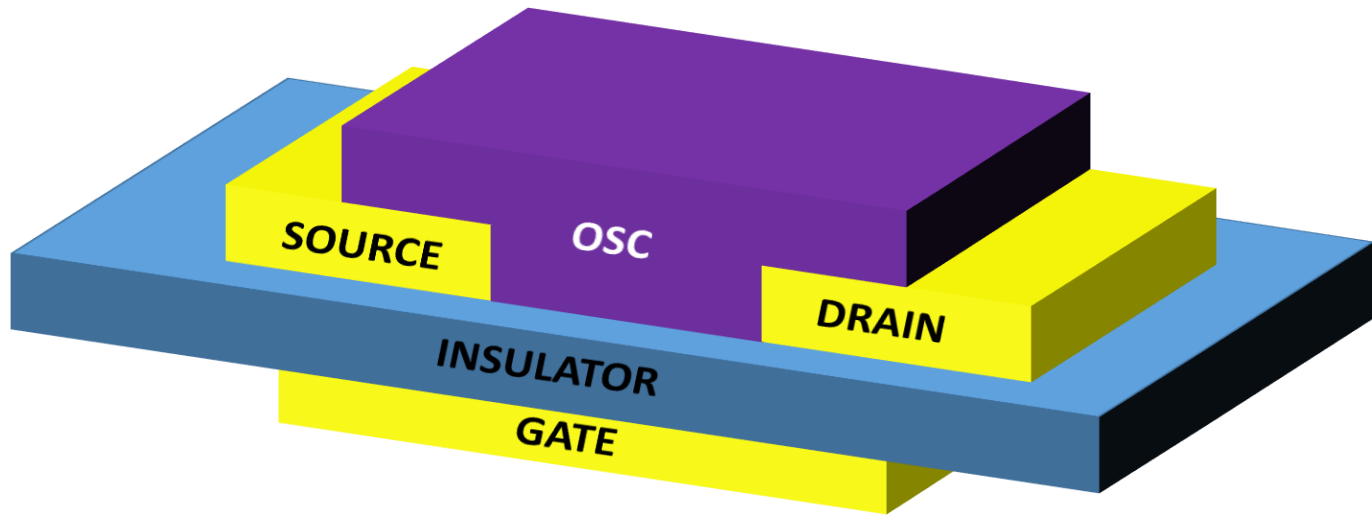
- ❖ Biodegradable
- ❖ Biocompatible
- ❖ Flexible
- ❖ Cost effective
- ❖ Large area production



OFET sensors



Sensing mechanisms



$$I_{DS} = f(\mu, C_{INS}, W, L, V_{GS}, V_{DS}, V_{TH}, R_C)$$

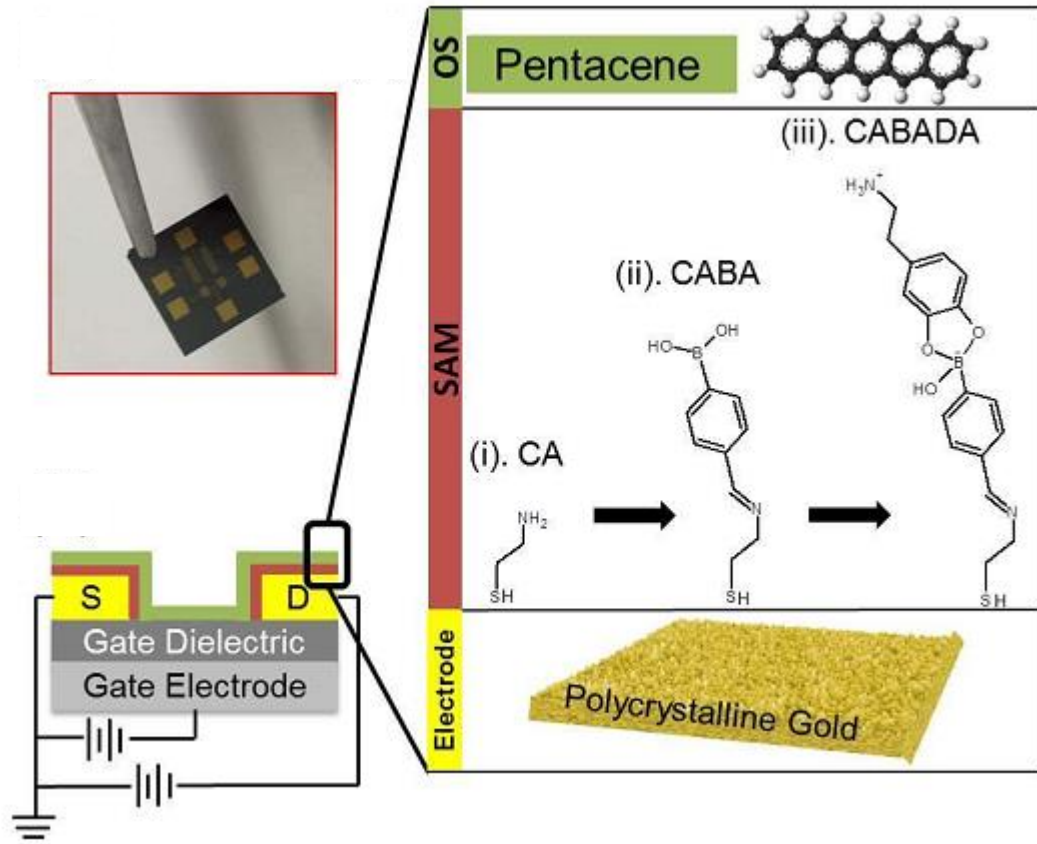
Sensing area:

- Active semiconductor/electrolyte
- Gate/electrolyte
- Semiconductor
- Electrodes

Sensing mechanisms:

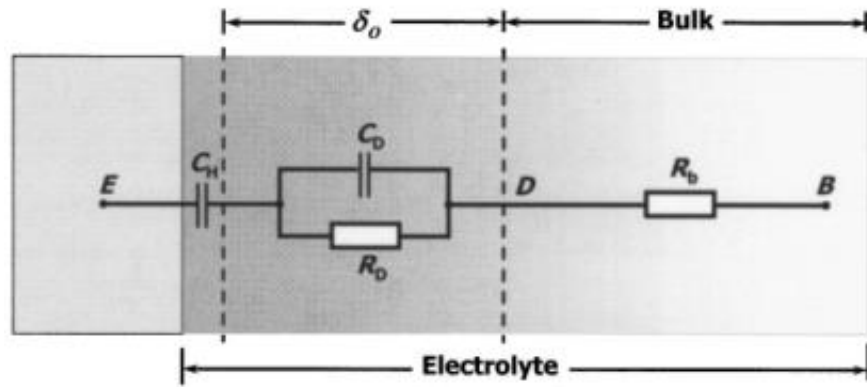
- Morphology variation
- Charge injection
- Field effect modulation

Charge injection modulation

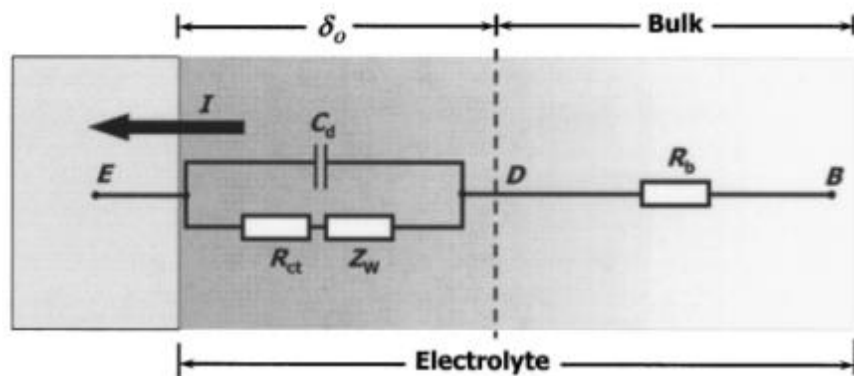


Charge-Injection Organic Gauges to Detect Dopamine Down to the Nanomolar Scale
Francesca Leonardi, Stefano Casalini, Cristiano Albonetti, Alessandro Kovtun, Andrea Liscio, and Fabio Biscarini (2015)

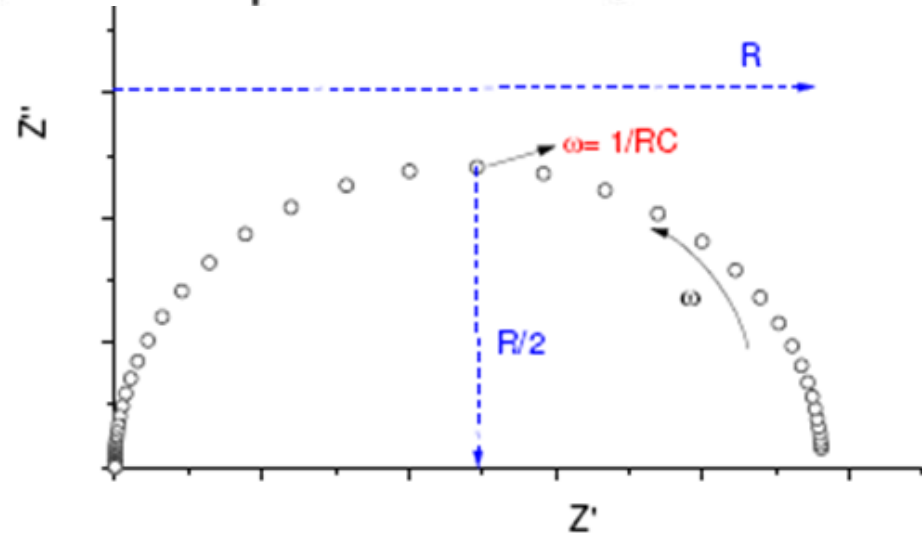
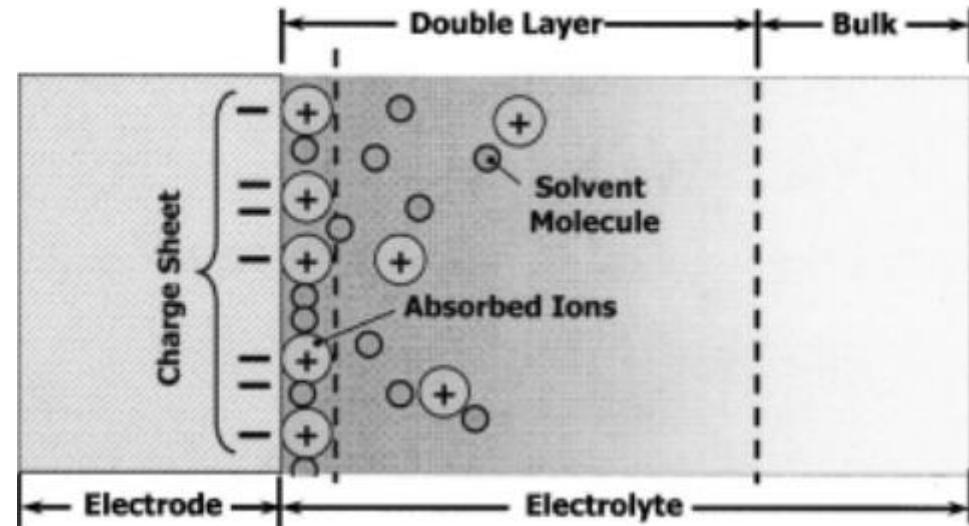
Electrode/Electrolyte interface



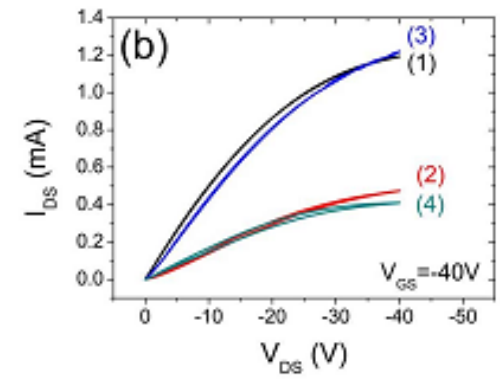
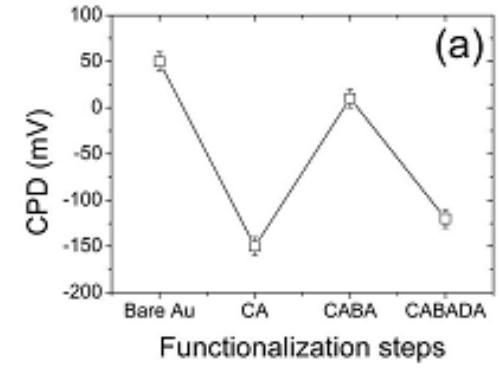
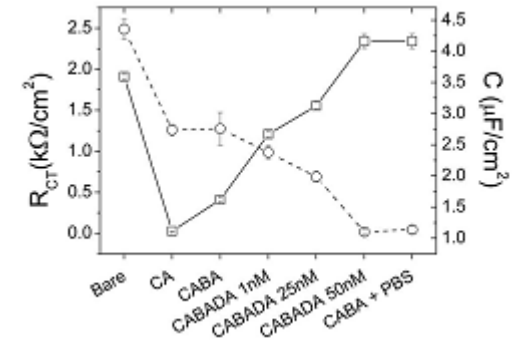
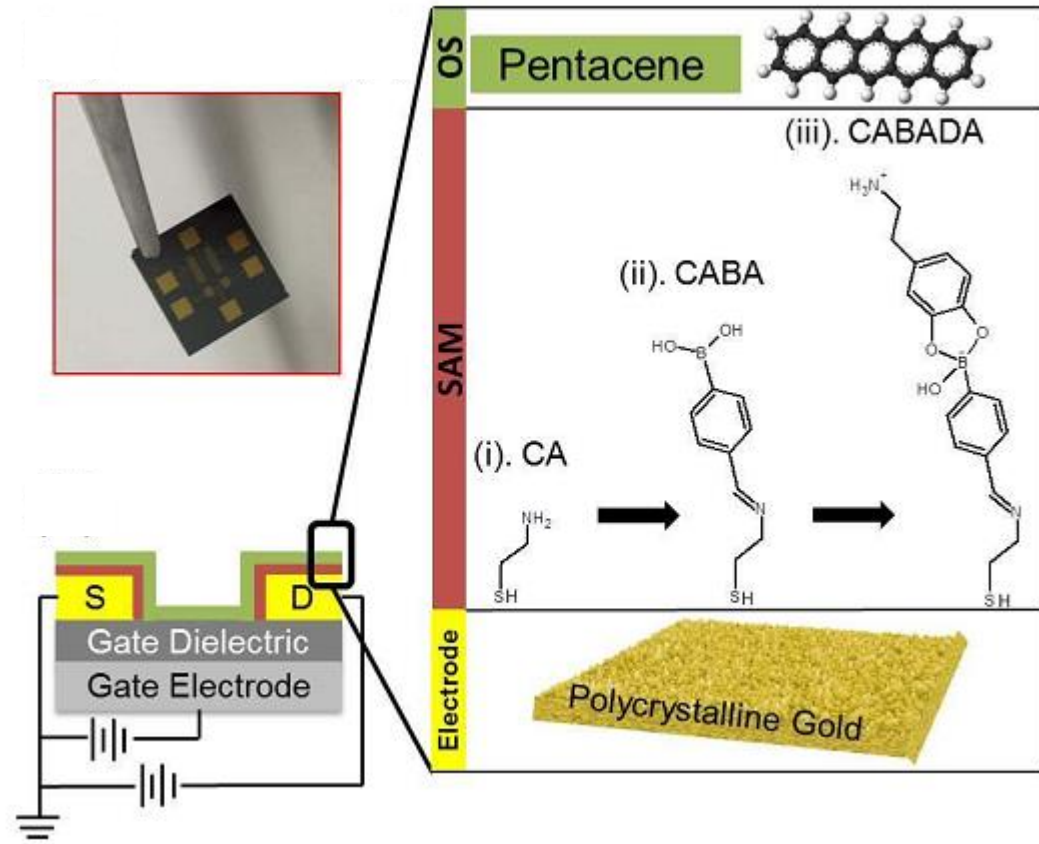
Perfectly Polarizable Electrode



Perfectly non Polarizable Electrode

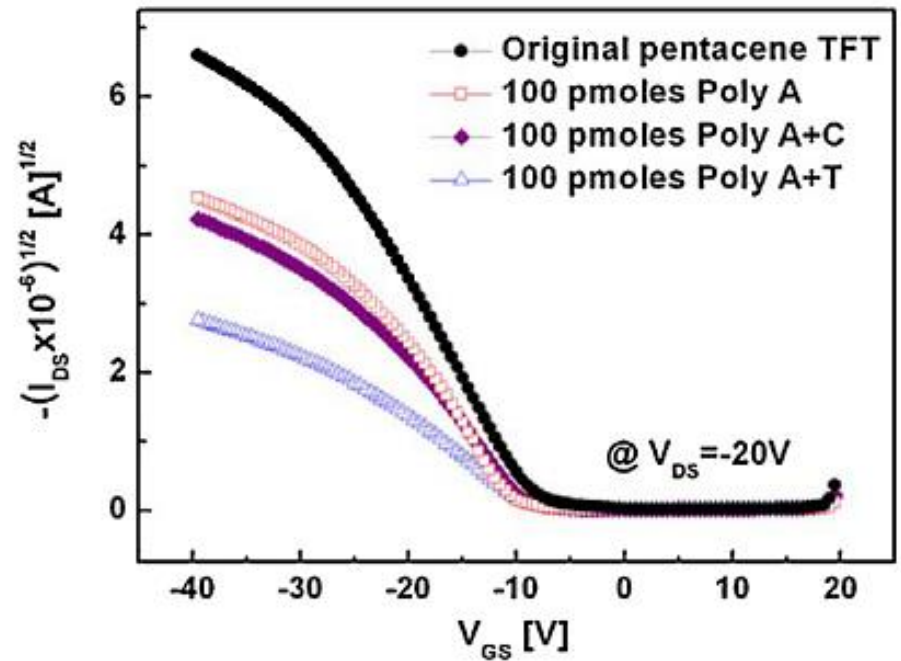
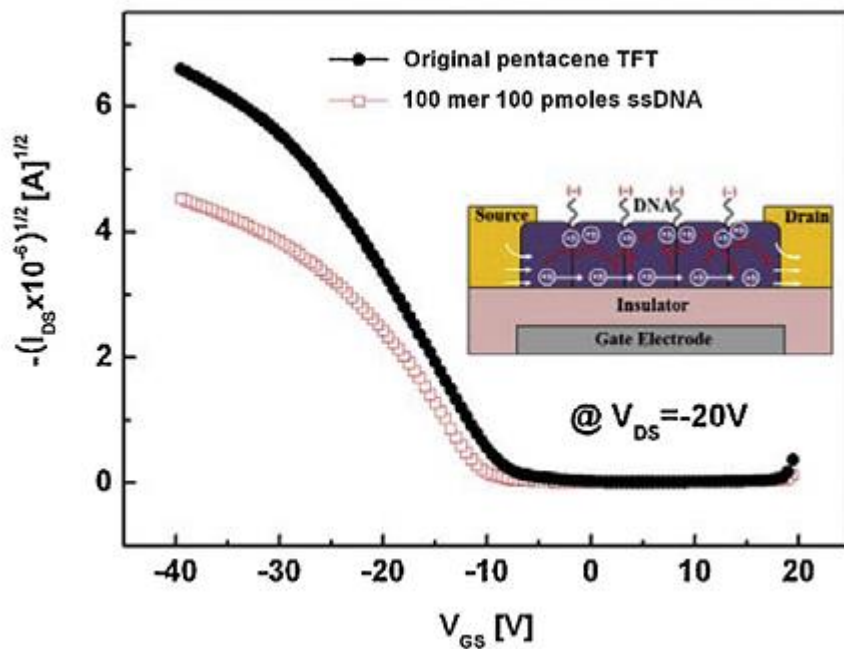
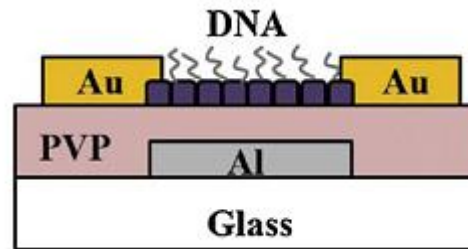


Charge injection modulation



Charge-Injection Organic Gauges to Detect Dopamine Down to the Nanomolar Scale
 Francesca Leonardi, Stefano Casalini, Cristiano Albonetti, Alessandro Kovtun,
 Andrea Liscio, and Fabio Biscarini (2015)

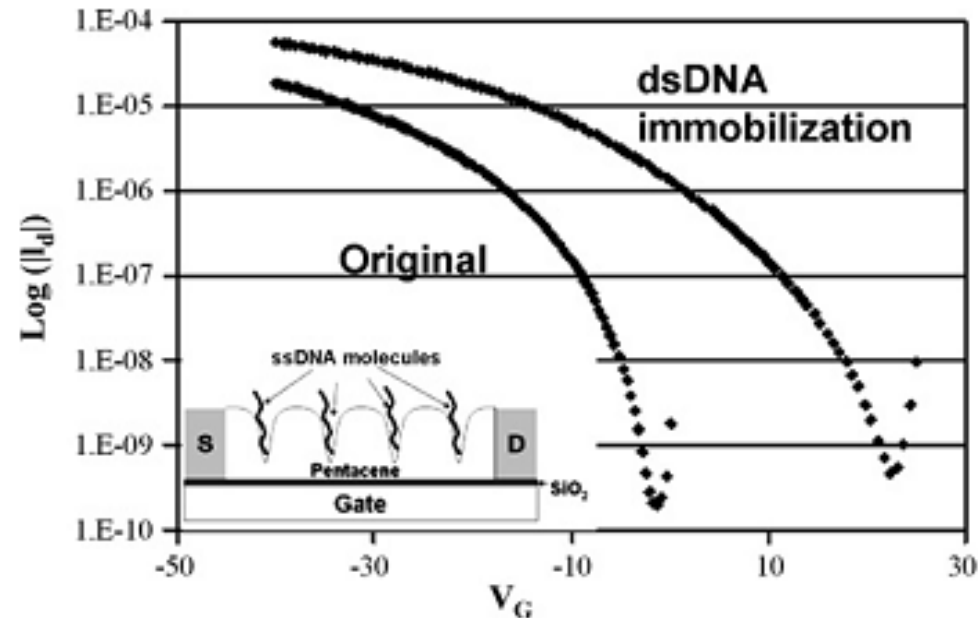
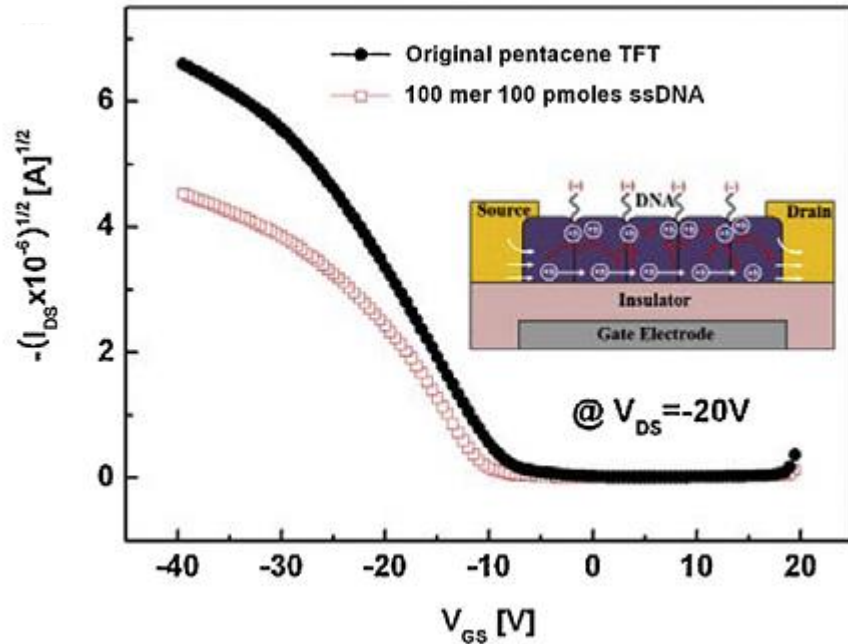
DNA hybridization based on pentacene TFTs



DNA hybridization sensor based on pentacene thin film transistor

Jung-Min Kim, Sandeep Kumar Jha, Rohit Chand, Dong-Hoon Lee, Yong-Sang Kim (2011)

DNA hybridization based on pentacene TFTs



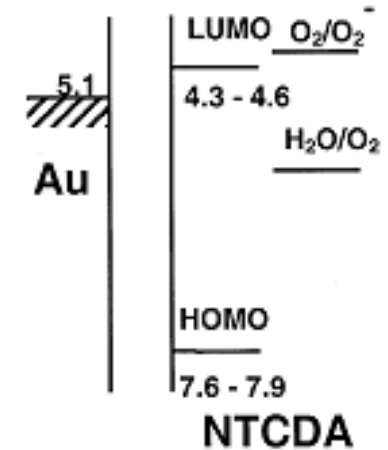
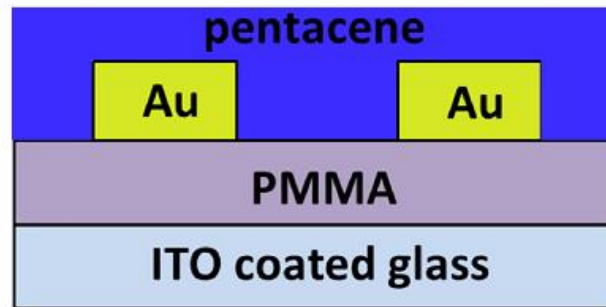
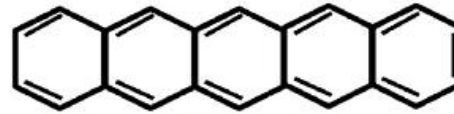
DNA hybridization detection with organic thin film transistors:
Toward fast and disposable DNA microarray chips
Qintao Zhang, Vivek Subramanian (2007)

DNA hybridization sensor based on pentacene thin film transistor
Jung-Min Kim, Sandeep Kumar Jha, Rohit Chand, Dong-Hoon Lee, Yong-Sang Kim (2011)

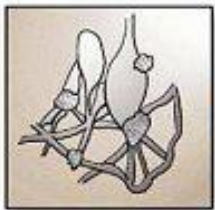
Gas sensors: an overview

Applications

- Nose
- Tongue
- ...



Receptor



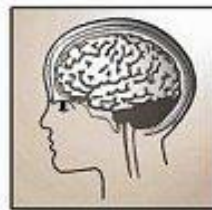
Neuron

Feature Extraction



Olfactory Bulb

Pattern Classification



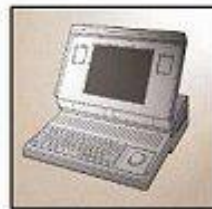
Brain



Sensor Array



Microprocessor



Software

- OSC molecular structure
- Degree of crystallization
- Grain boundaries
- Surface roughness

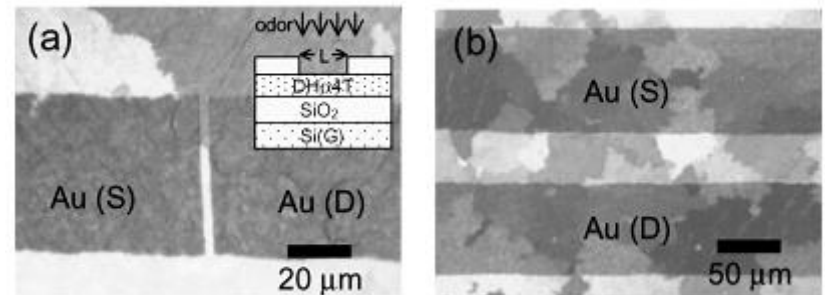
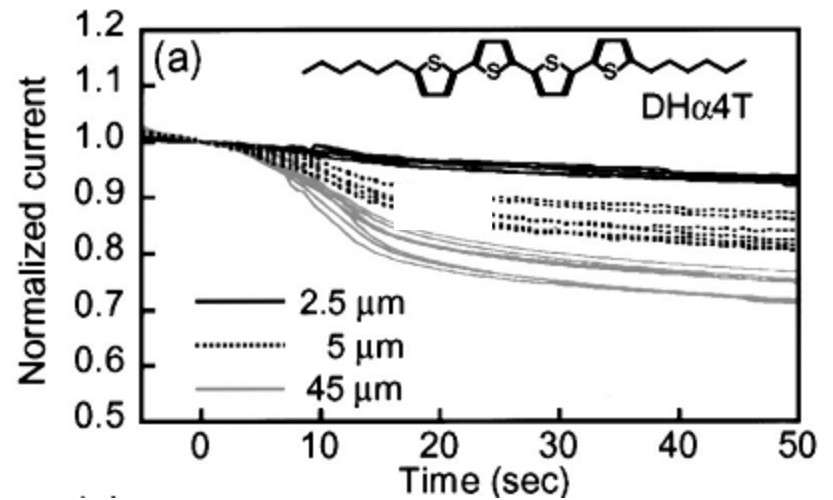
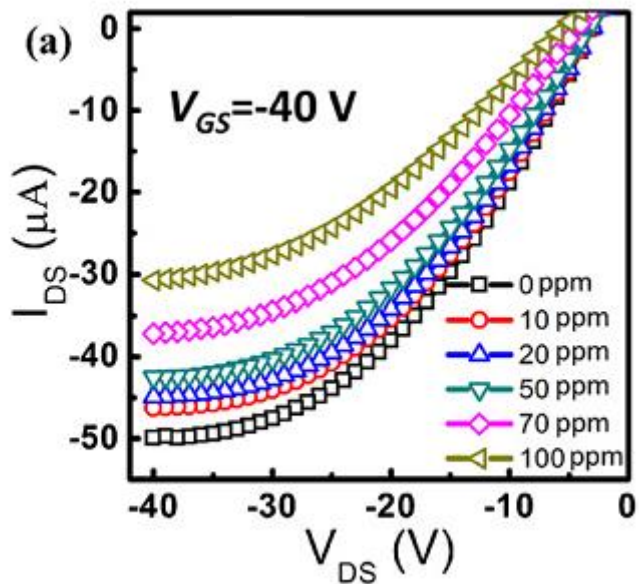
Changing parameters

- Off state current
- V_{TH}
- μ

Multi-parameter gas sensors based on organic thin-film-transistors

L. Torsi, A. Dodabalapur, L. Sabbatini, P.G. Zamboni (2000)

Gas sensors

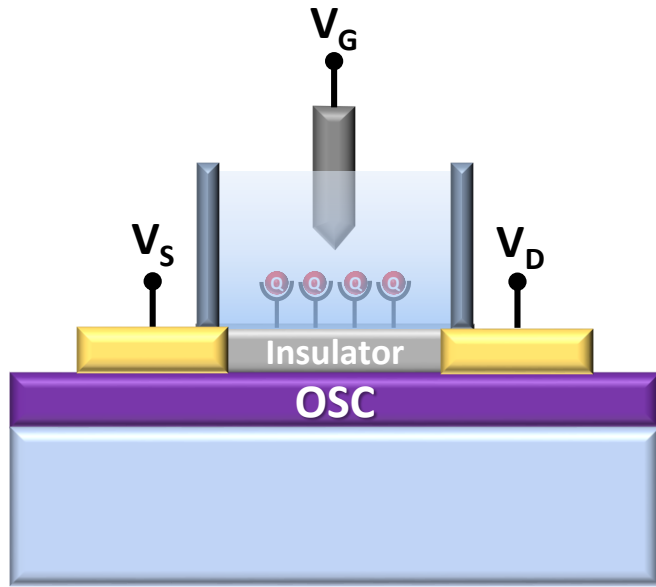


Vapor sensing with α,ν -dihexylquarterthiophene field-effect transistors: The role of grain boundaries

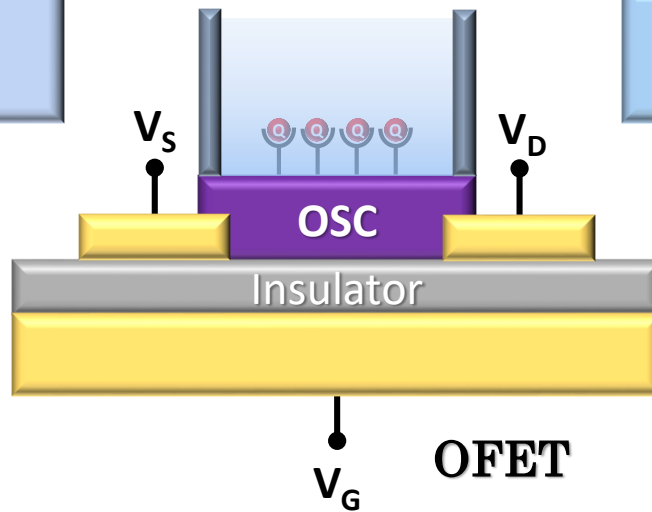
Takao Someya, Howard E. Katz, Alan Gelperin, Andrew J. Lovinger, and Ananth Dodabalapur (2002)

Ammonia gas sensor based on pentacene organic field-effect transistor
Junsheng Yu, Xing Yu, Lin Zhang, Hongjuan Zeng (2015)

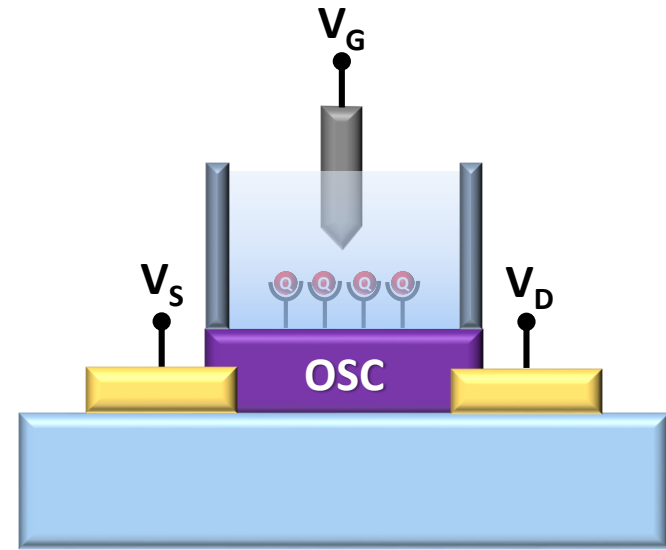
Structures



ISOFET

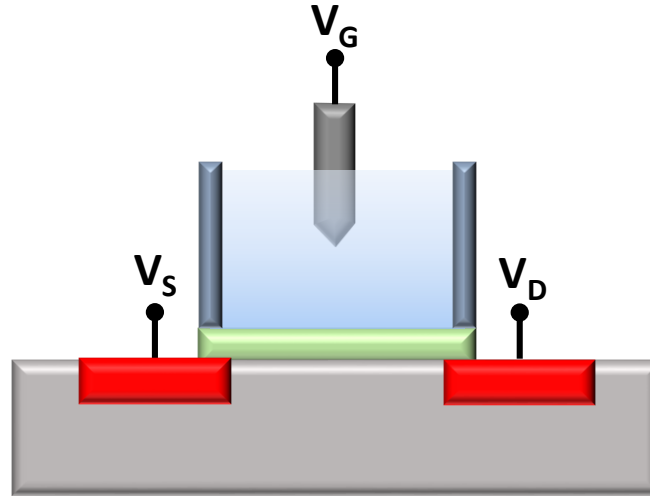


OFET



EGOFET

ISFET



$$V_{FB} = (E_{ref} + \phi_{ij}) - (\phi_{eo} - \chi_e) - \chi_{Si} - Q_0/C_{ox}$$

$$V_T^* = V_T + E_{ref} + \phi_{ij} + \chi_e - \phi_{eo}(pH) - \Phi_m/q$$

ϕ_{ref} : reference electrode potential referred to the vacuum level;

ϕ_{ij} : potential difference (liquid-junction) between the reference solution and the electrolyte;

ϕ_{eo} : potential drop in the electrolyte at the interface with the insulating oxide;

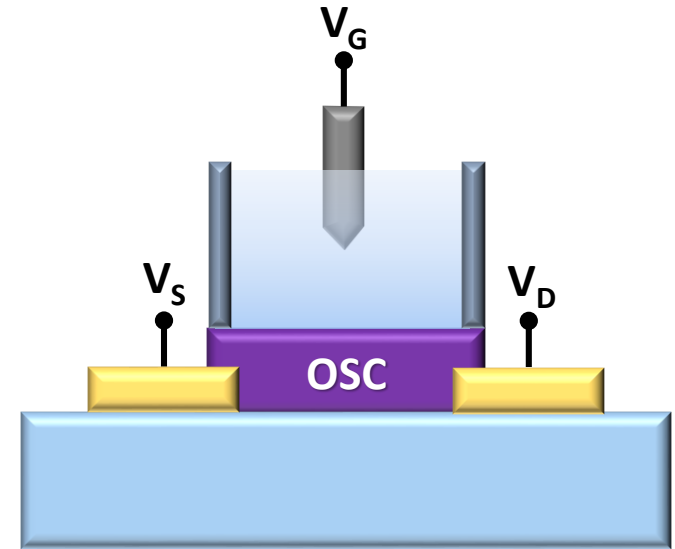
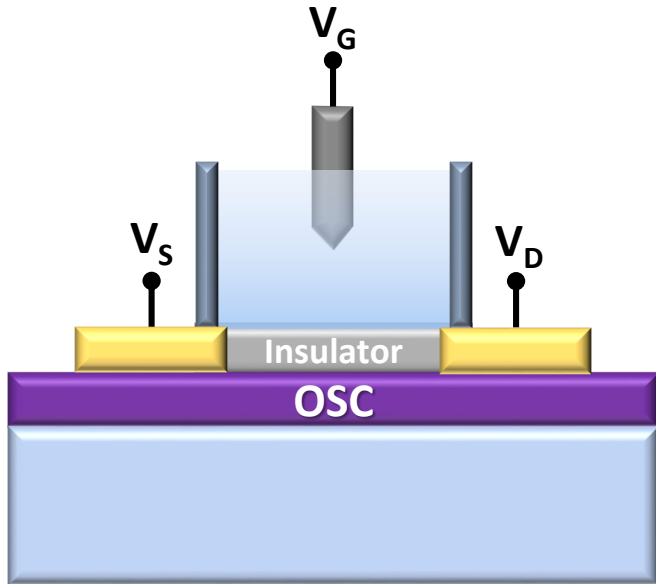
χ_e : dipole surface potential in the solution;

χ_{Si} : semiconductor work function;

Q_0 : charge (per unit area);

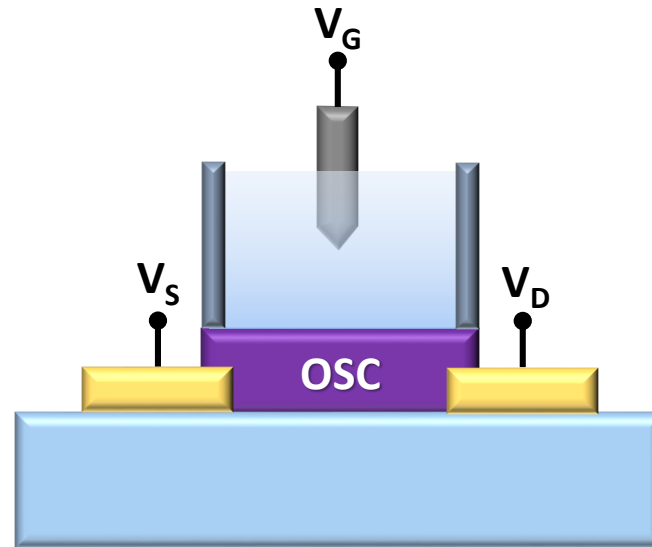
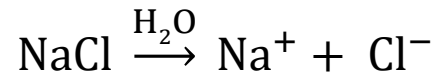
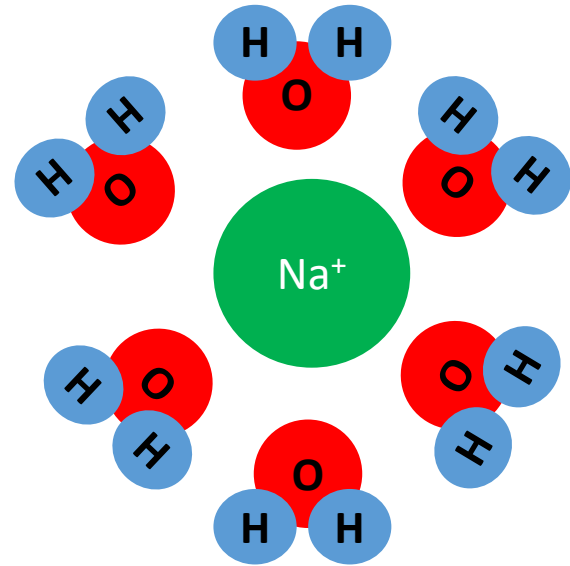
C_{ox} : oxide capacitance (per unit area);

From ISFET to EGOFET

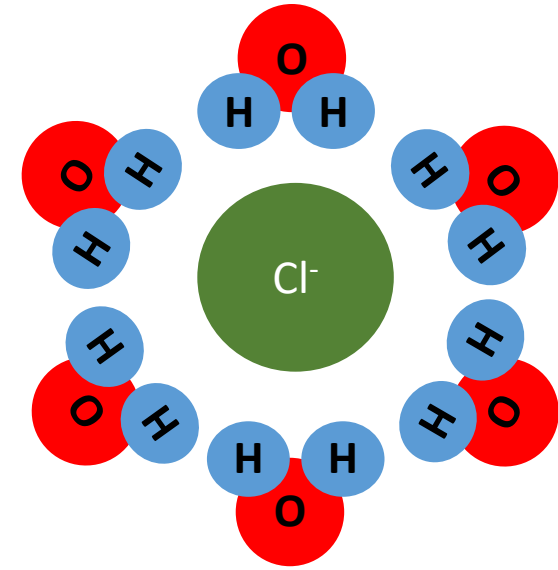


EGOFET

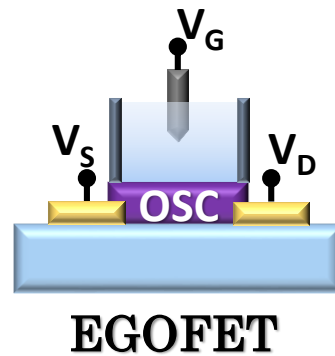
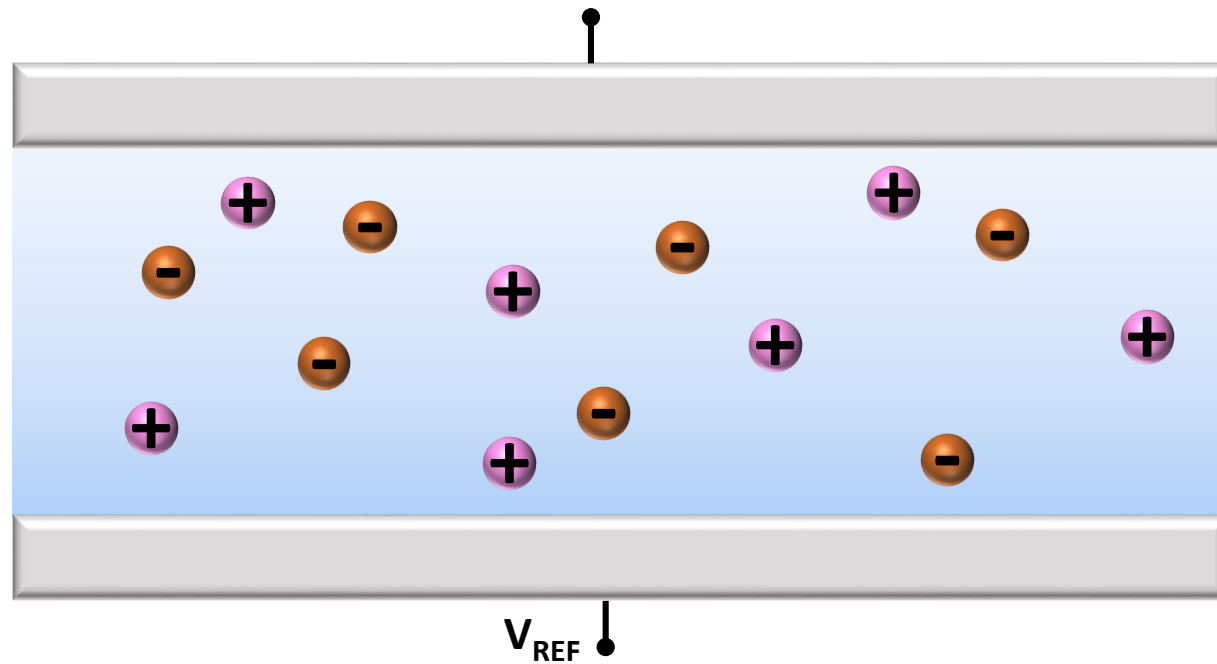
Electrolyte: solvation



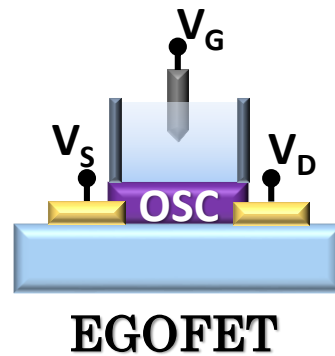
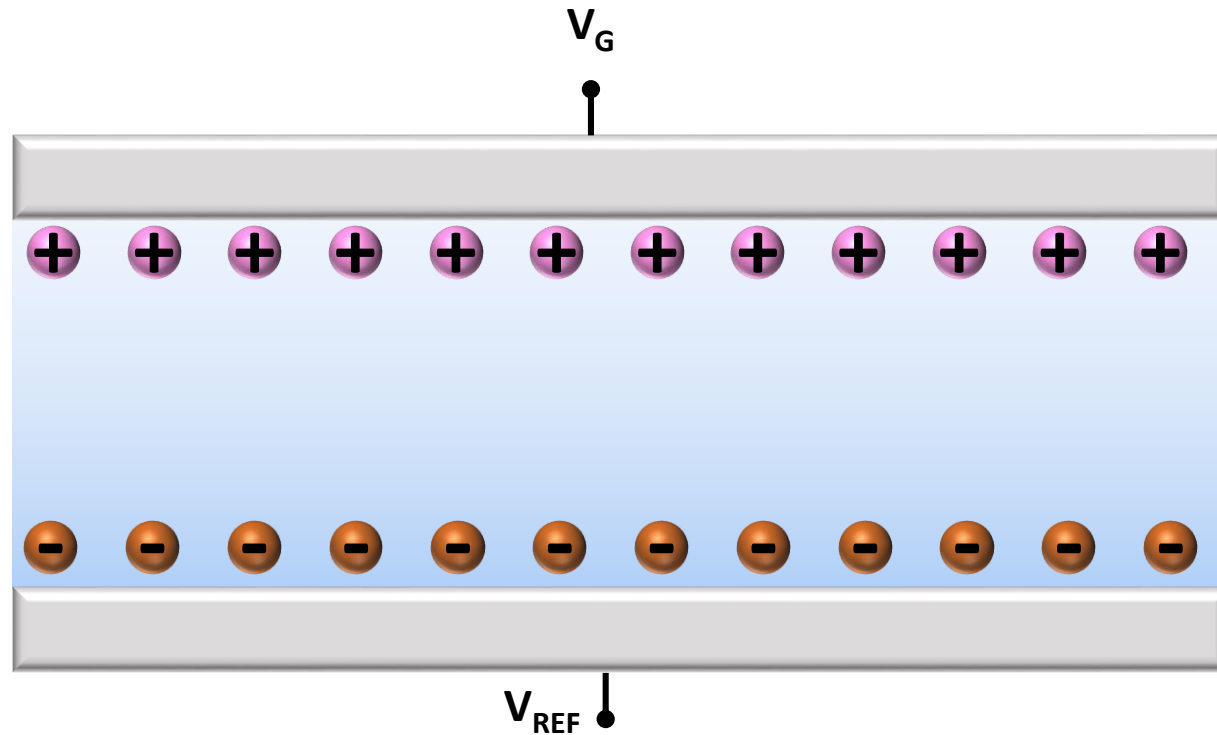
EGOFET



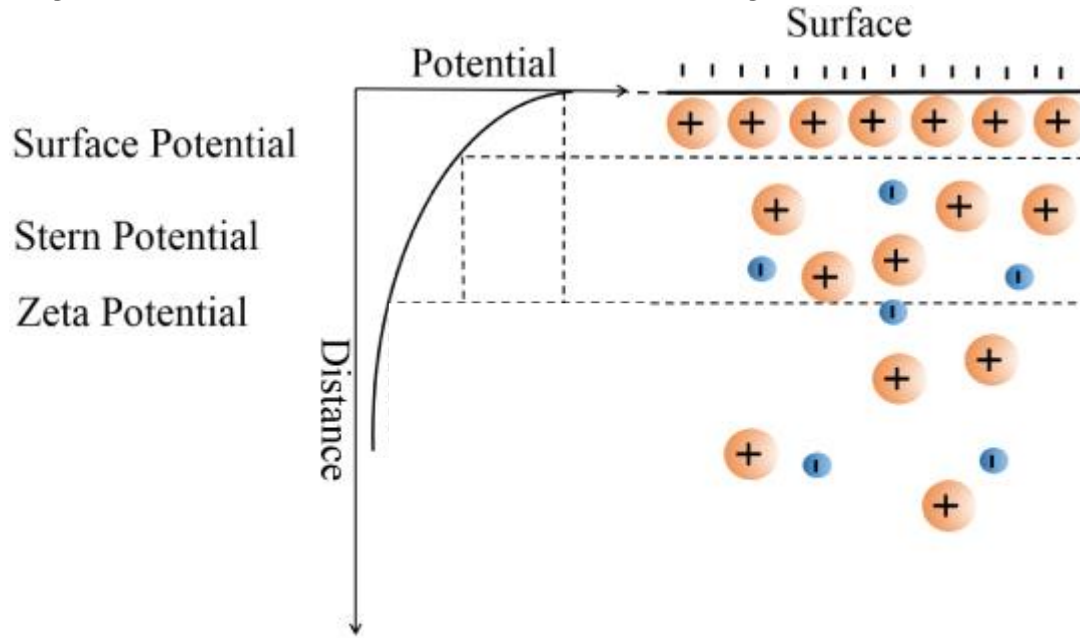
Electrolyte: polarization



Electrolyte: polarization



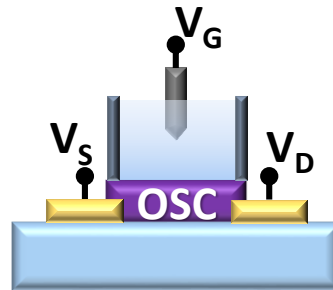
Electrolyte: double layer



$$\frac{d^2\varphi(x)}{dx^2} = -\frac{\rho(x)}{\varepsilon}$$

$$q_{dl} = \int_0^{+\infty} \rho(x) dx$$

$$C_{dl} \cong \frac{\varepsilon}{\lambda_D} A$$

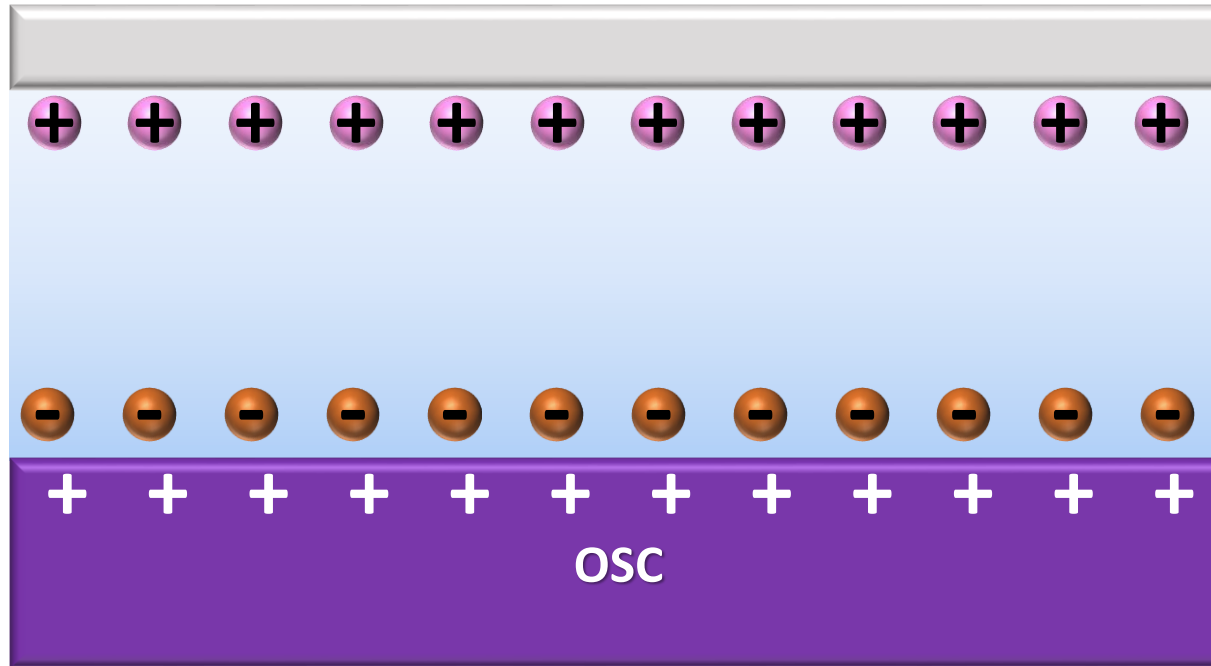


EGOFET

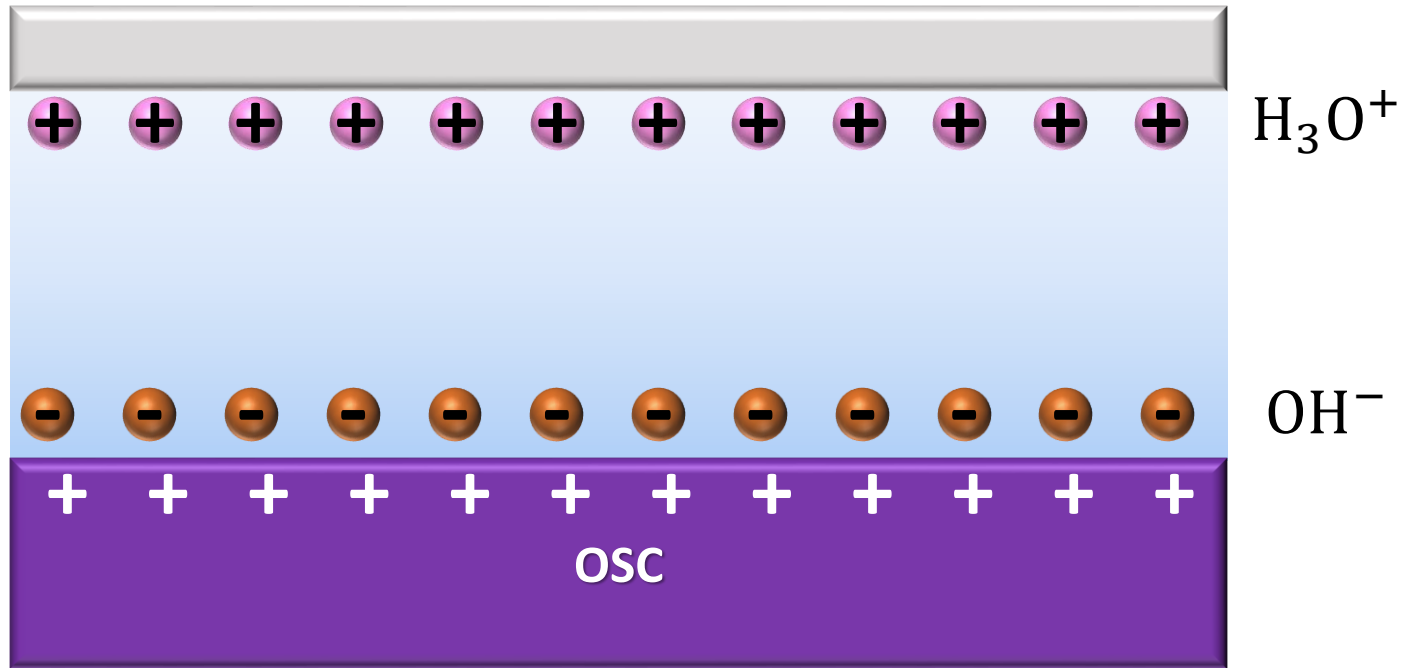
$$C_{dl} : 10 - 100 \mu\text{F} \cdot \text{cm}^{-2}$$

$$C_{ins} : 10 \text{ nF} \cdot \text{cm}^{-2}$$

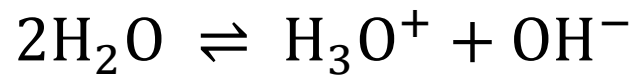
EGOFET: working principle



WGOFET



Water self ionization:

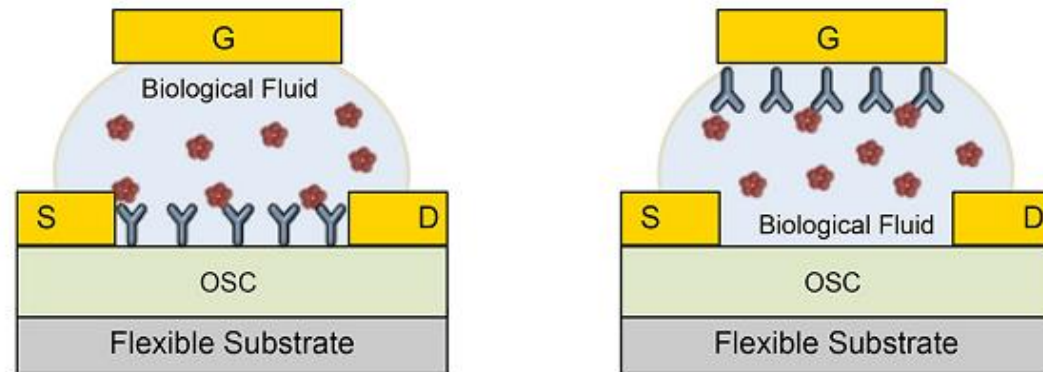




A T = 300 K

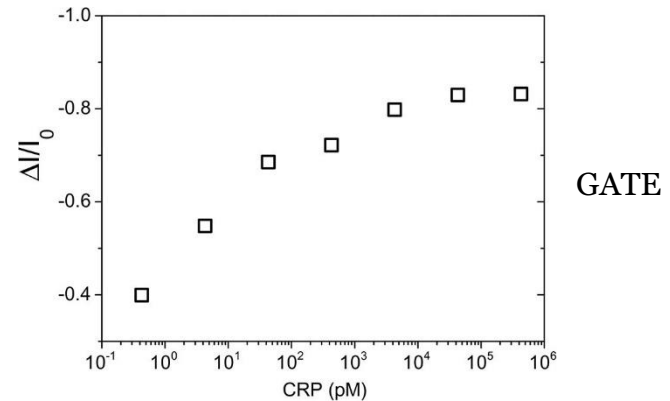
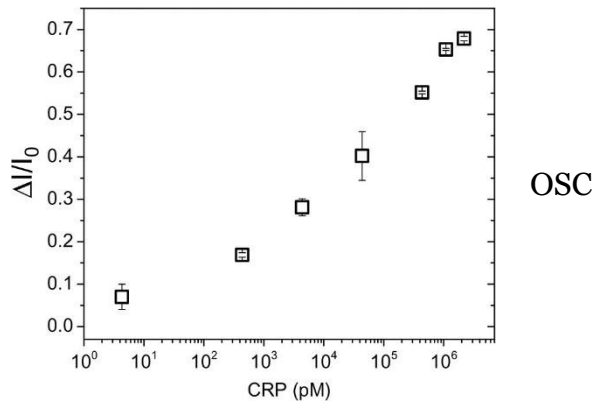
$$[H_3O^+] = [OH^-] = 10^{-7} \text{ M}$$

POC biosensors: EGOFET

Point-of-care (POC) biosensors are integrated diagnostic devices that allow the detection of clinically relevant biomarkers in biological fluids (blood, urine, saliva, sweat, and tears) outside conventional laboratories.



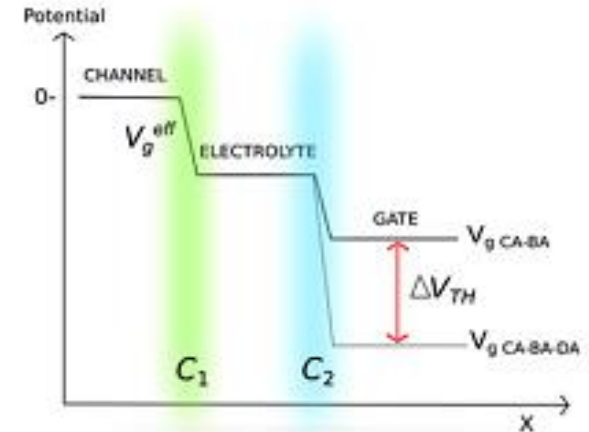
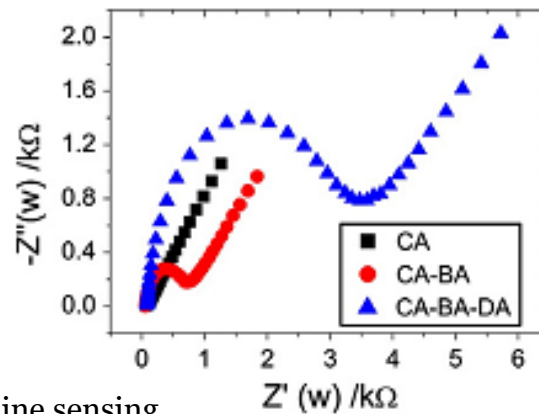
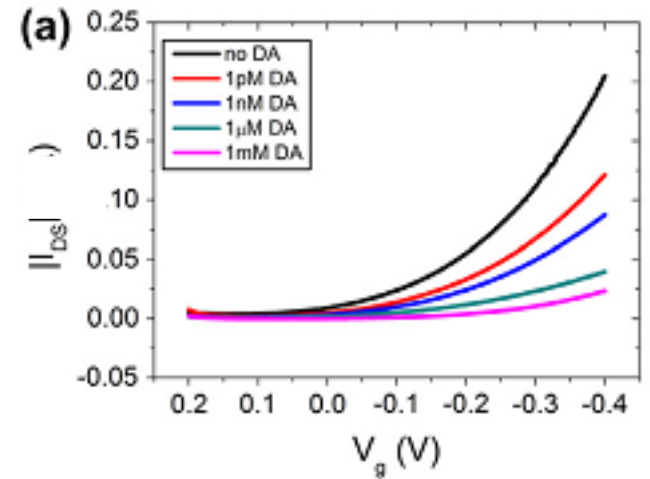
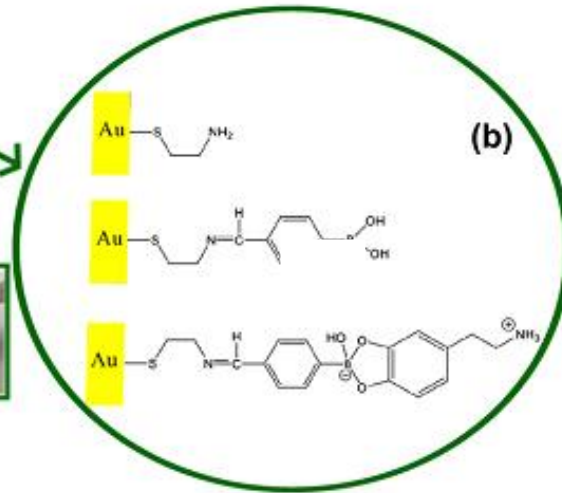
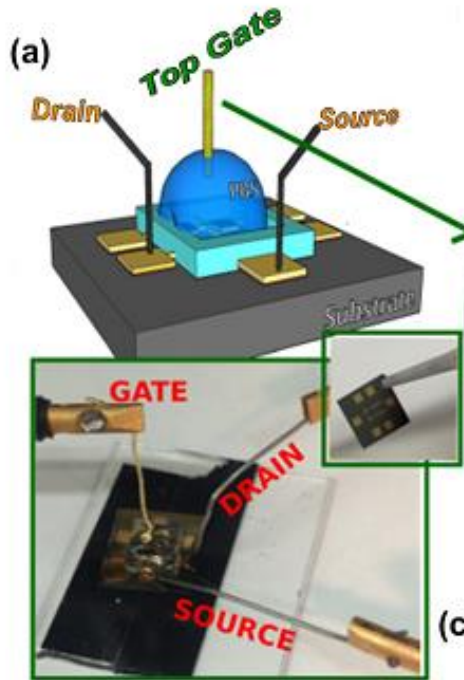
 Anti-CRP recognition element
 CRP target ligand



Ultrasensitive printable biosensors for point-of-care applications

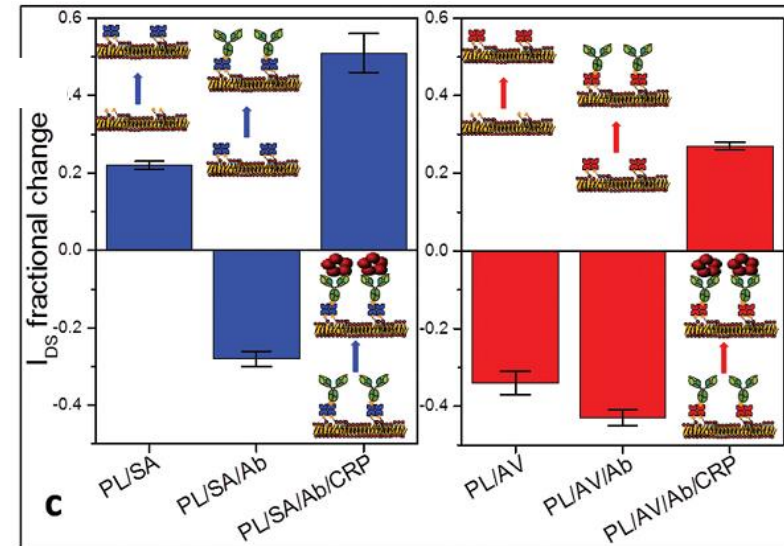
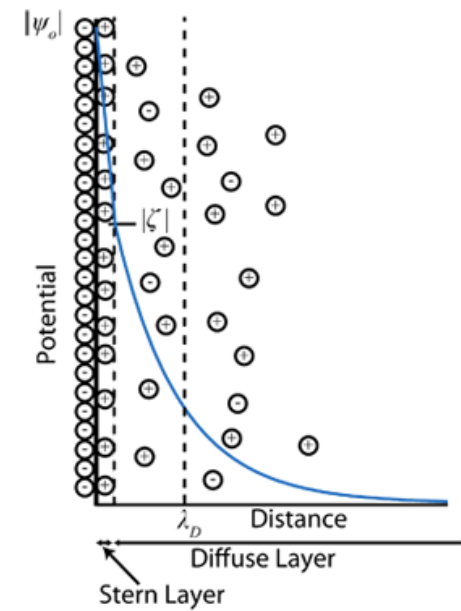
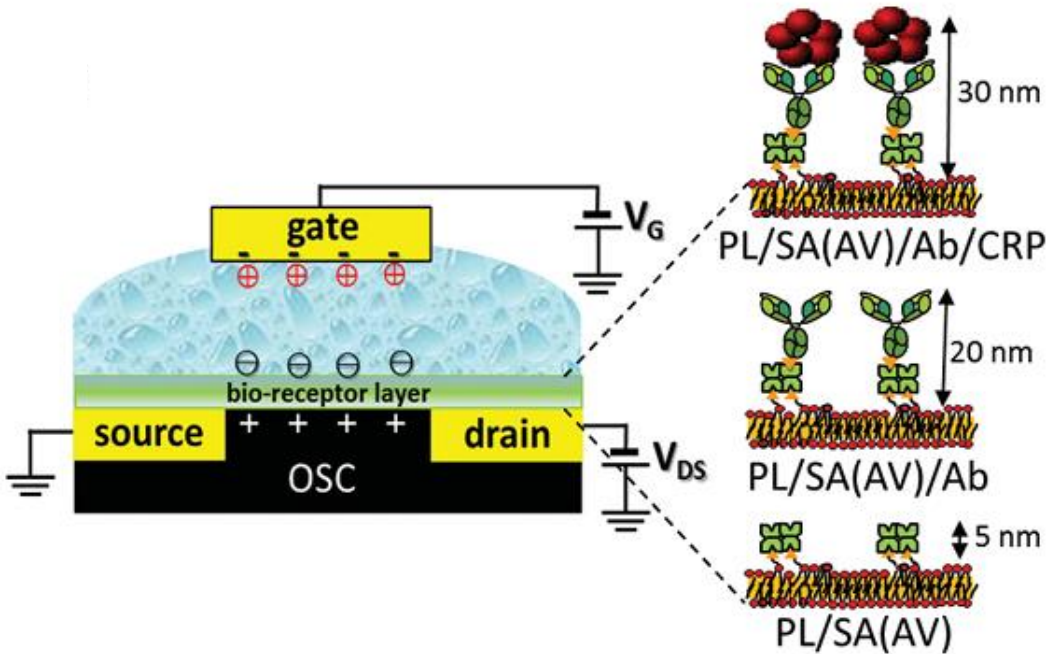
Maria Magliulo, Mohammad Yusuf Mulla, Kyriaki Manoli, Donato De Tullio, Preethi Seshadri, Gaetano Scamarcio, Gerardo Palazzo and Luisa Torsi (2012)

POC biosensors: dopamine



Organic field-effect transistor for label-free dopamine sensing
 S. Casalini, F. Leonardi, T. Cramer, F. Biscarini (2013)

Debye Length



Detection Beyond Debye's Length with an Electrolyte-Gated Organic Field-Effect Transistor

Gerardo Palazzo , * Donato De Tullio , Maria Magliulo , Antonia Mallardi , Francesca Intranuovo , Mohammad Yusuf Mulla , Pietro Favia , Inger Vikholm-Lundin , and Luisa Torsi (2015)

OCMFET: DNA hybridization

OTFT

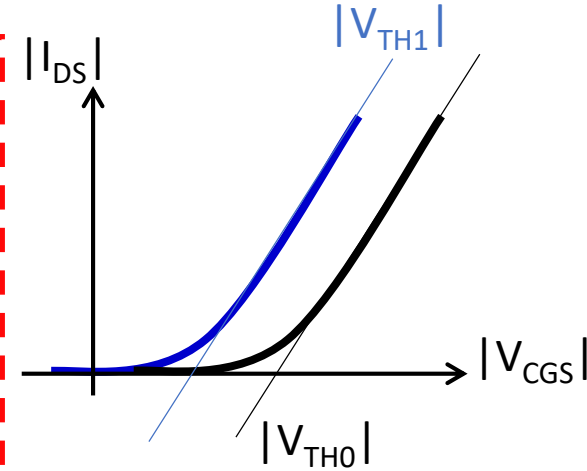
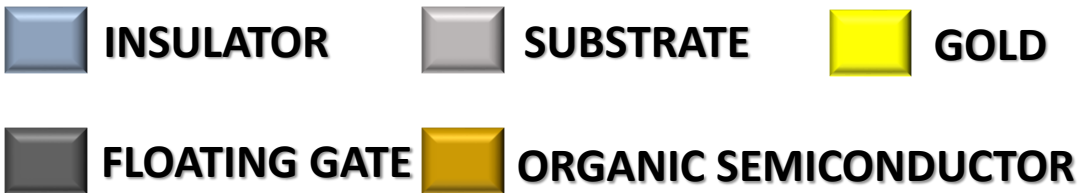
SENSING AREA

SOURCE

DRAIN

CONTROL GATE

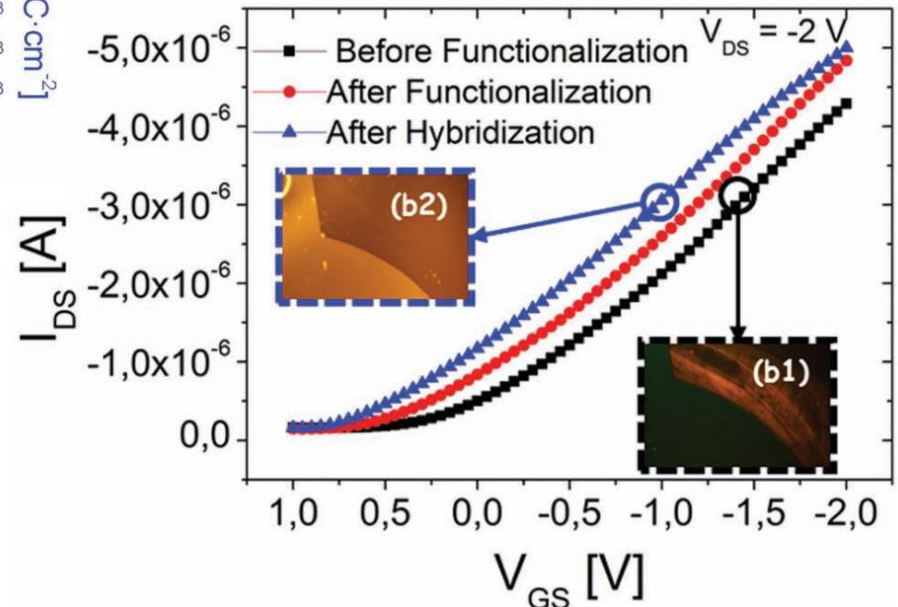
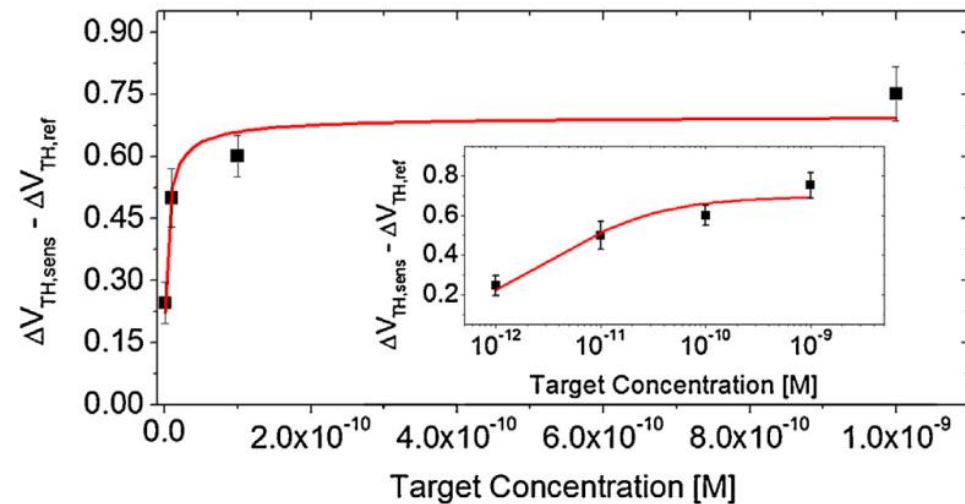
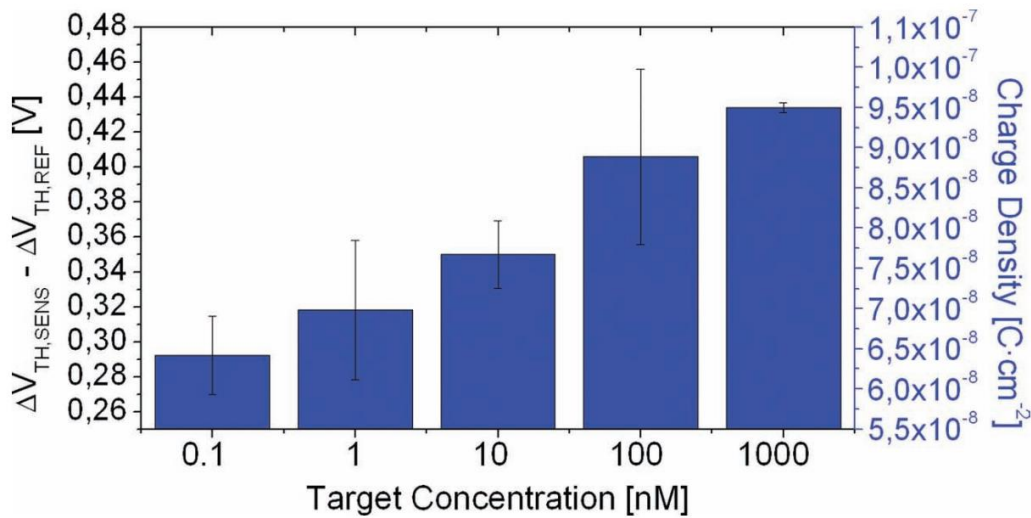
FLOATING GATE



$$\Delta V_{TH} = \frac{\Delta Q_{SENS}}{C_{CG} + C_{DF} + C_{SF}}$$

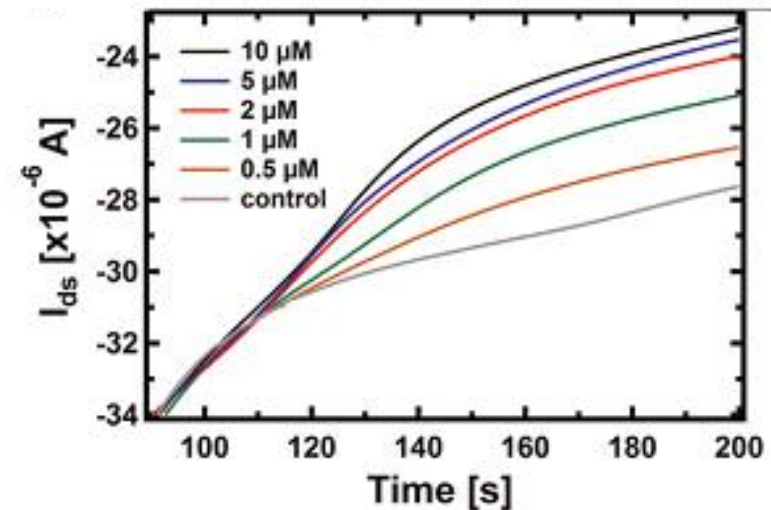
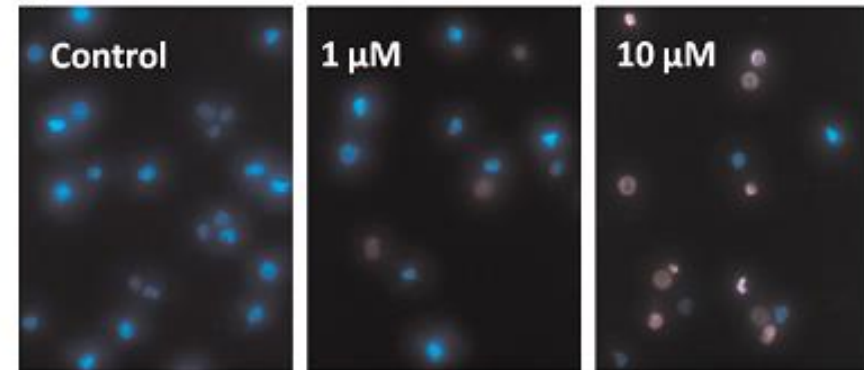
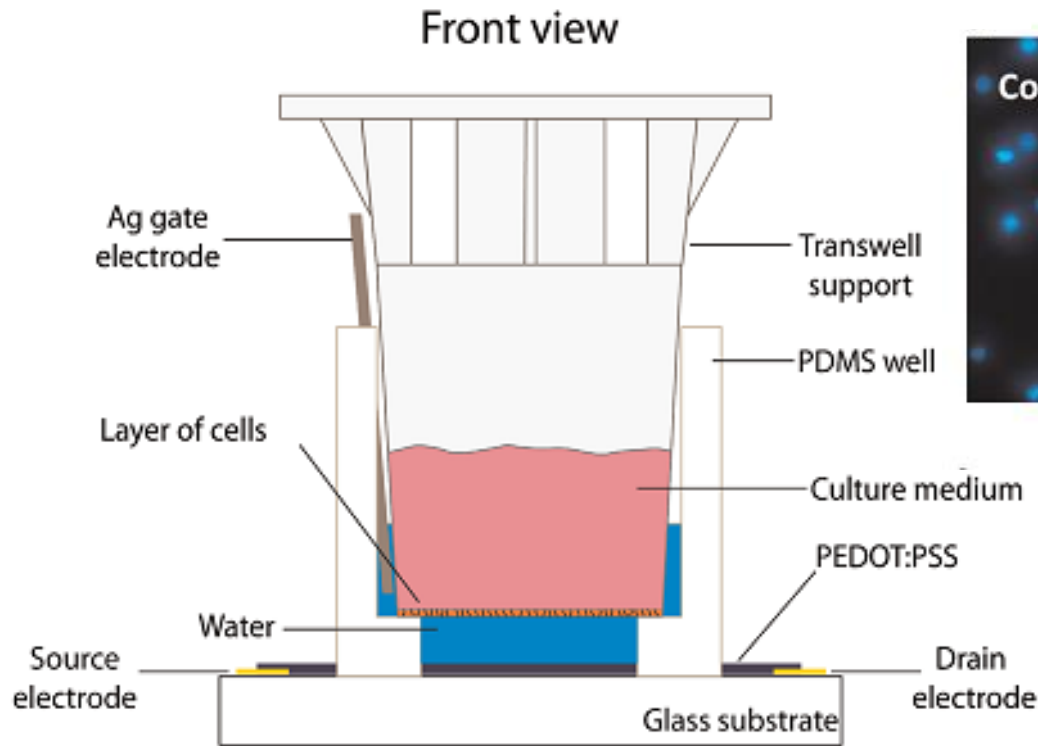
$$V_{FG} \approx \frac{C_{CG}}{C_{CG} + C_{DF} + C_{SF}} V_{CGS} + \frac{Q_{SENS}}{C_{CG} + C_{DF} + C_{SF}} + \frac{Q_0}{C_{CG} + C_{DF} + C_{SF}}$$

OCMFET: DNA hybridization



S. Lai, M. Demelas, G. Casula, P. Cosseddu, M. Barbaro, and A. Bonfiglio, **Adv. Mater.** 25, 103 (2013)

Membrane: cell death monitoring



Drug-induced cellular death dynamics monitored by a highly sensitive organic electrochemical system

Agostino Romeo, Giuseppe Tarabella, Pasquale D'Angelo, Cristina Caffarra, Daniele Cretella, Roberta Alfieri, Pier Giorgio Petronini, Salvatore Iannotta (2015)

Summary

1. (Bio)sensor figures of merit:
features, properties, issues

- Materials
- Chemical properties
- Surface functionalization

2. Transistor-based structures
sensing

- Structures: working principle
- Transduction mechanisms
- Applications
- Advantages/Disadvantages