

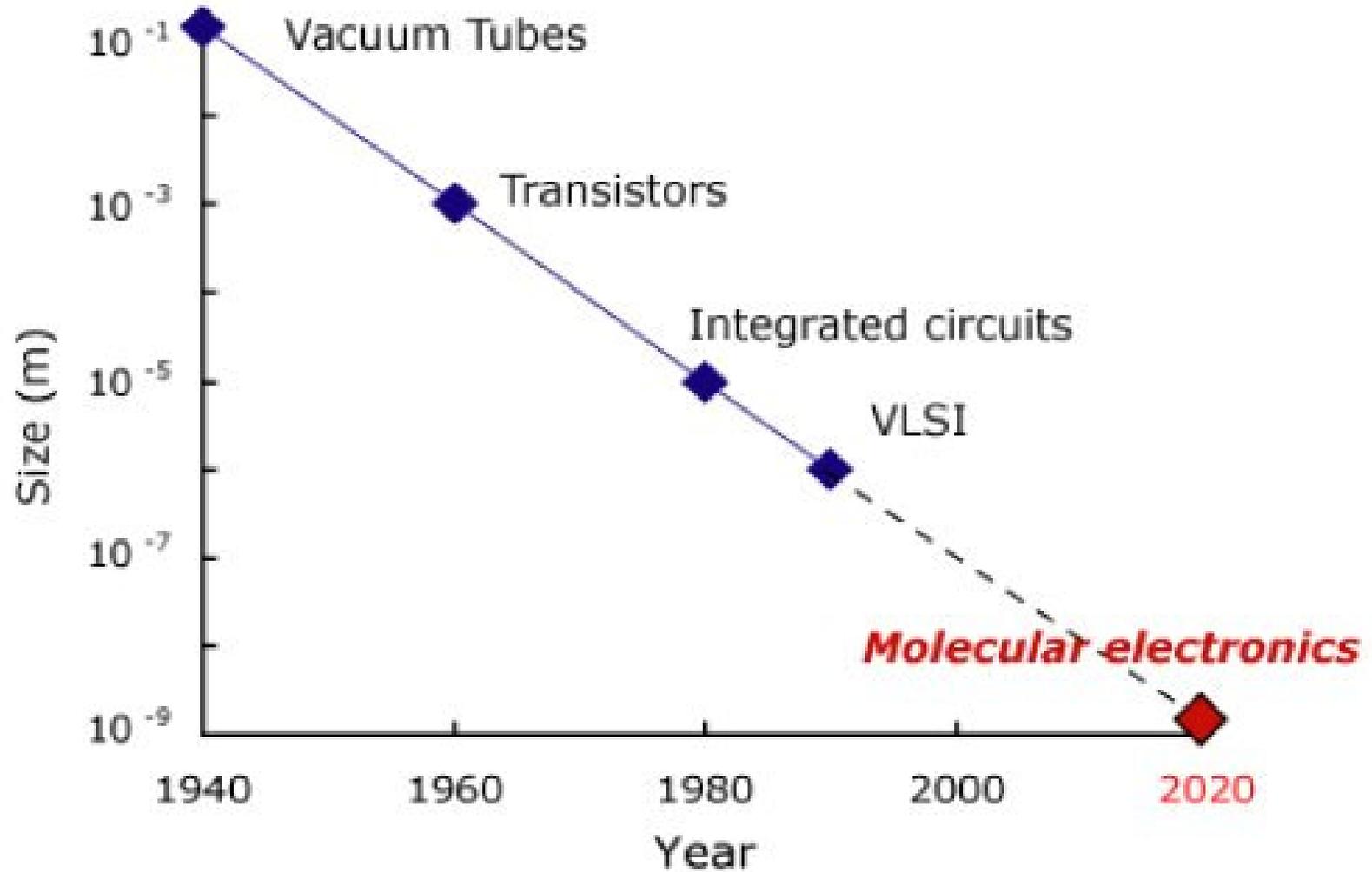
PMT 2200

Eletrônica Orgânica

Fernando Josepetti Fonseca

Depto de Eng de Sistemas Eletrônicos (PSI)

Lei de Moore



The Scale of Things – Nanometers and More



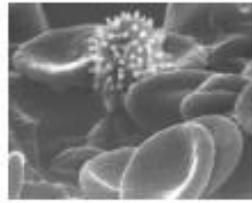
Things Natural



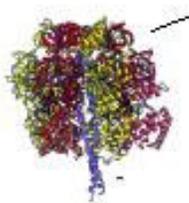
Dust mite
200 μm



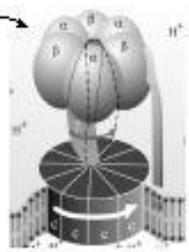
Human hair
 $\sim 60\text{-}120 \mu\text{m}$ wide



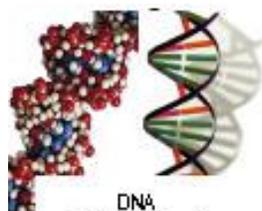
Red blood cells with white cell
 $\sim 2\text{-}5 \mu\text{m}$



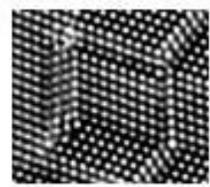
$\sim 10 \text{ nm}$ diameter



ATP synthase



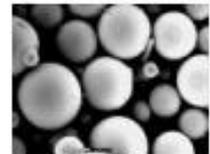
DNA
 $\sim 2\text{-}12 \text{ nm}$ diameter



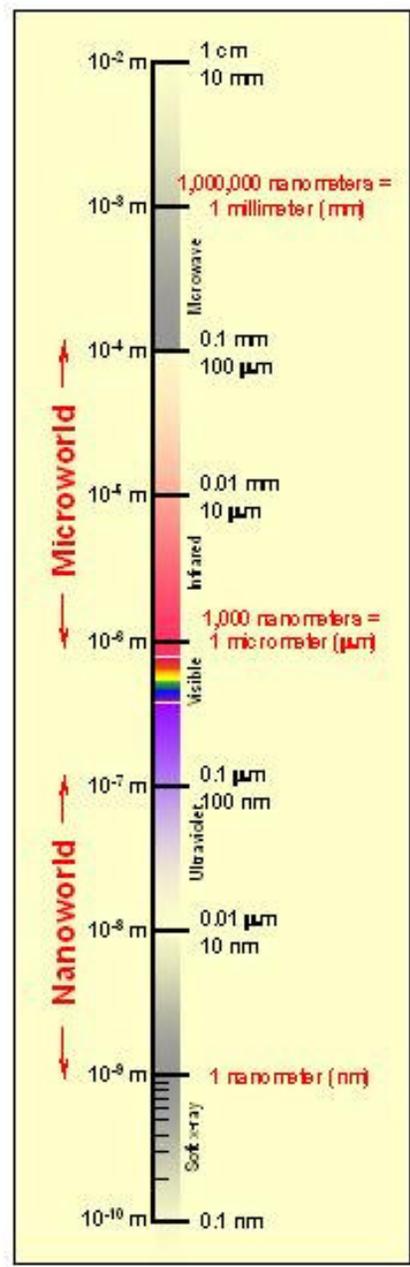
Atoms of silicon
spacing \sim tenths of nm



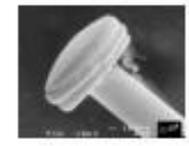
Ant
 $\sim 5 \text{ mm}$



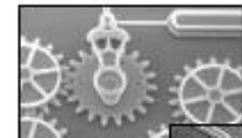
Fly ash
 $\sim 10\text{-}20 \mu\text{m}$



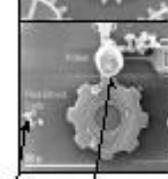
Things Manmade



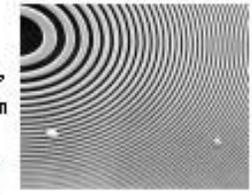
Head of a pin
1-2 mm



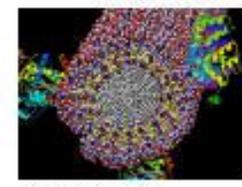
Micro Electro Mechanical (MEMS) devices
10 - 100 μm wide



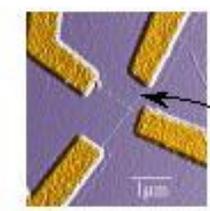
Pollen grain
Red blood cells



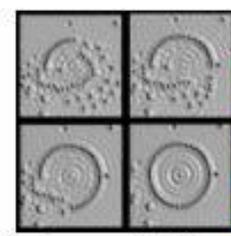
Zone plate x-ray "lens"
Outer ring spacing $\sim 35 \text{ nm}$



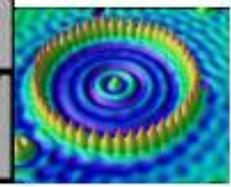
Self-assembled, Nature-inspired structure
Many 10s of nm



Nanotube electrode



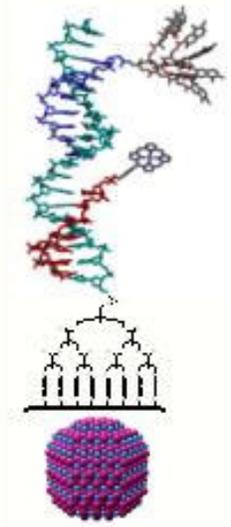
Quantum corral of 48 iron atoms on copper surface
positioned one at a time with an STM tip
Conal diameter 14nm



Carbon nanotube
 $\sim 1.3 \text{ nm}$ diameter

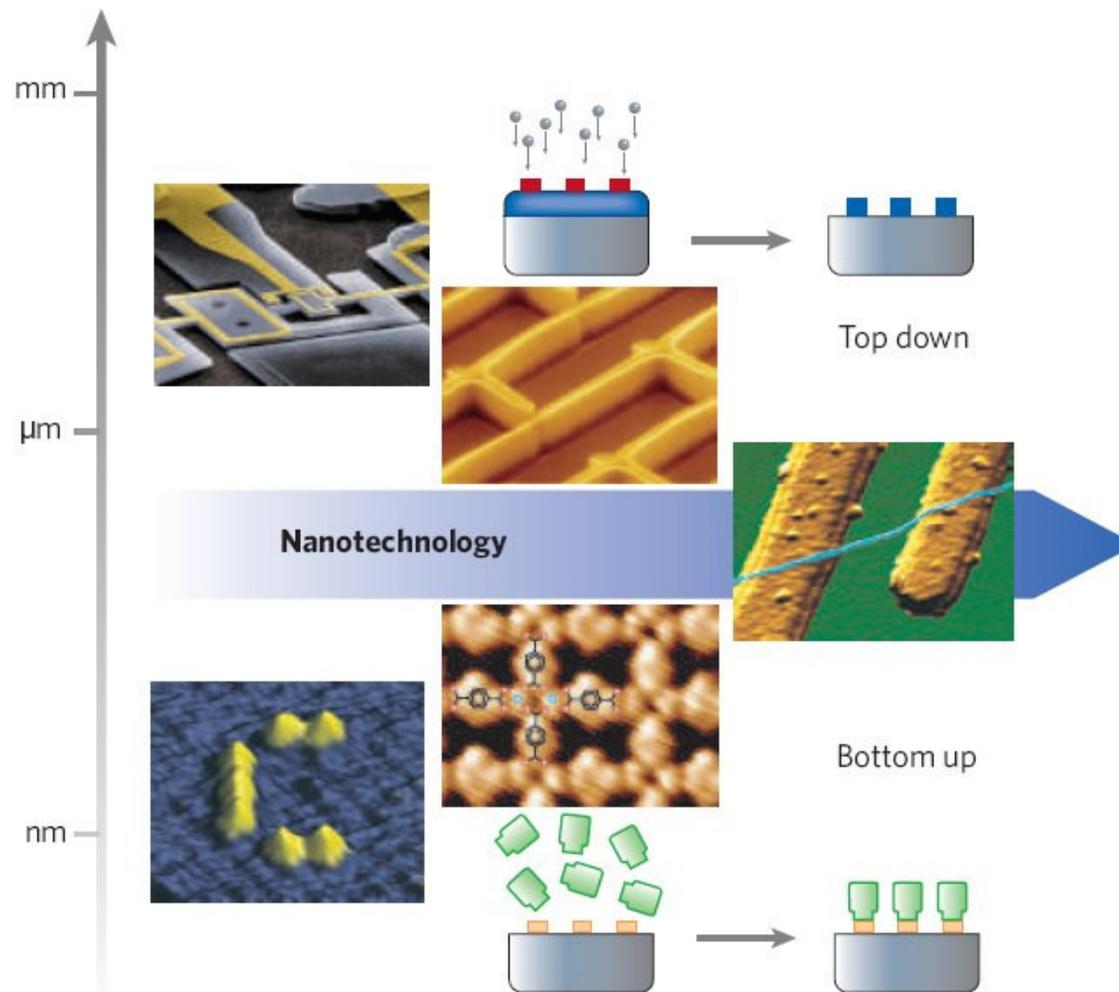
Carbon buckyball
 $\sim 1 \text{ nm}$ diameter

The Challenge



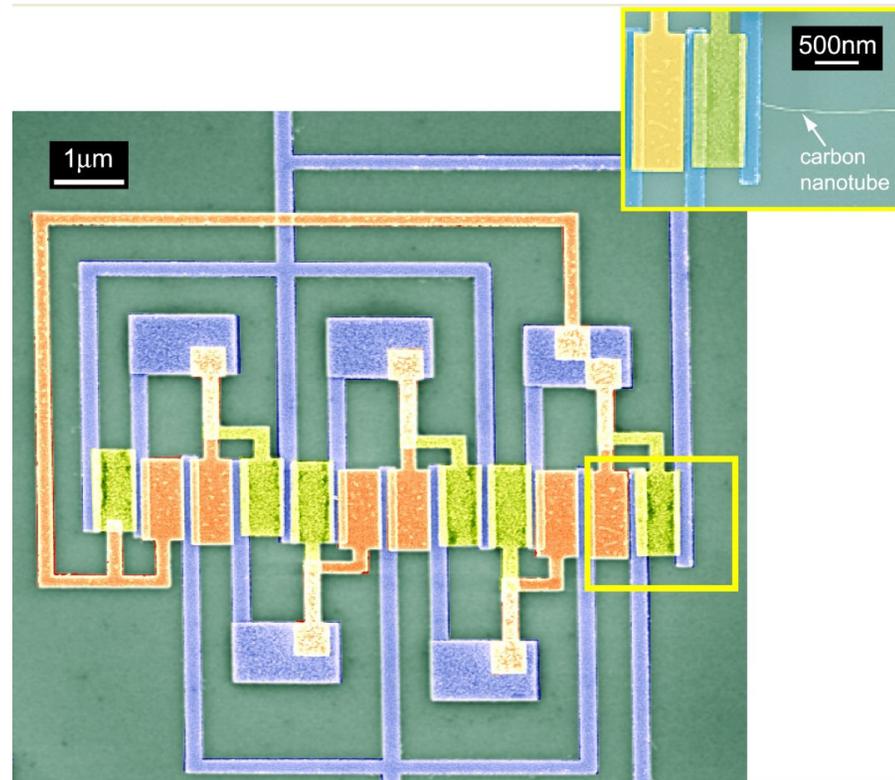
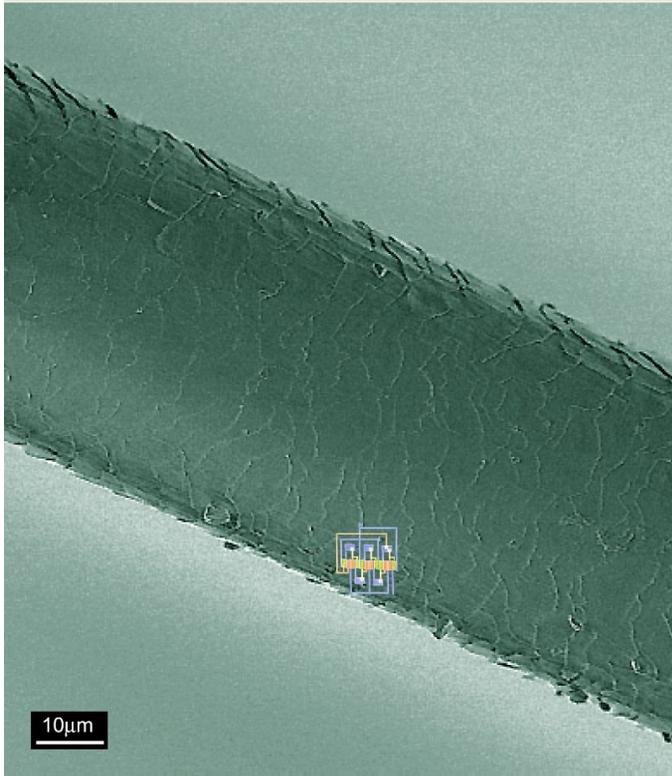
Fabricate and combine nanoscale building blocks to make useful devices, e.g., a photosynthetic reaction center with integral semiconductor storage.

Top-down x Bottom-up ?



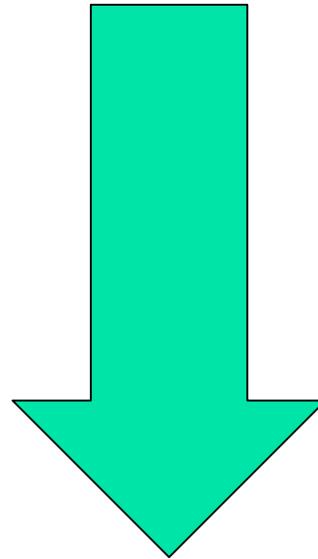
Nanotubos de Carbono

(CNT = Carbon NanoTube)



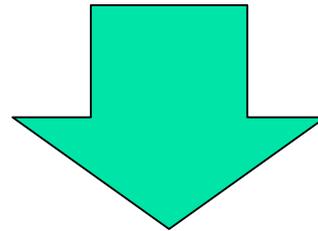
Source: IBM

Como continuar a fabricar dispositivos cada vez menores?

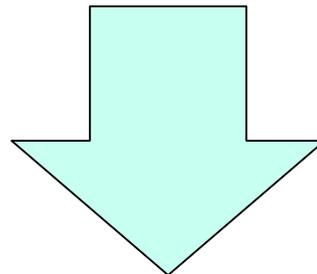


Eletrônica Molecular

Como continuar a fabricar dispositivos cada vez menores?



Eletrônica Orgânica



Eletrônica Molecular

Eletrônica Orgânica

Nova oportunidade para a fabricação de dispositivos eletrônicos de filmes finos.

Os materiais orgânicos conjugados podem apresentar características condutoras, semicondutoras e optoeletrônicas muito interessantes.

Com condições de processamento muito mais fáceis e baratas para serem utilizadas.

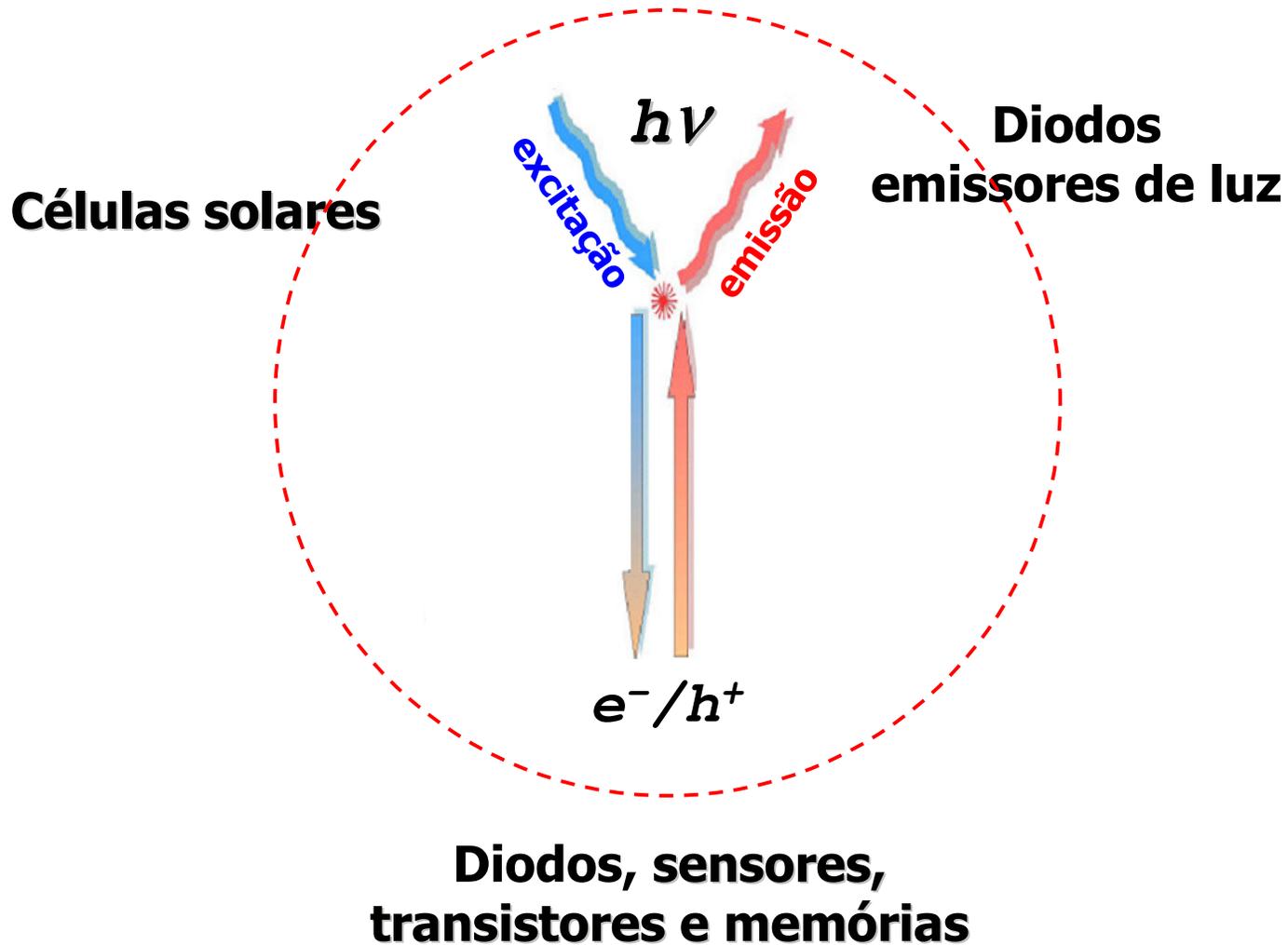
Possuem também a vantagens de serem processadas

- à temperatura ambiente,
- com maior velocidade,
- com custos potencialmente menores.

Aplicações da Eletrônica Orgânica

- As principais aplicações desenvolvidas são:
 - *Organic light emitting diodes (OLED)*
 - *Organic thin-film transistors (OTFT)*
 - *Organic photovoltaics (OPV)*
- Além de
 - *Sensores*
 - *Memórias*
 - *RFID*

Eletrônica Orgânica



Mercado de LEDs

iSuppli
Applied Market Intelligence

iLibrary Login

Who

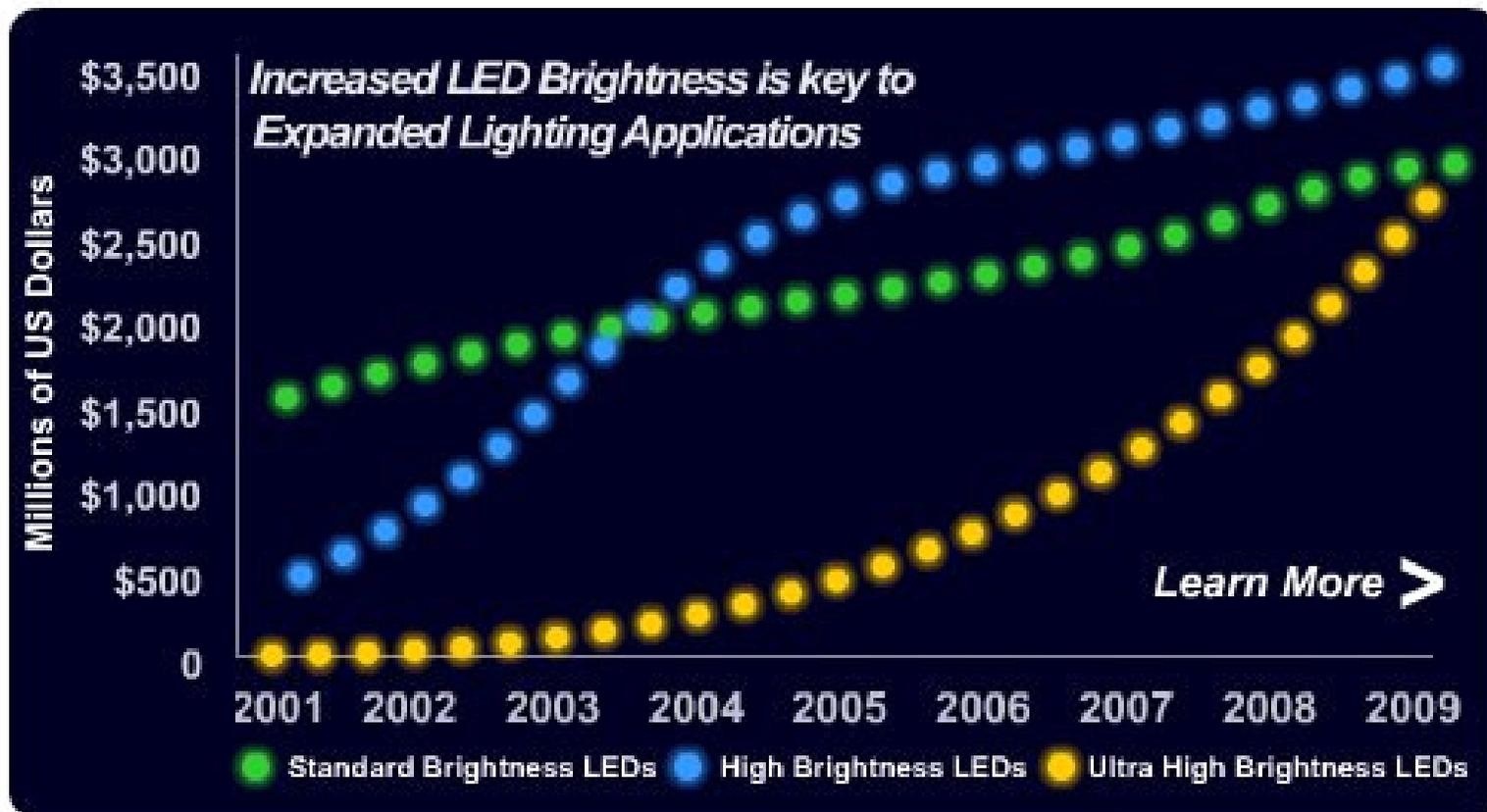
Products

Analysts

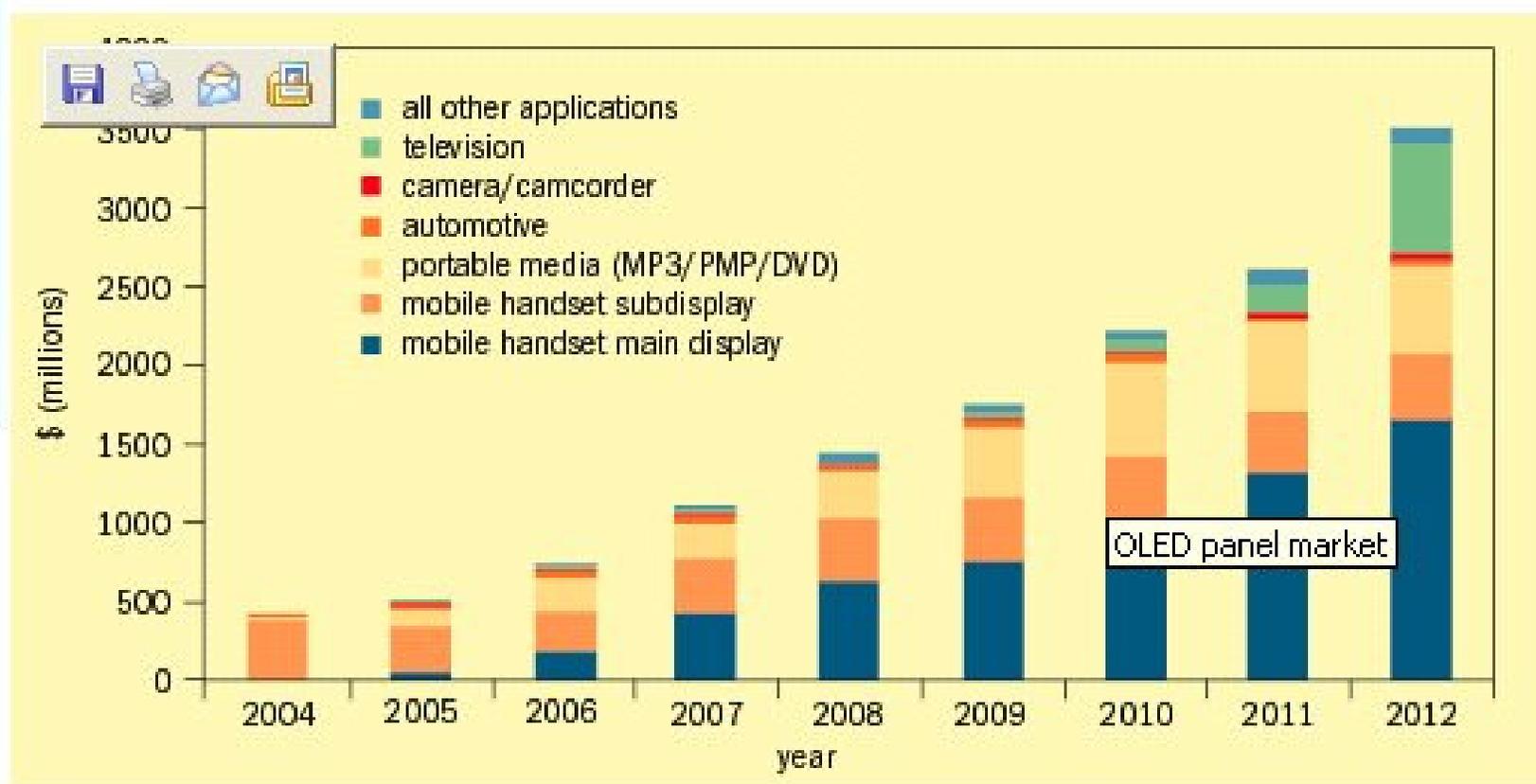
Events

News

A



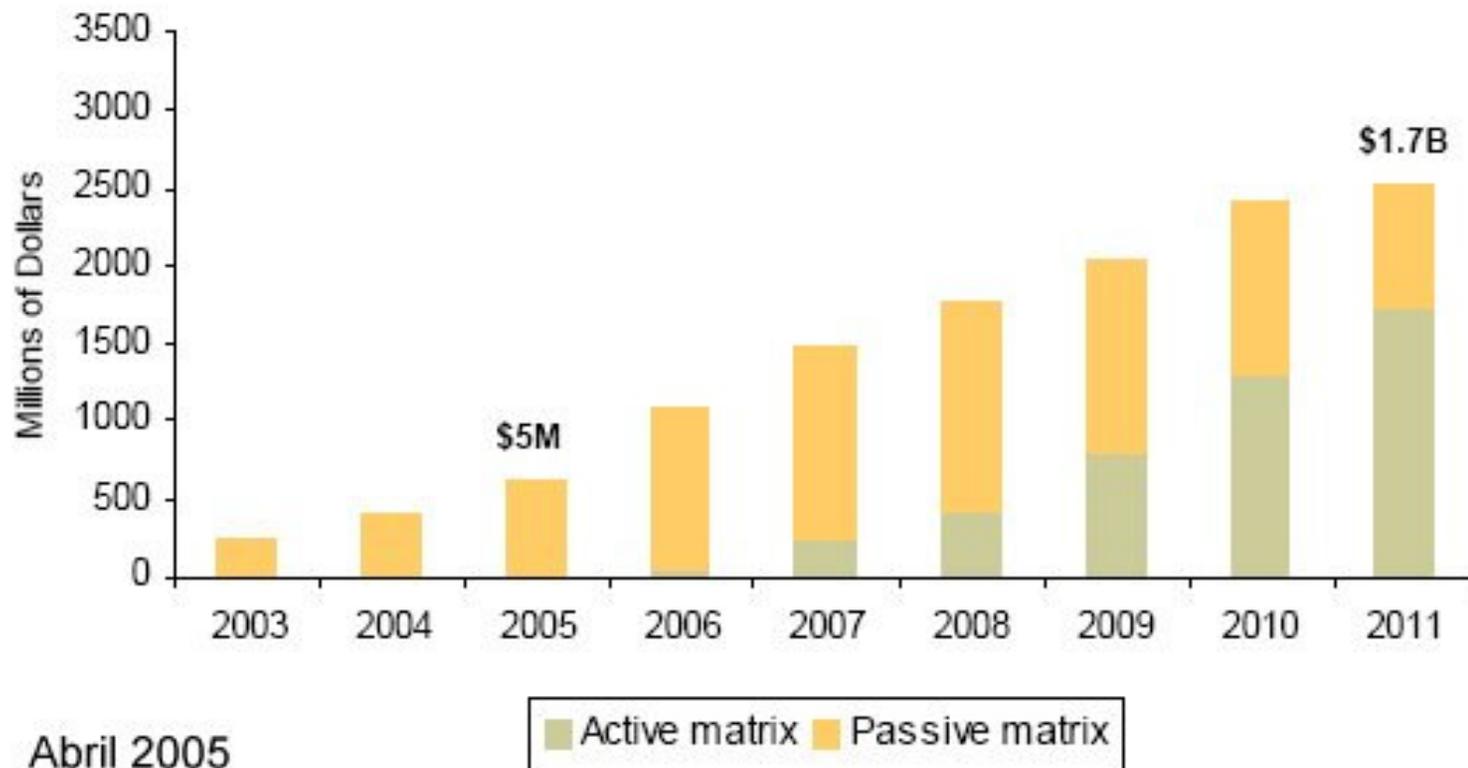
Mercado de OLEDs



Worldwide OLED panel market, 2004-2012: TV could take off around 2010 if backed by major players. Image: iSuppli Corp, Organic Light-Emitting Diode Displays, 1H 2006

Active x Passive Matrix OLEDs

AMOLED: A Whisper to a Roar



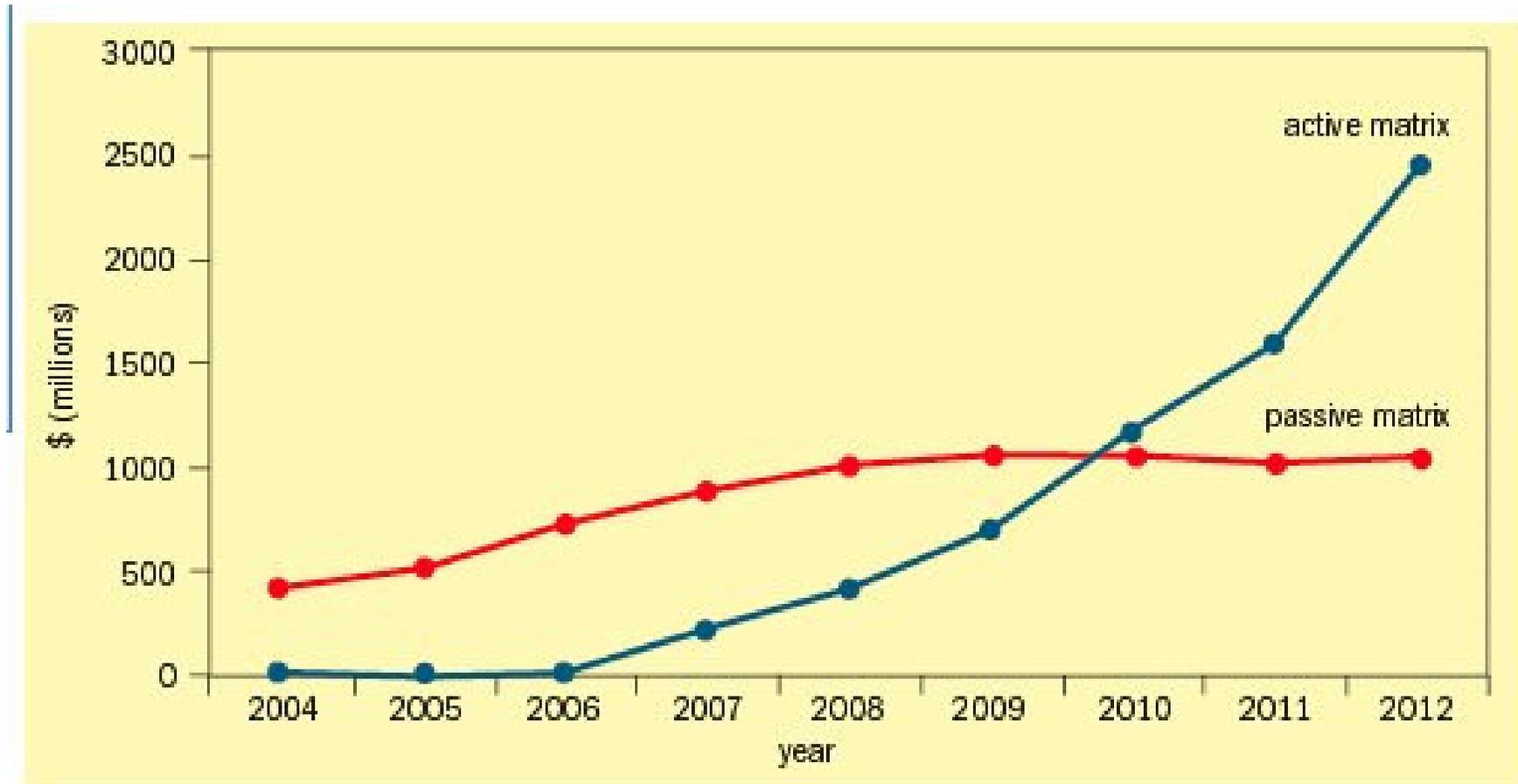
Abril 2005

iSuppli

Emerging Display Technologies

By Kimberly Allen, Ph.D., Director of Strategic Display Research

Mercado de OLEDs



The growth of the OLED market depends heavily on the success of active matrix OLED technology. Image: iSuppli Corp, Organic Light-Emitting Diode Displays, 1H 2006

Desejamos fabricar displays
finos, leves e flexíveis



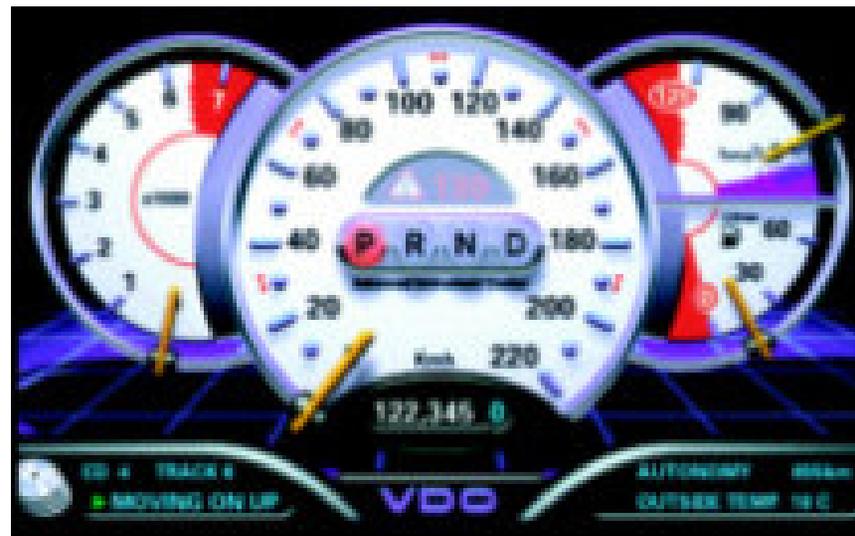
**Tela retrátil,
flexível e/ou
dobrável**



**Tela
Retrátil**

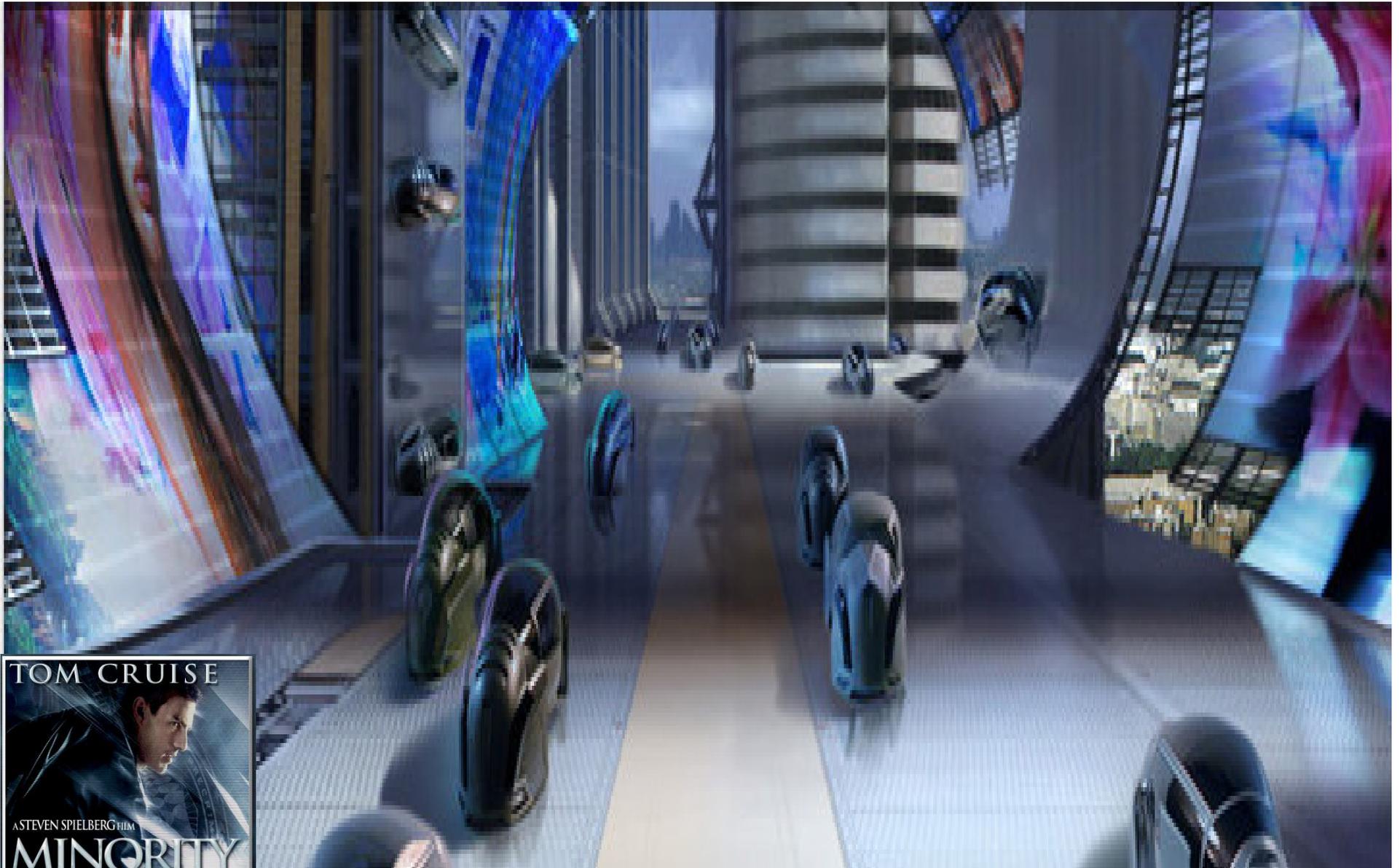


Aplicação: Indústria automobilística



Painel
Automotivo

Motivação: Painéis grandes, externos e flexíveis



Aplicações de OLED

TV OLED Sony 11"
dez 2007
US\$ 2.500,00

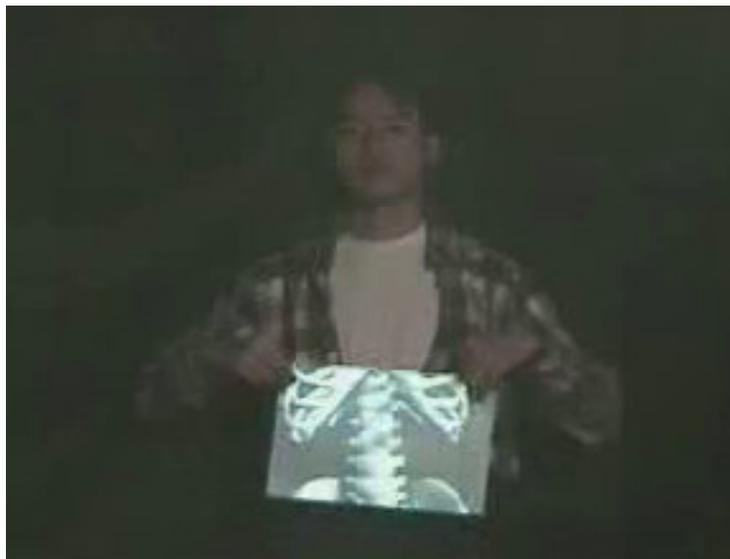


Motivação: Entretenimento



Brinquedos
e cartões

Motivação: Inovação tecnológica



Jaqueta Invisível, *Isto É* 1741,
Fev 2003

Como tudo começou?

1977: o nascimento dos polímeros eletrônicos

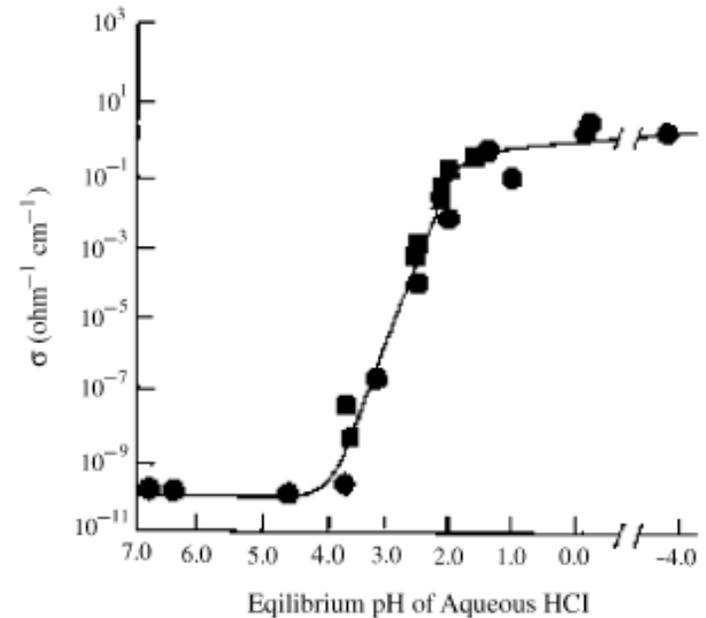
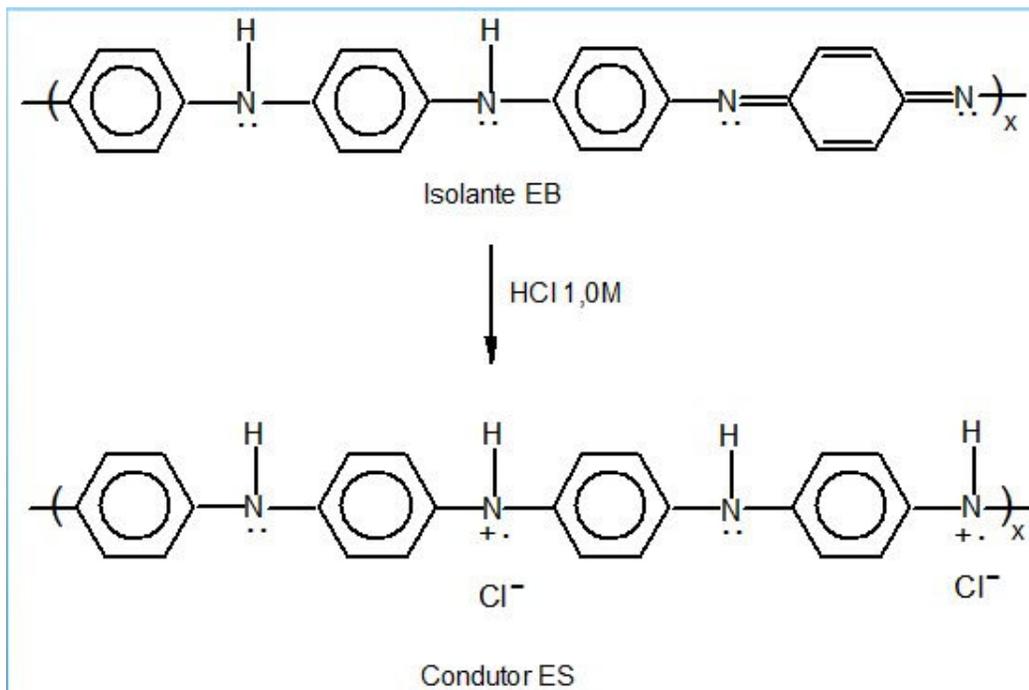


2000 - Prêmio Nobel em Química
(A. J. Heeger, H. Shirakawa e A. G. MacDiarmid)

***"for the discovery and development of conductive
polymers"***

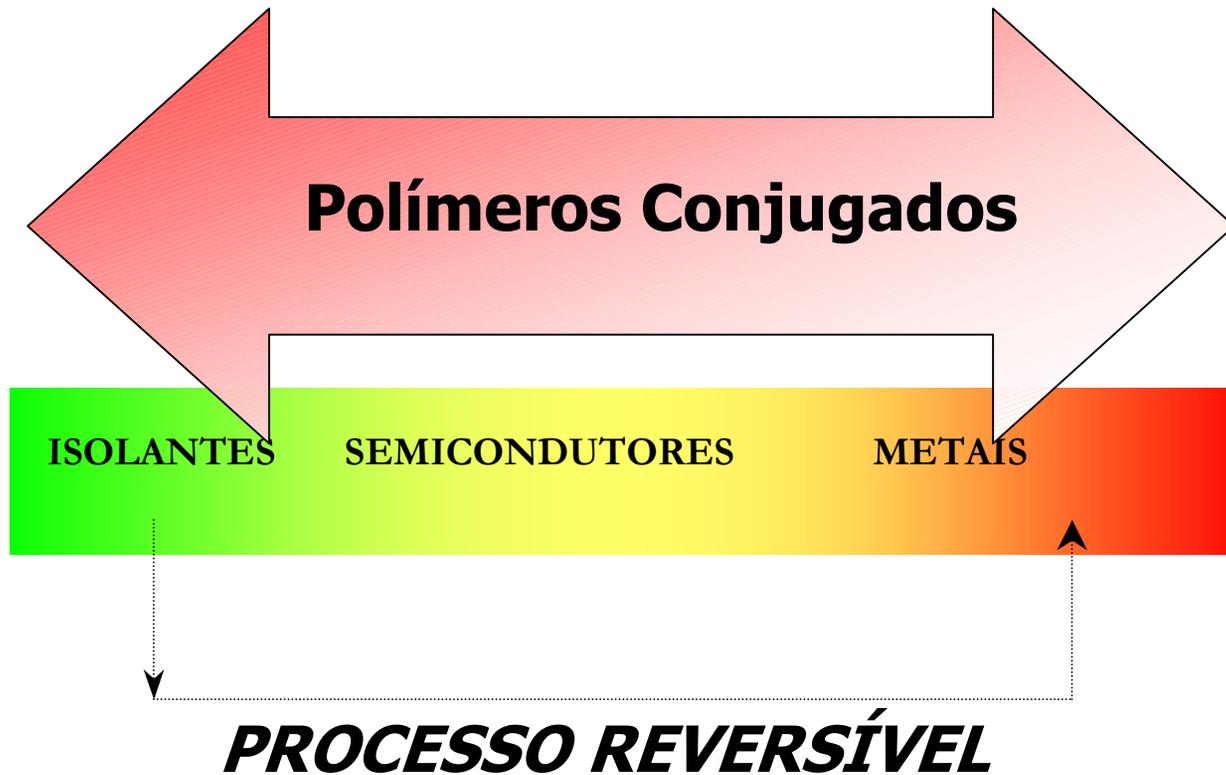
Polímeros condutores

Materiais cuja condutividade elétrica depende das características físico-químicas do ambiente que os cerca
→ transdutores em sensores químicos

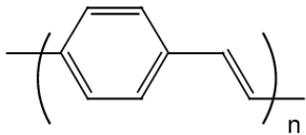


A condutividade depende do meio e é reversível!

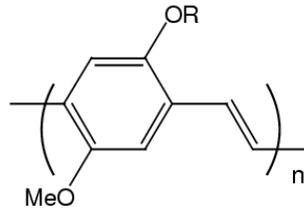
Propriedades Inovadoras



Alguns Polímeros conjugados

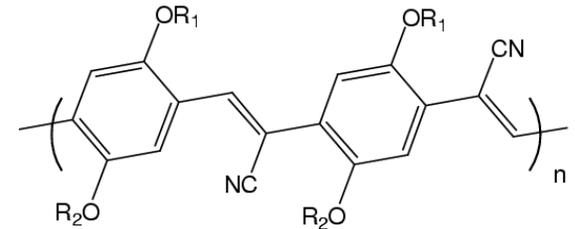


PPV

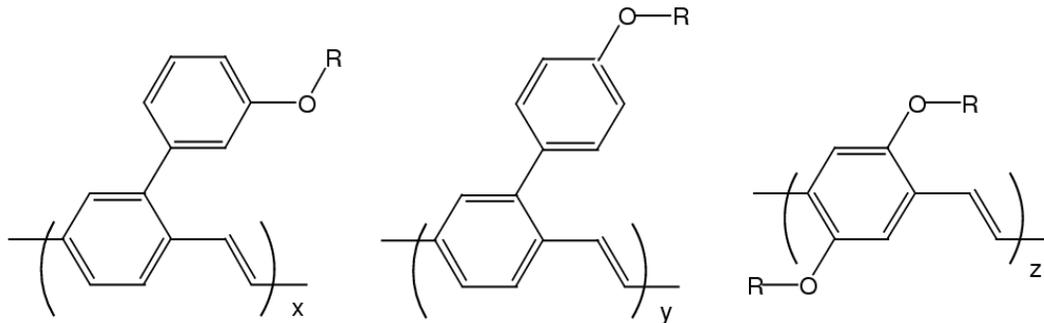


MEH-PPV $R = \text{CH}_2\text{CH}(\text{Et})\text{Bu}$
 "OC₁C₁₀" PPV $R = (\text{CH}_2)_3\text{CH}(\text{Me})(\text{CH}_2)_2\text{CHMe}_2$

Soluble PPV's

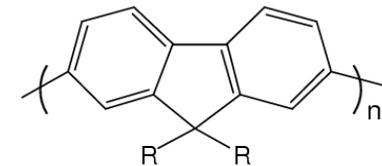


Cyano-PPV



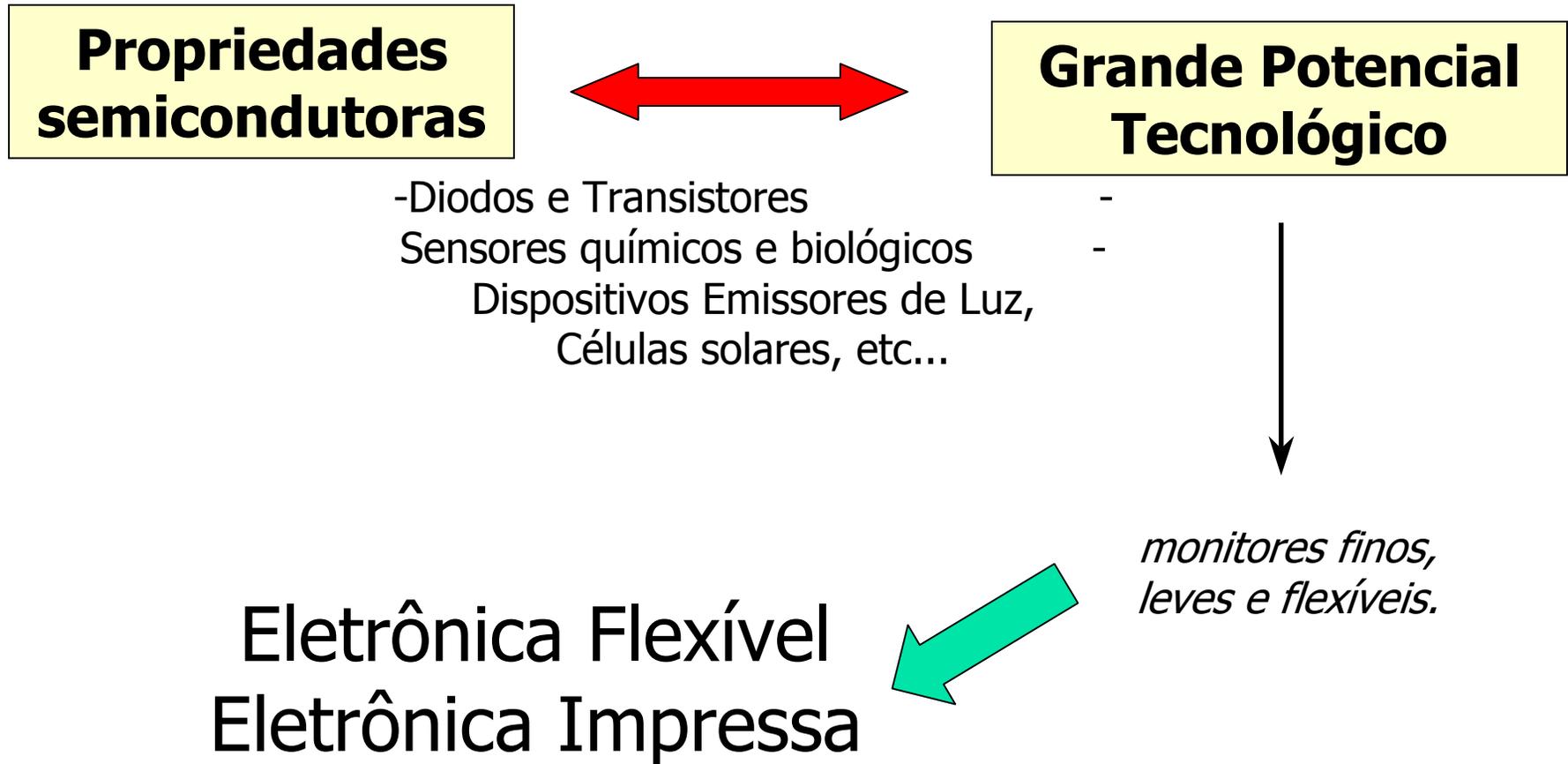
$R = (\text{CH}_2)_3\text{CH}(\text{Me})(\text{CH}_2)_2\text{CHMe}_2$

Hoechst/Aventis/Covion PPV co-polymers



Polyfluorene

Novos horizontes:



Equipamentos flexíveis!!!!

Lap Top



TV

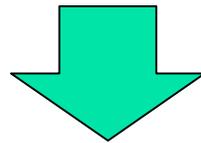
Vantagens “potenciais”

Baixo custo e *fácil preparação*

Baixo consumo de energia

Grandes áreas de emissão

Flexibilidade / Espessura



Nova tecnologia

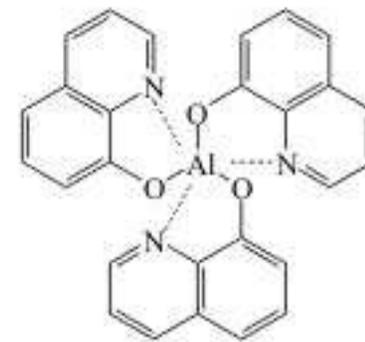
Dispositivos de camadas finas de pequenas moléculas orgânicas ou polímeros conjugados

Primeira demonstração de LED com pequena molécula orgânica

(camadas preparadas por evaporação térmica)

C.W. Tang, S.A. Vanslyke, Appl. Phys. Lett. 51 (1987) 913

Alq₃ = tris(8-hydroxyquinoline) aluminum (III)



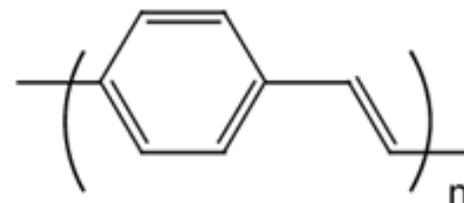
Primeira demonstração de eletroluminescencia de um polímero conjugado

(camadas preparadas por *spin-coating*)

J.H. Burroughes et al., Nature 347 (1990) 539

Patente USA 5.247.190

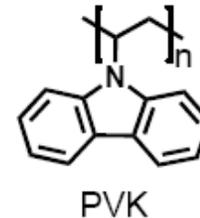
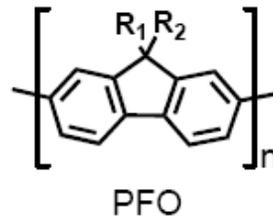
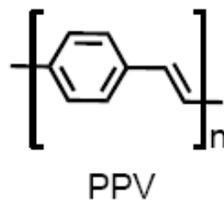
PPV = poly(para-phenylene vinylene)



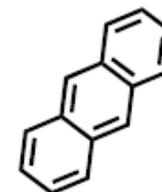
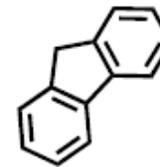
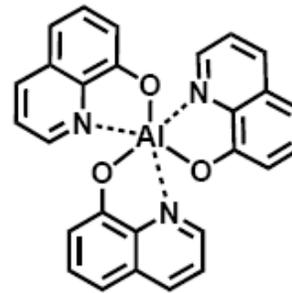
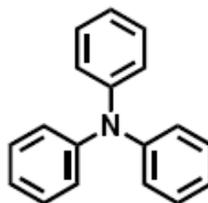
Tipos de OLEDs

Atualmente, os tipos mais usuais de OLEDs são os poliméricos (PLEDs) e as pequenas moléculas organometálicas (OLEDs)

Polymer
PLEDs



Organic
OLEDs



O primeiro produto comercial usando um polímero luminescente
(PLED monocromático)



**Norelco 8894XL Spectra
"James Bond's Shaver of
Choice" with Polymer
Display**

\$179.99

Lançado em 2002

Primeiro produto utilizando display de OLED

OLED

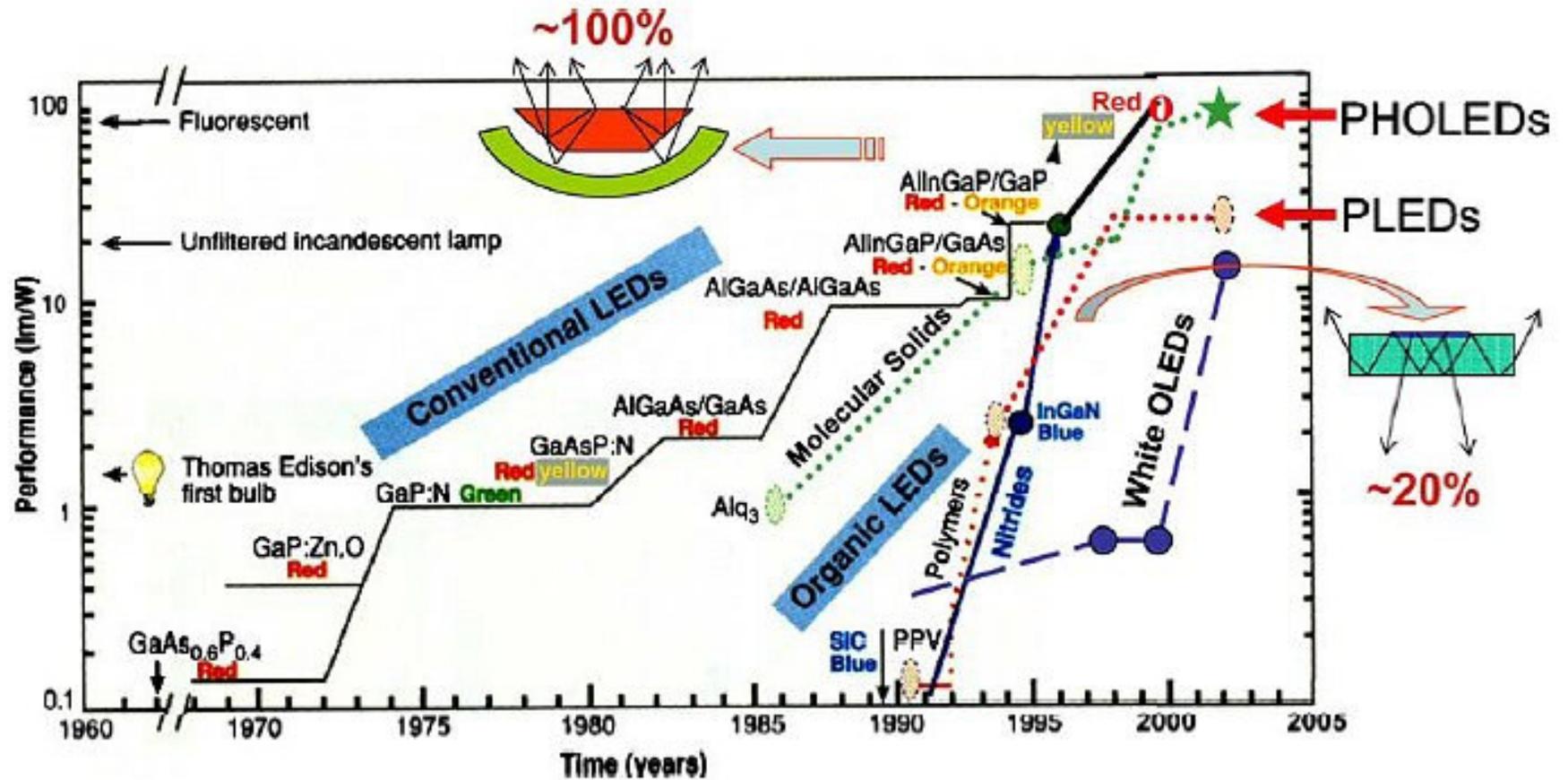
Organic Light-Emitting Diodes



- Baixo consumo
- Alta Resolução
- Custo de Produção competitivo
- **Limitação** 15" de diâmetro

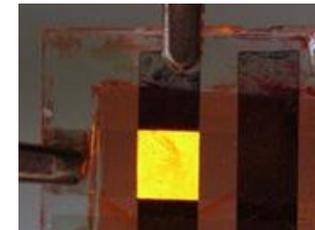
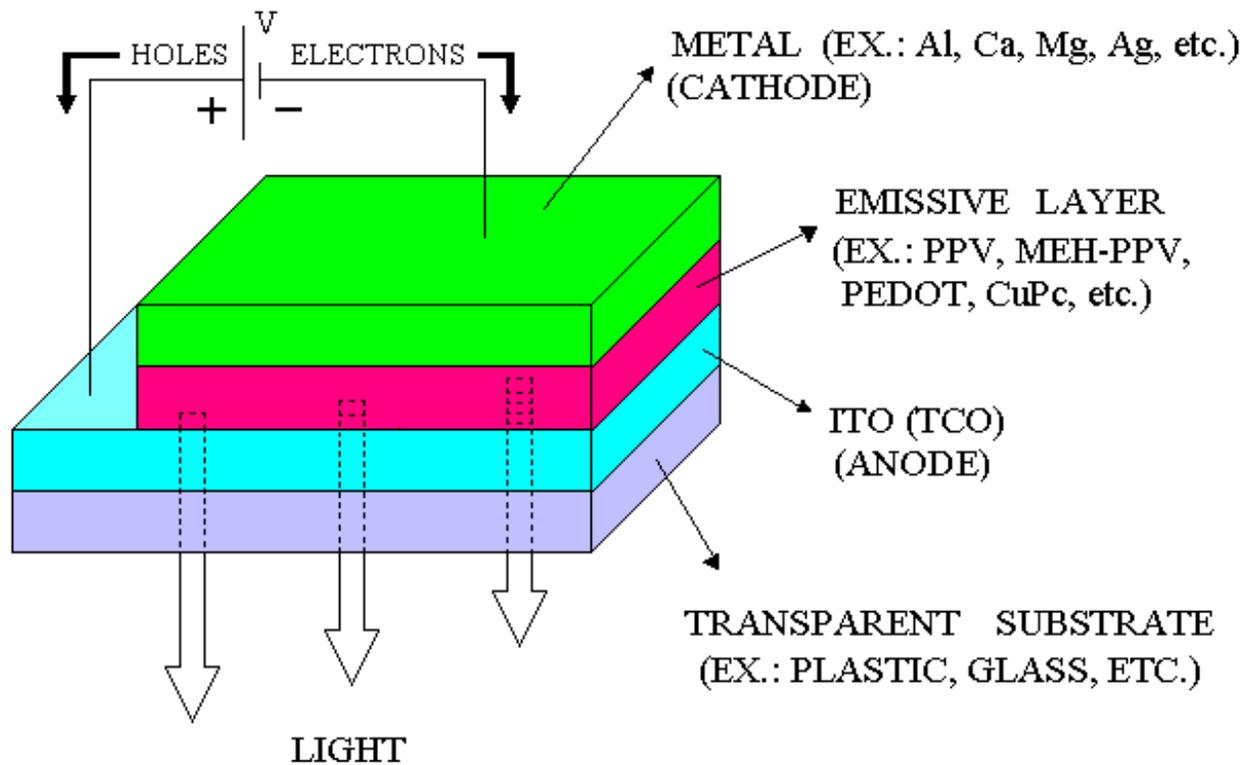
Lançamento KODAK 2003 !

Progresso do desempenho dos LEDs orgânicos e inorgânicos nos últimos 45 anos

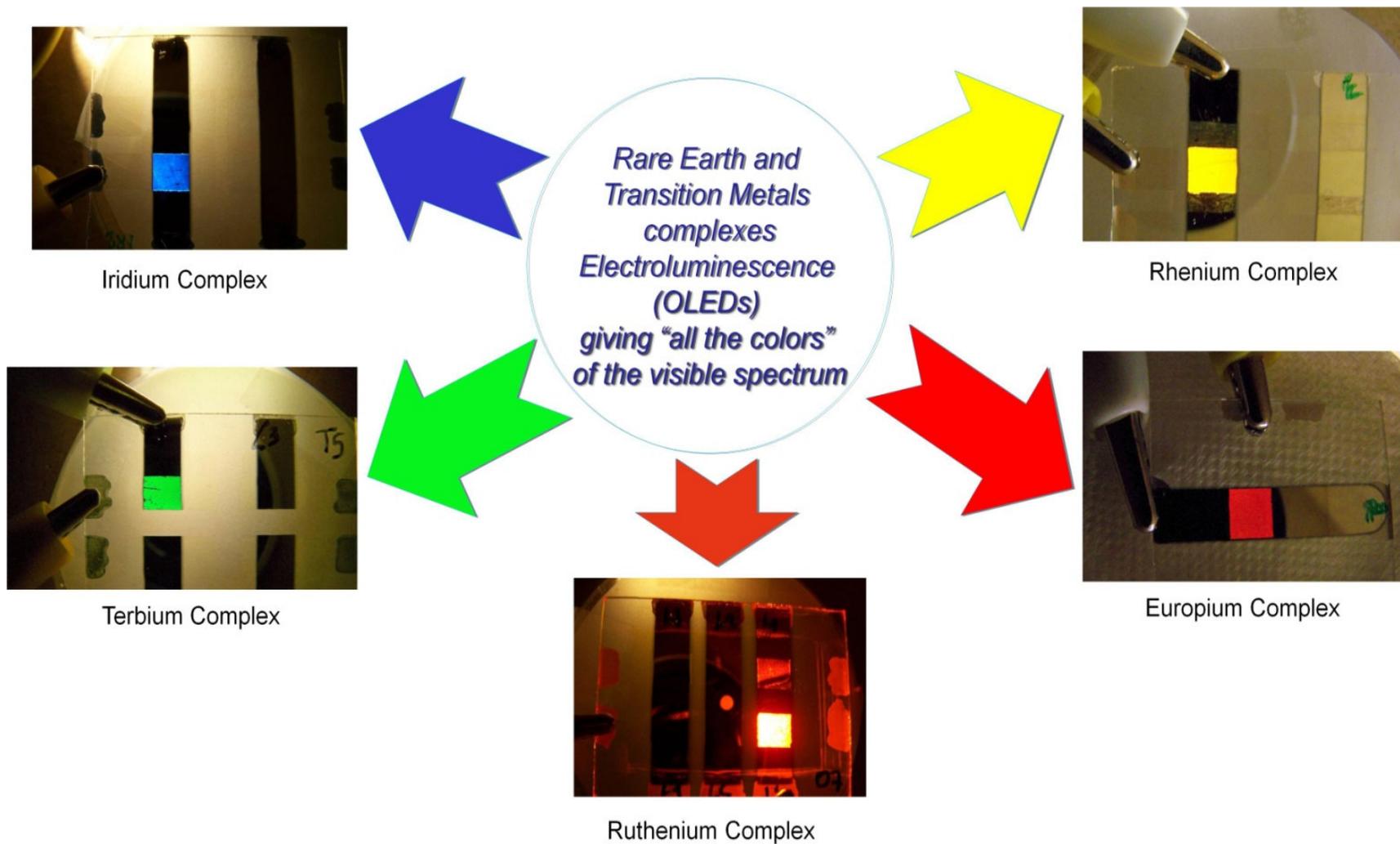


Fonte: Stephen R. Forrest, The road to high efficiency organic light emitting devices, *Organic Electronics*, 4, p. 45-48, 2003.

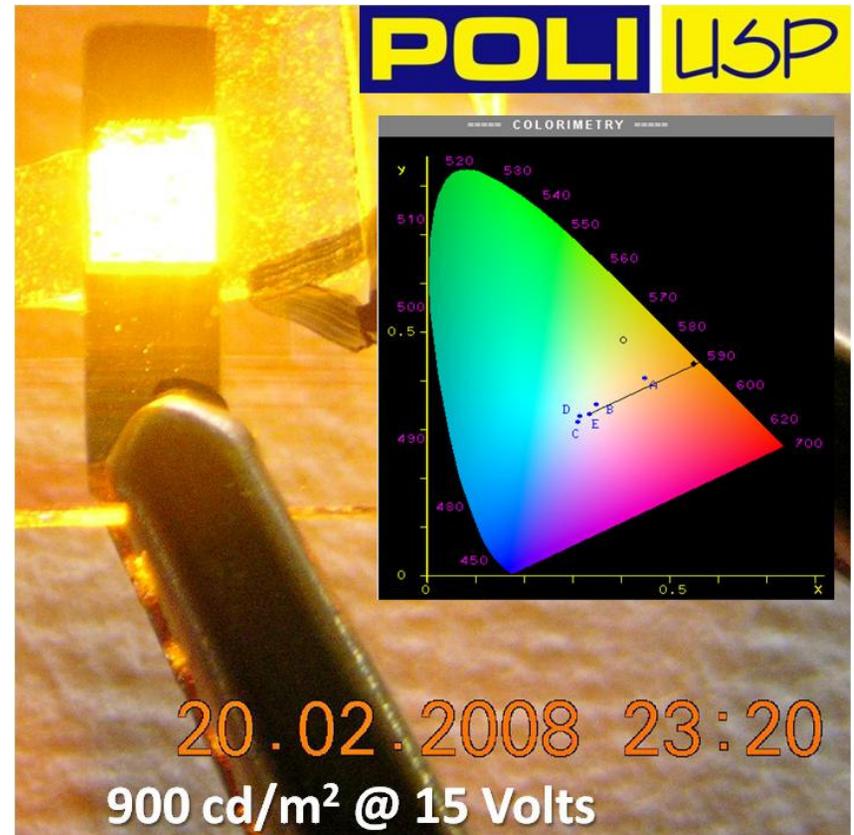
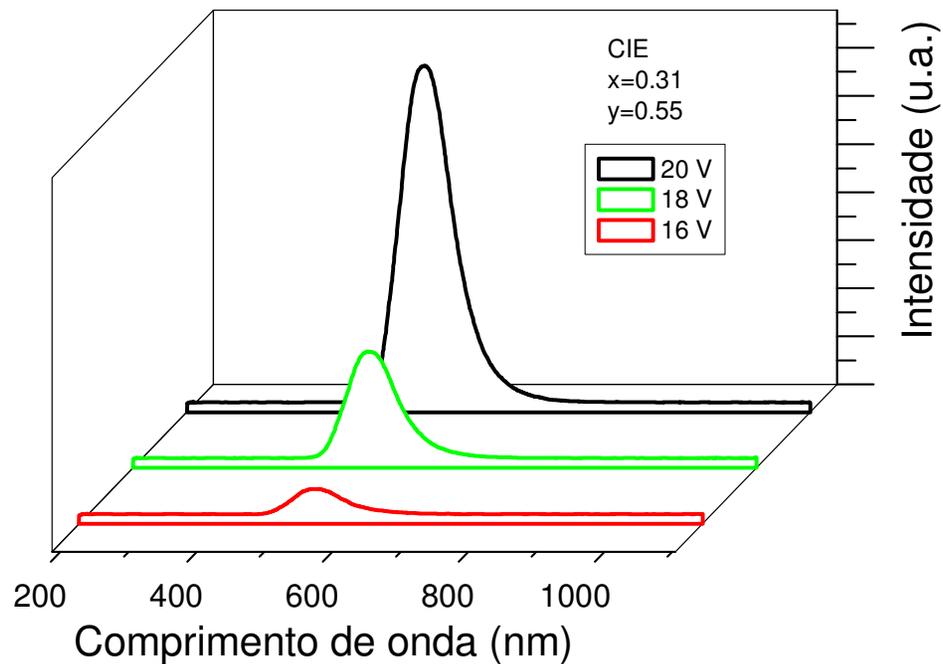
Polymeric Light-Emitting Diodes (PLED)



PLEDs, OLEDs e LECs

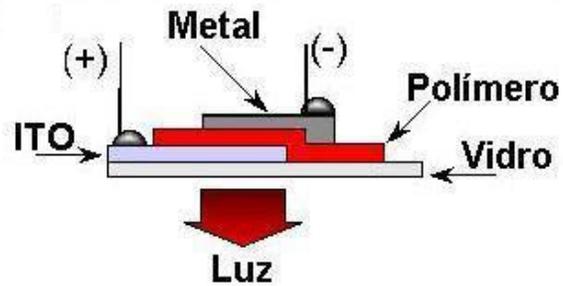


Caracterização Óptica



H. Gimaiel, G. Santos, E. T. A. Dirani, F. J. Fonseca,
e A. M. Andrade

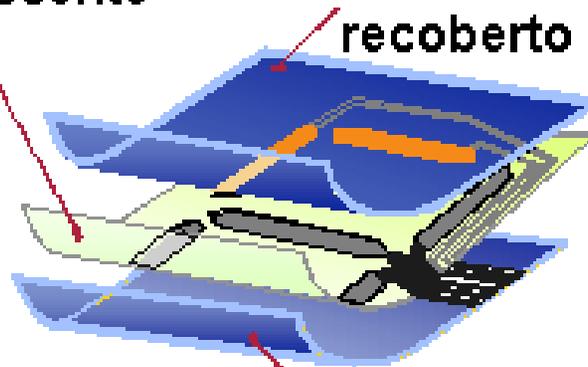
Fabricação de dispositivos



Dispositivo típico

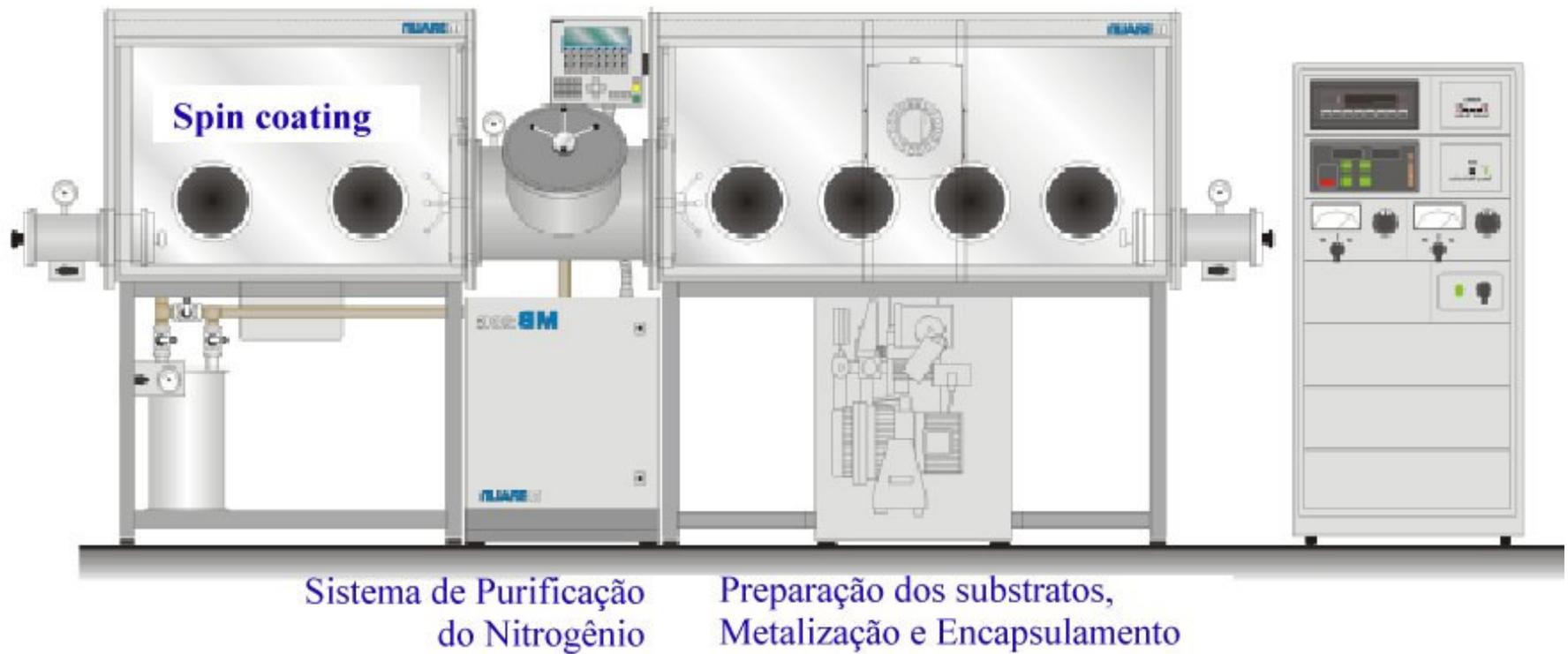
Polímero Luminescente e metalização

Filme Polimérico Flexível recoberto com ITO



Filme Polimérico Protetor

Fabricação de *displays*



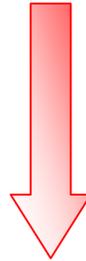
Infraestrutura

Glove Box com atmosfera controlada com spinner e evaporadora



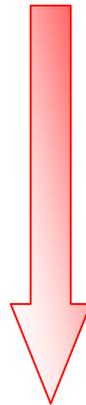
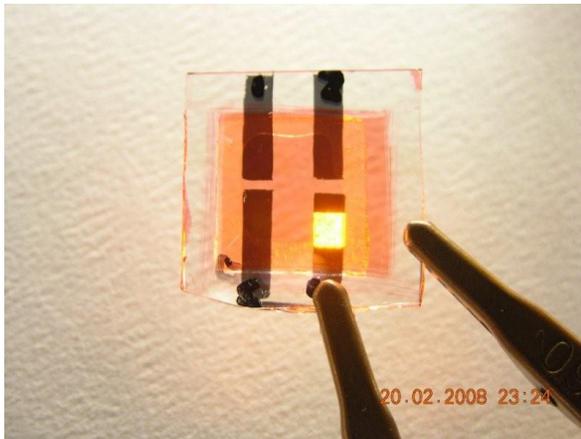
Cadeia de desenvolvimento

Produção de Materiais
(Polímeros)



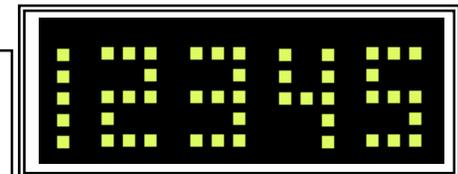
Correlacionar as propriedades elétricas e ópticas dos dispositivos com a estrutura dos polímeros.

Dispositivos



Combinar estudos experimentais com modelamentos.

Integração dos dispositivos
(Displays, CI, painéis solares)



Dispositivos Eletrônicos Poliméricos

Dispositivos Emissores de Luz (PLEDs)

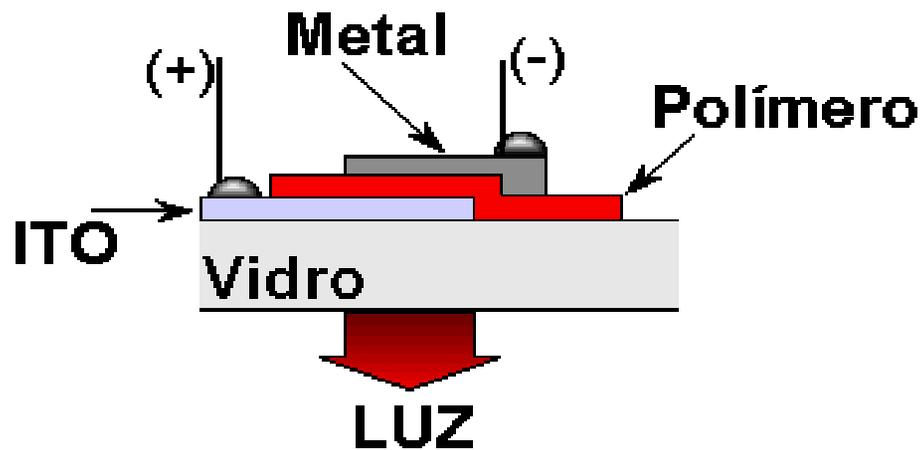
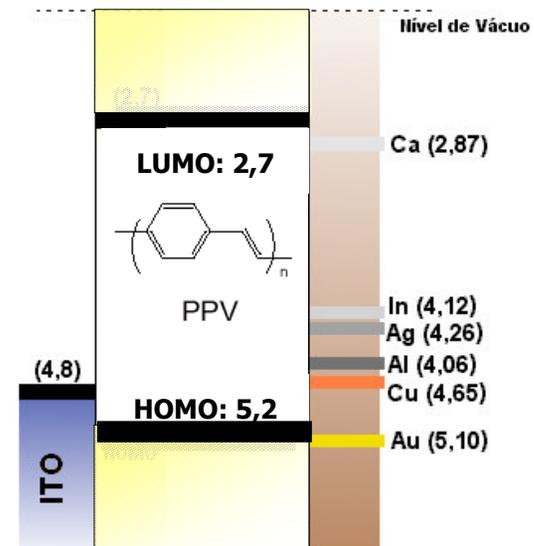
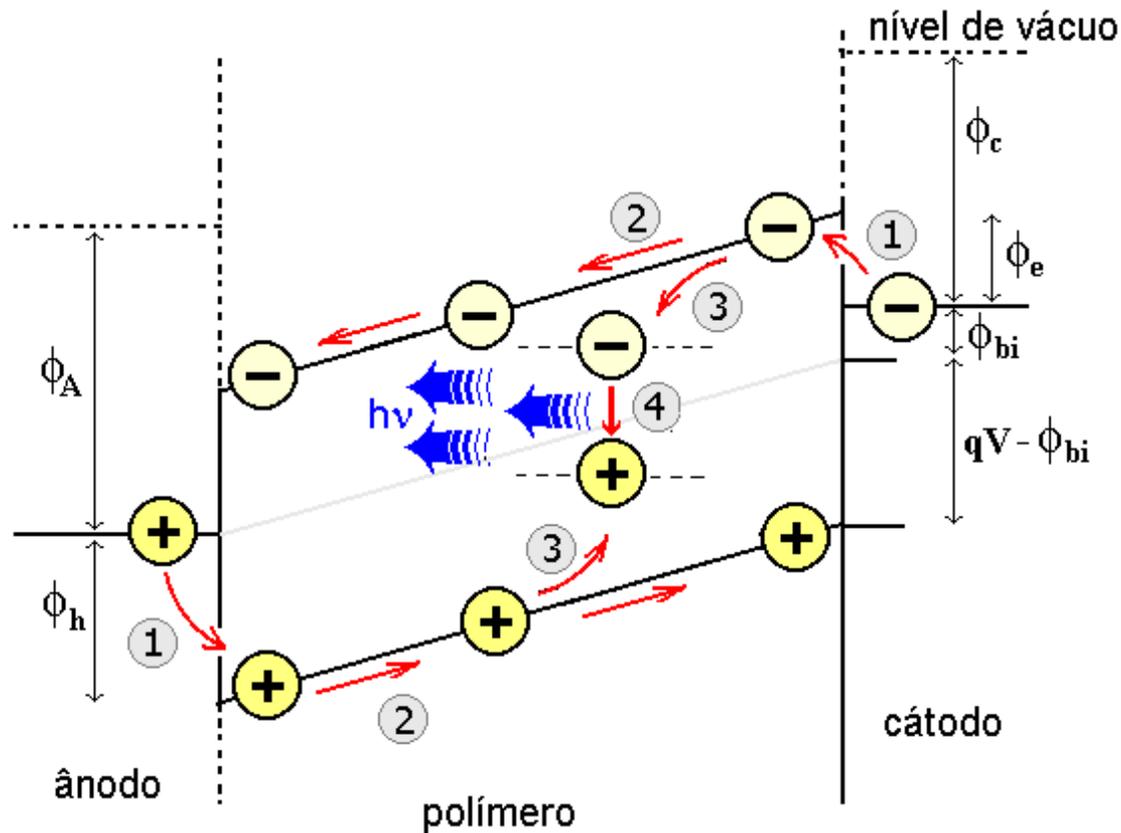


Diagrama de Energias



Princípios de Funcionamento

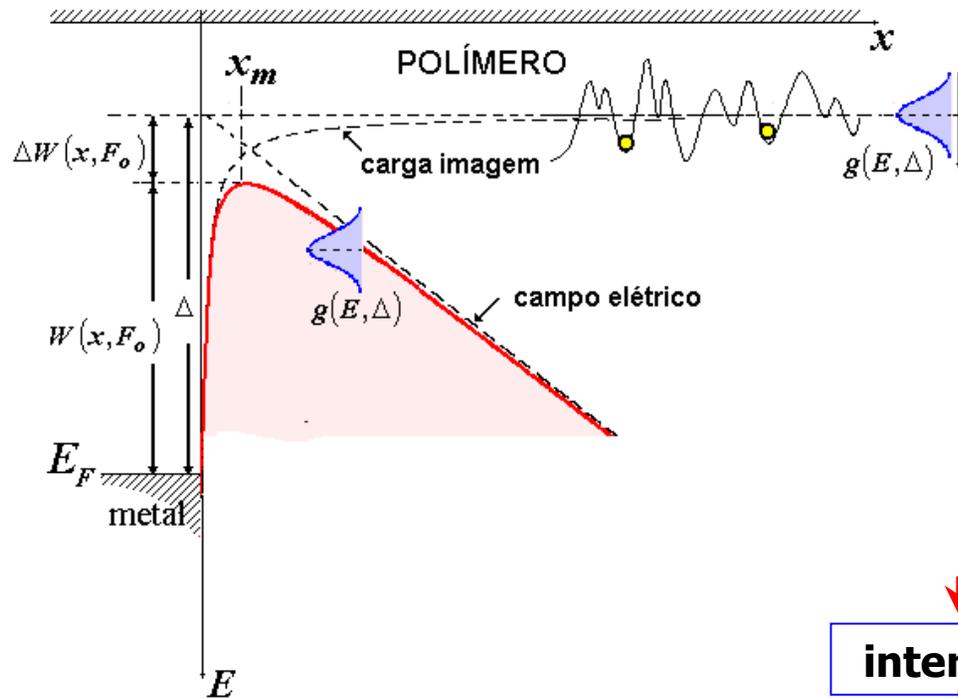


Passos básicos da eletroluminescência:

- (1) injeção dos portadores,
- (2) transporte dos portadores,
- (3) formação do éxciton e
- (4) processo de decaimento radiativo.

Mecanismos de Injeção e Transporte de Portadores

Interface metal-polímero

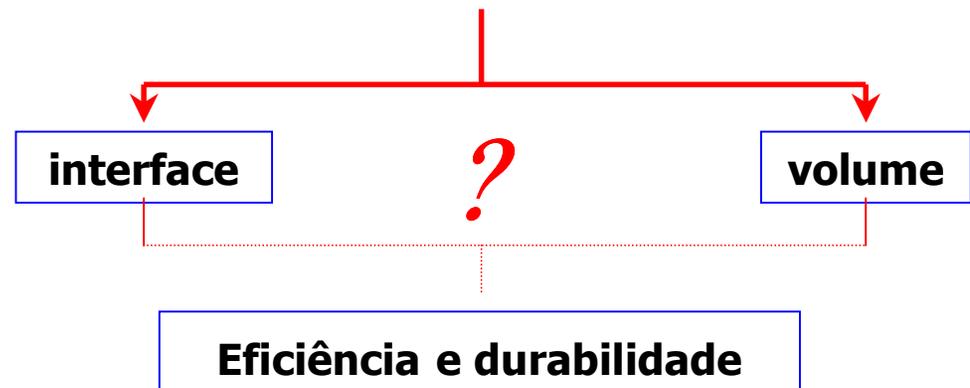


Transporte: Sistema sólido desordenado



CORRENTE ELÉTRICA

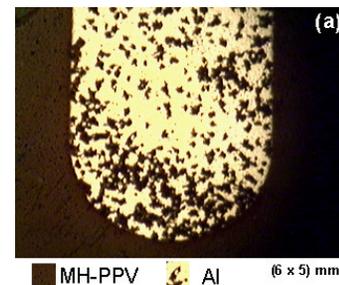
Contribuições



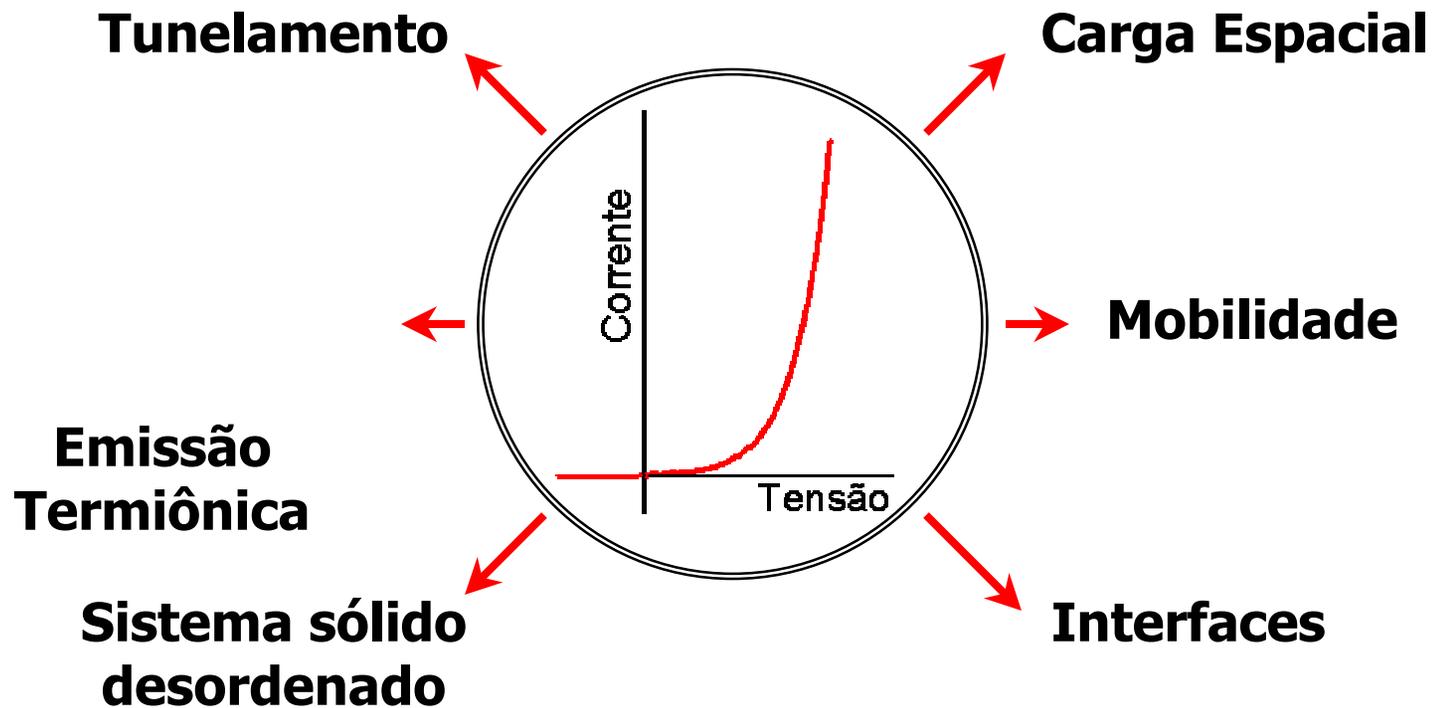
Injeção, Transporte e Eficiência

INFLUÊNCIAS

- Características dos substratos.
- Estrutura Química do polímero.
- Mobilidade dos portadores ($\mu_h > \mu_e$).
- Morfologia dos filmes.
- Temperatura.
- Degradações do polímero e das interfaces.



Processos envolvidos



Caracterizações

Contribuições do volume e das interfaces

- **I vs. V**
- **Impedância Complexa**
- **Capacitância**
- **Tempo de vôo**

Estrutura eletrônica

- **Fotoluminescência**
- **Eletroluminescência**
- **Radiância espectral**

Morfologia

- **Microscopia de Força Atômica**
- **Espectroscopia de Elipsometria**

Eficiência

- **Eficiência quântica**
- **Tempo de vida (*degradação*)**

Síntese de Polímeros e novos materiais



Displays



RED: MEH-PPV 1 g \$ 220

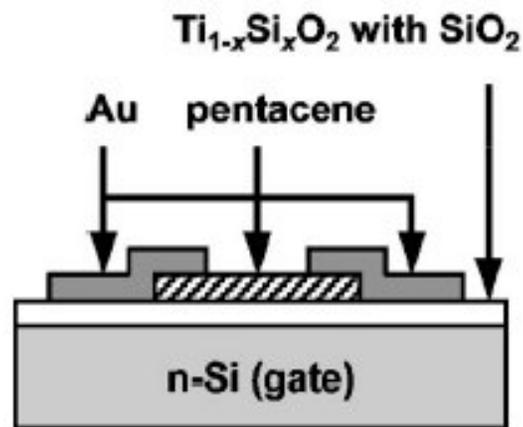
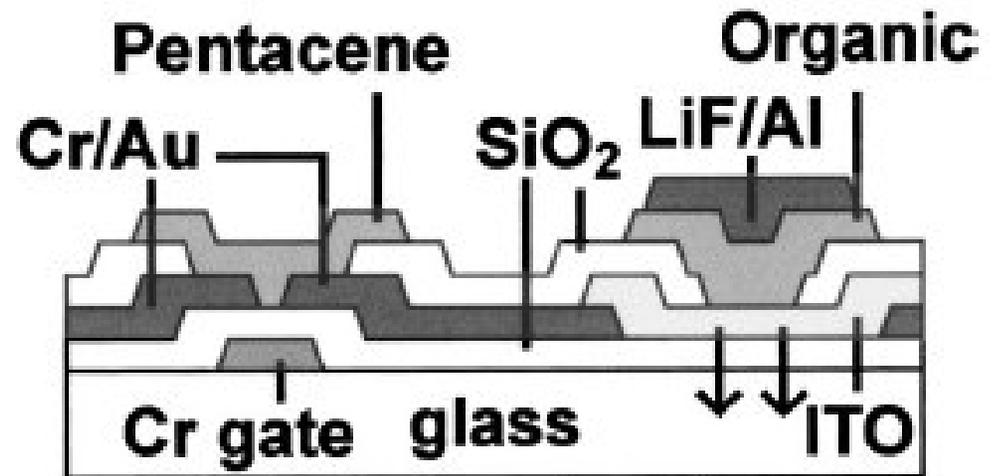
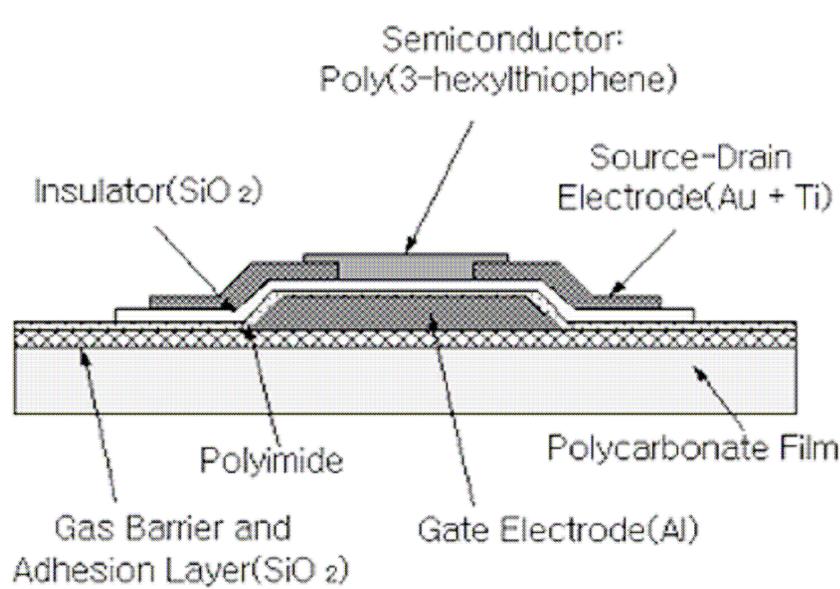
GREEN: BEHP-PPV 1 g \$ 560

BLUE: PFE 1 g \$ 564

Desenvolvimento de Tintas Luminescentes e “descartáveis”

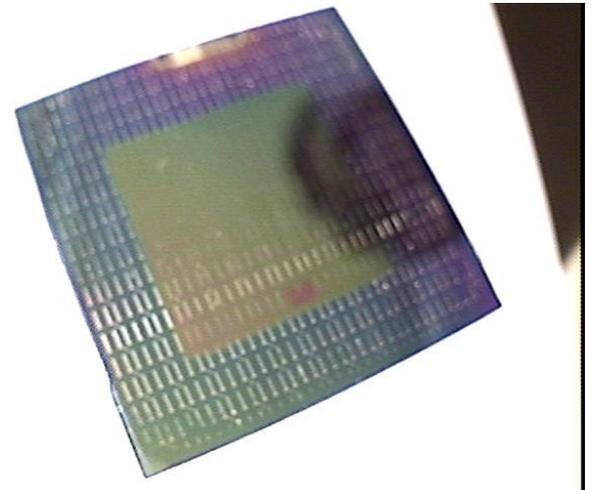
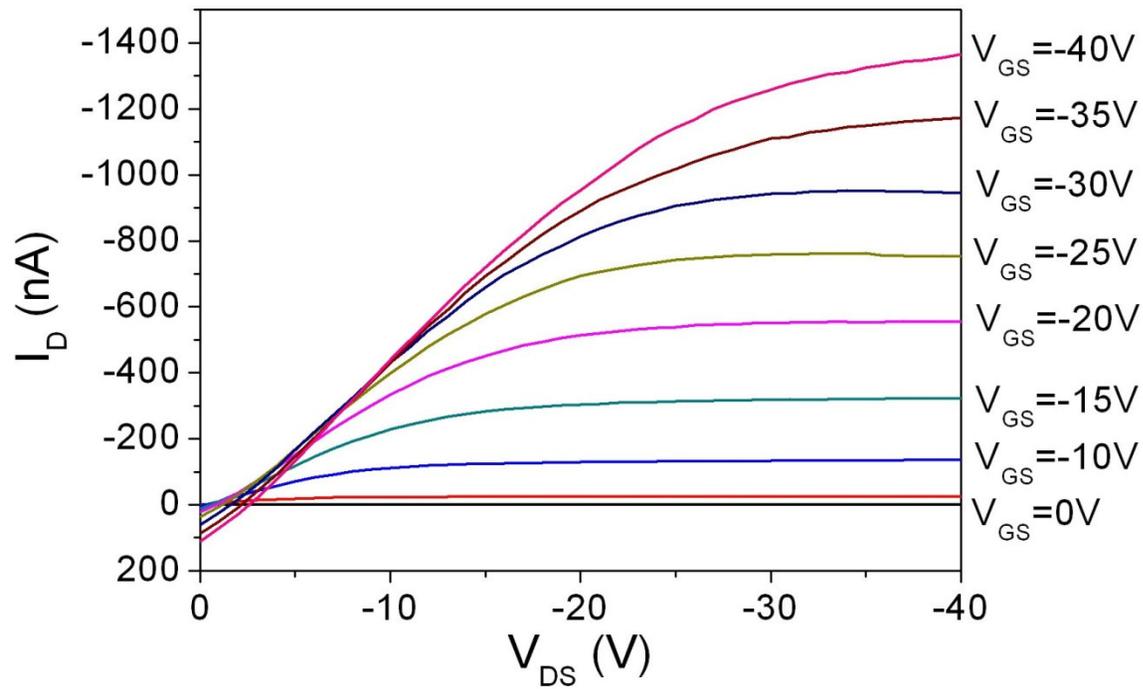


Organic Thin Film Transistor (OTFT)

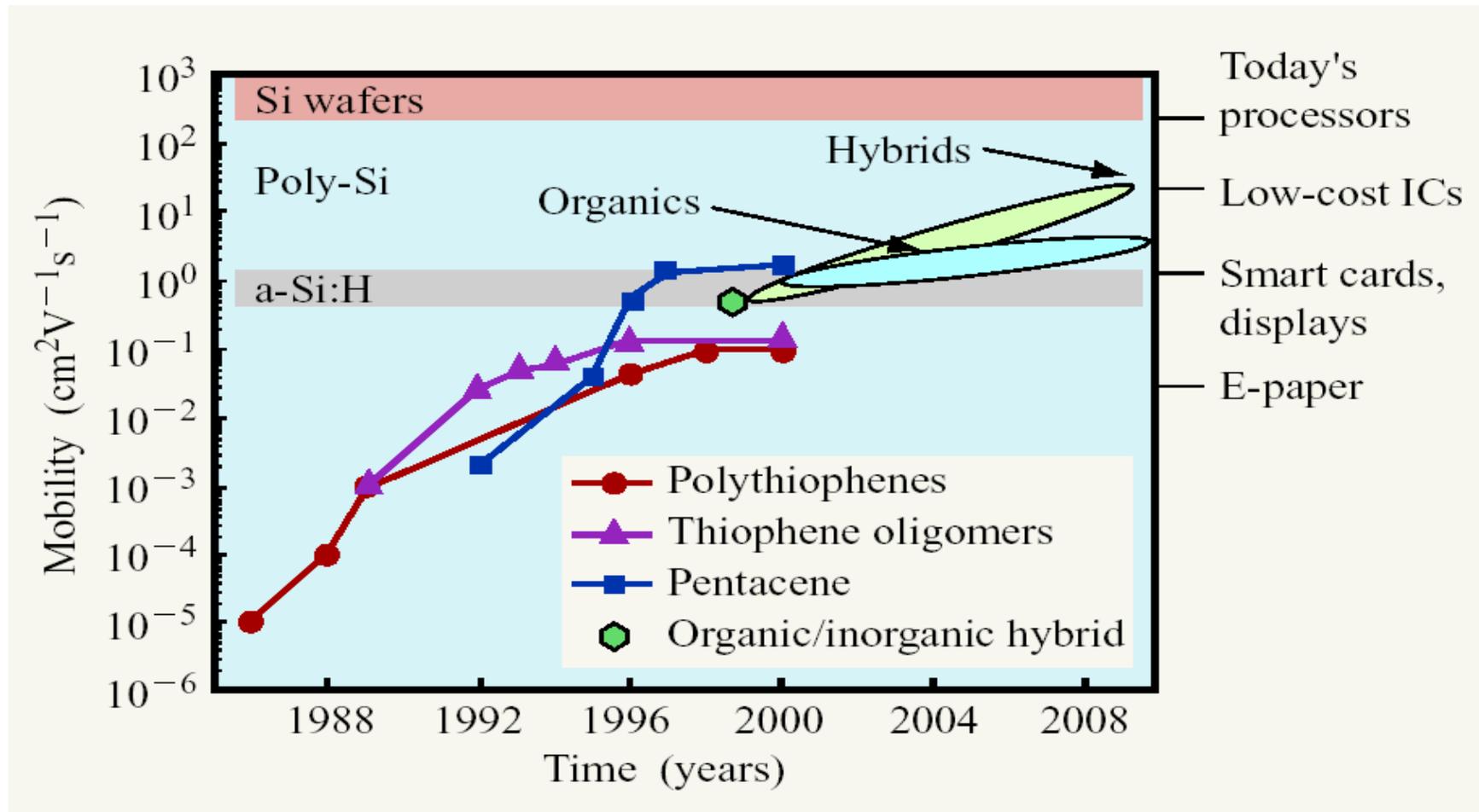


OTFT

OTFT bottom contact bottom gate - Si/SiO_xN_y/Au/Pentacene



Mobilidade de portadores



Mobilidades dos semicondutores orgânicos melhoraram cinco ordens de grandeza nos últimos 15 anos. Grandes esforços em pesquisa em novos materiais são responsáveis por este aumento.

Tipos de sensores químicos

Específico

- ✓ *Sensor específico*
- ✓ *Um único sensor*
- ✓ *Análise quantitativa*
 - Amônia
 - Radiação UV e Gamma

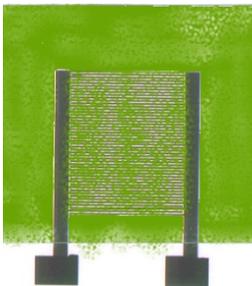
Seletividade Global

- ✓ *Sensores NÃO específicos*
 - ✓ *Arranjos de sensores*
- ✓ *Análise de dados multivariada*
- ✓ *Necessita "degustar/cheirar" analitos padrões*
- ✓ *Comparação de desempenhos*
- ✓ *Correlação com análise sensorial*
 - Língua Eletrônica
 - Nariz Eletrônico
 - LE + NE

Caracterização de sensores

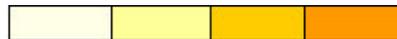
Teste de:

- **Sensibilidade;**
- **Reprodutibilidade;**
- **Repetibilidade;**
- **Life-time;**
- **Response time;**
- **Reset.**



Testes de Fabricação:

Microeletrodos
Envelhecimento
Monitoramento de Processos

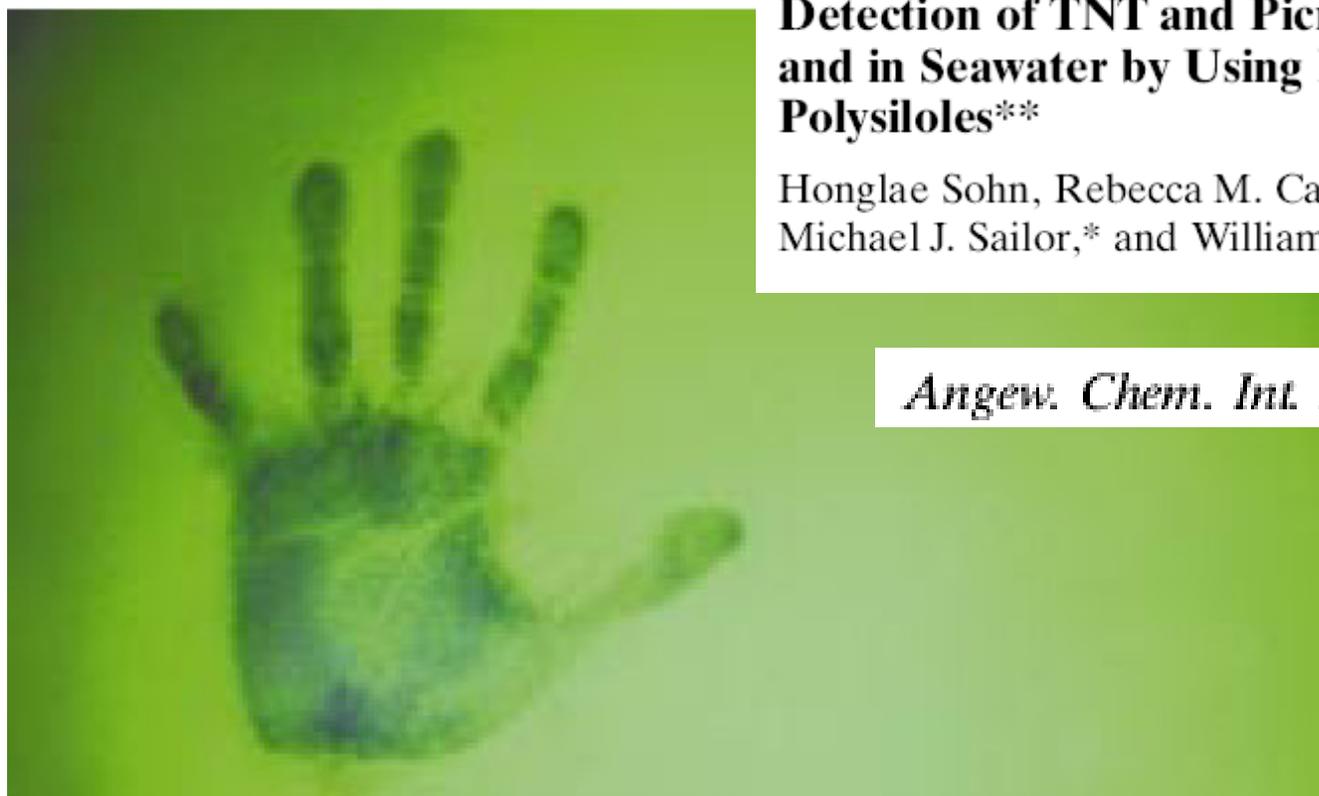


Desenvolvimento de sensores químicos

**Detection of TNT and Picric Acid on Surfaces
and in Seawater by Using Photoluminescent
Polysiloles****

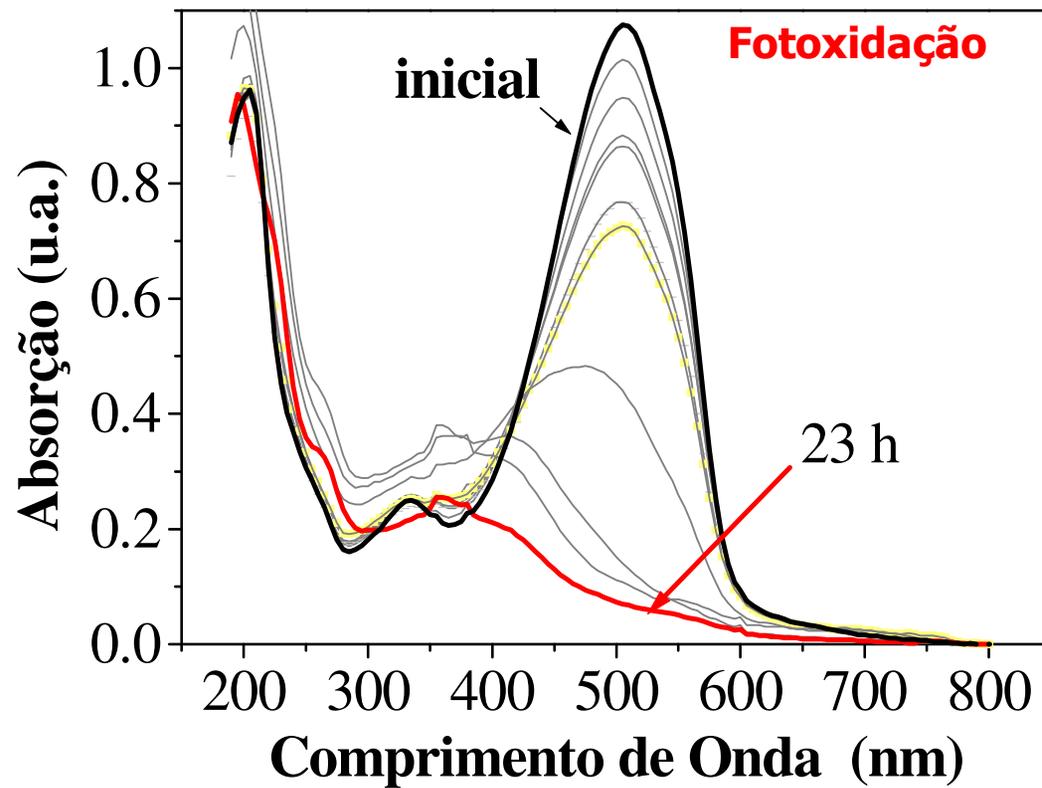
Honglae Sohn, Rebecca M. Calhoun,
Michael J. Sailor,* and William C. Trogler*

Angew. Chem. Int. Ed. **2001**, *40*, No. 11



TNT: 2,4,6-trinitrophenol (picric acid)

Dosímetros

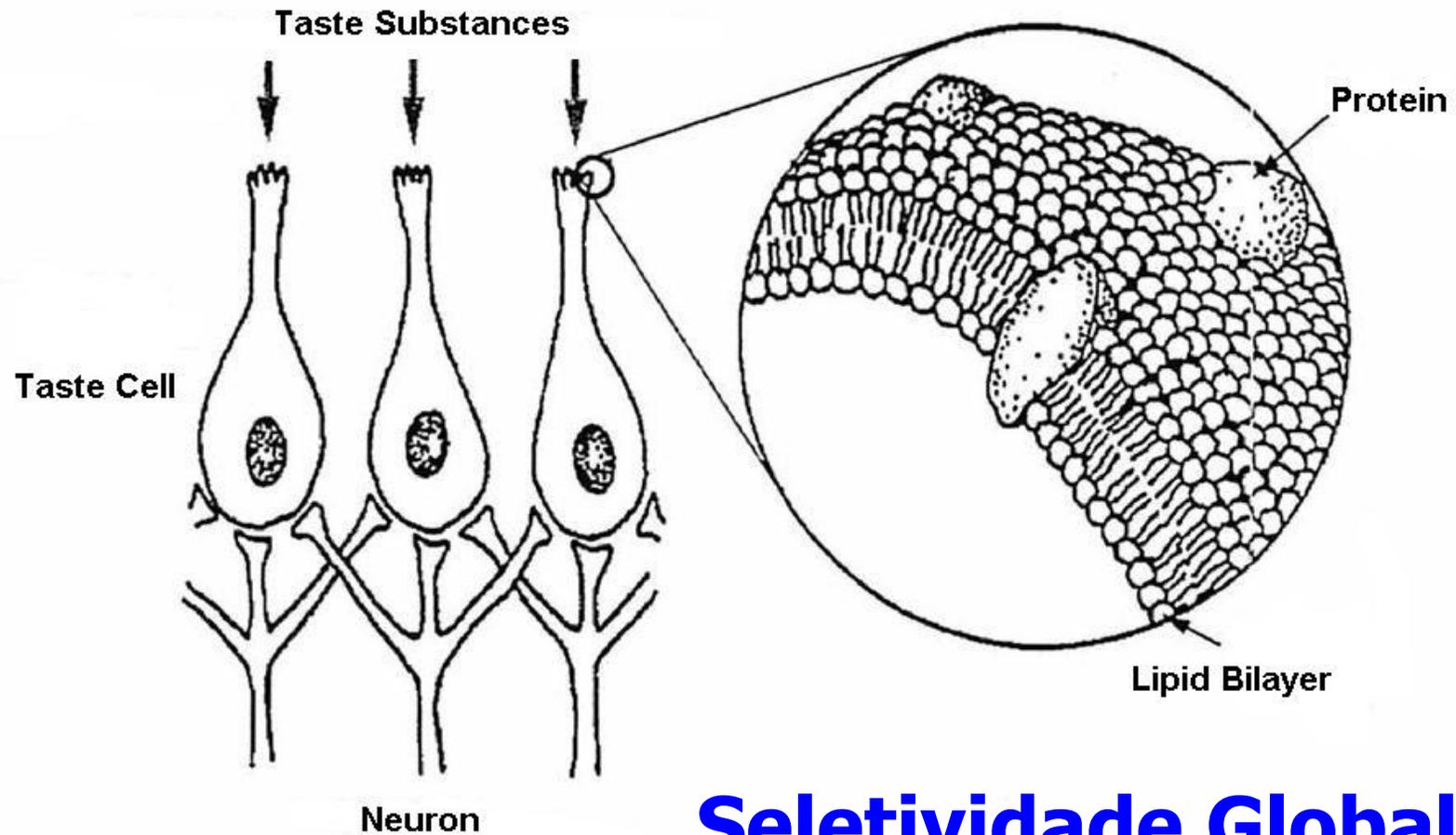


Raios *x*, gama, etc...



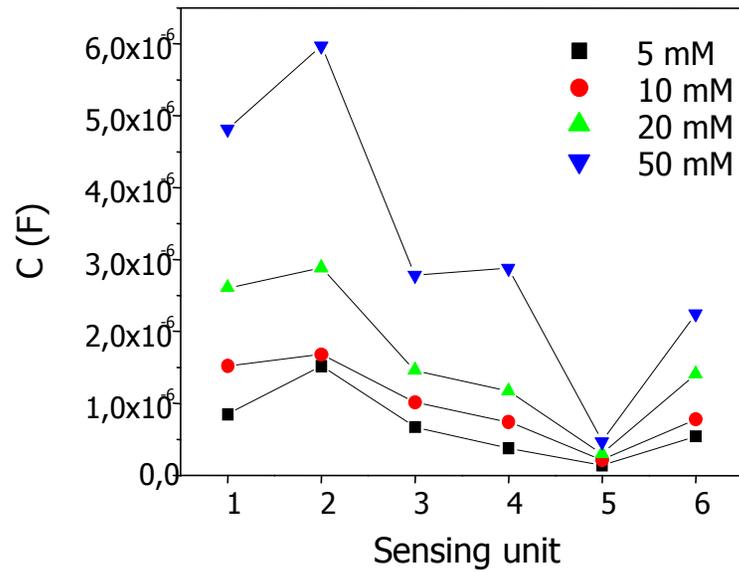
colorímetro

Língua Humana

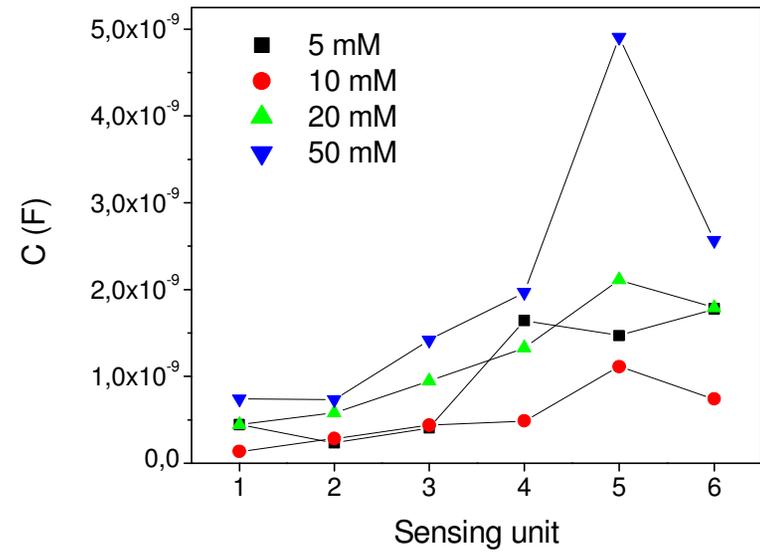


Seletividade Global

“Impressão digital” dos líquidos



NaCl



sucrose

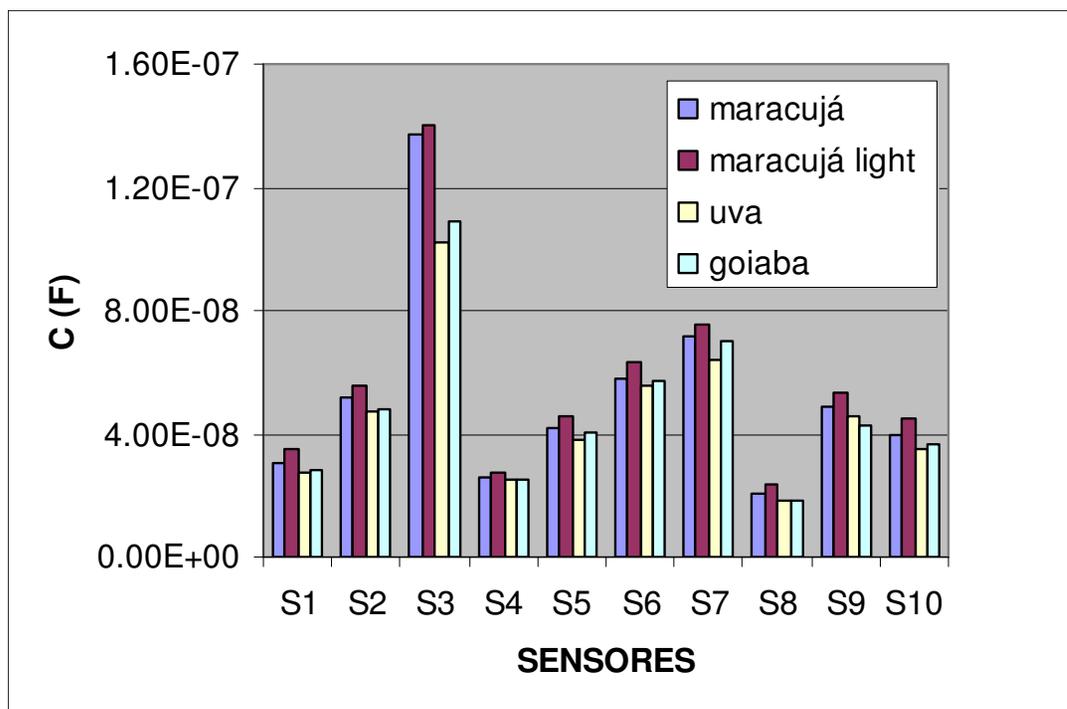
Língua Eletrônica e Seletividade Global



Arranjo de sensores não-específicos
+ análise multivariada

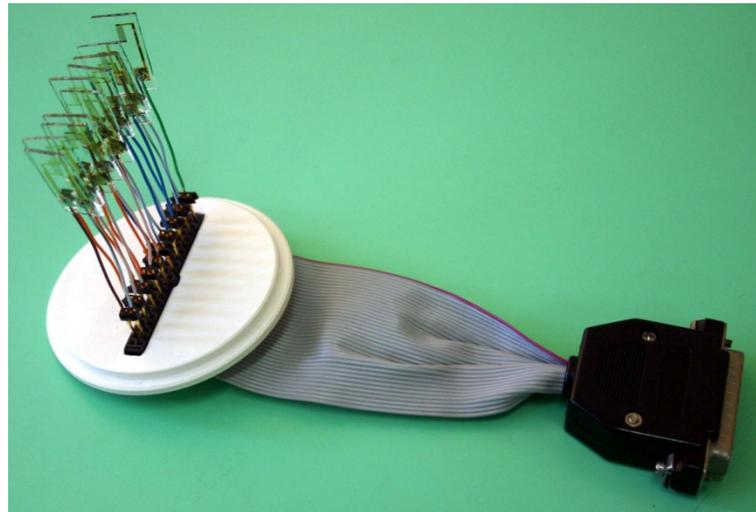
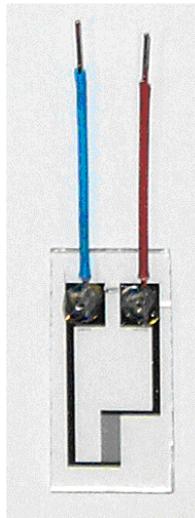
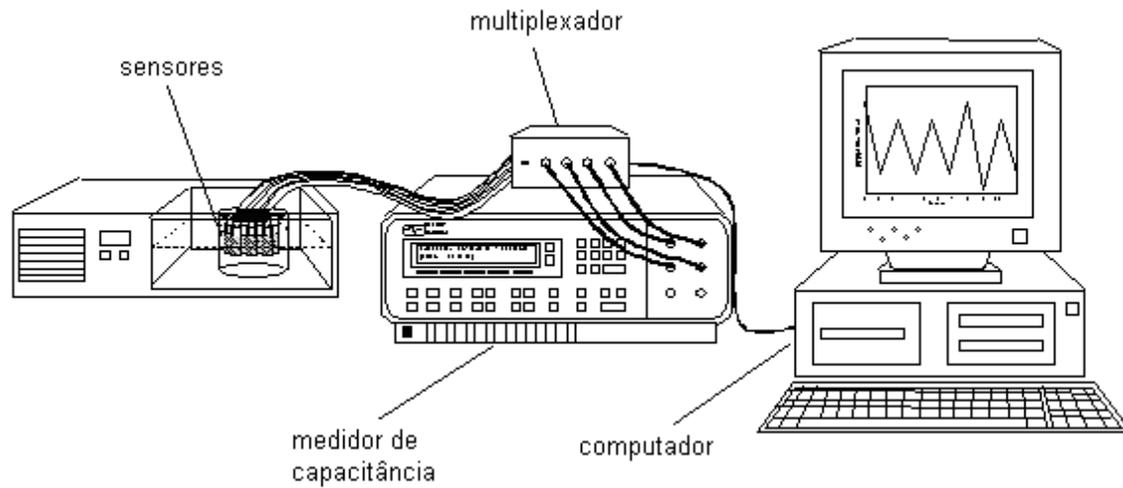


Impressão digital dos líquidos



**Impressões
digitais de sucos
de diferentes
frutas, obtidas
com a LE**

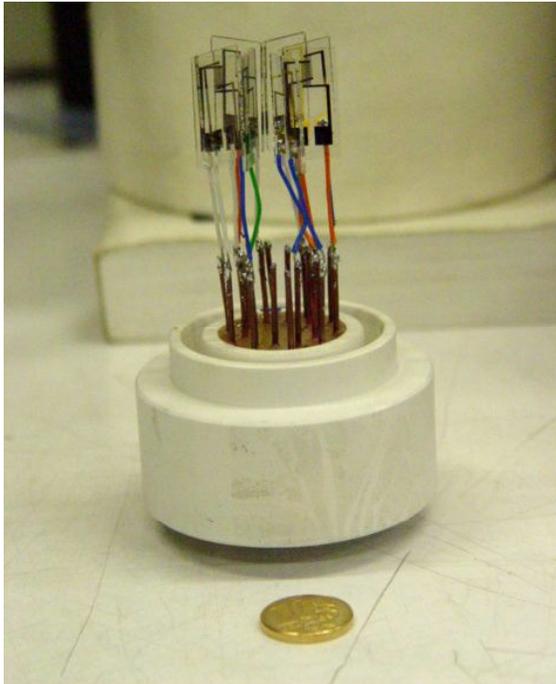
Língua Eletrônica – “Hardware”



Motivação



Língua Eletrônica



Applications

✓ **Water**

Control of contaminants in water reservoirs used for human supplying.

Monitoring sea water desalinization for human consumption.

- Measurements in real time improving time response
 - Low cost
- Data acquisition *in locu* and sending via wireless system

Nariz Eletrônico

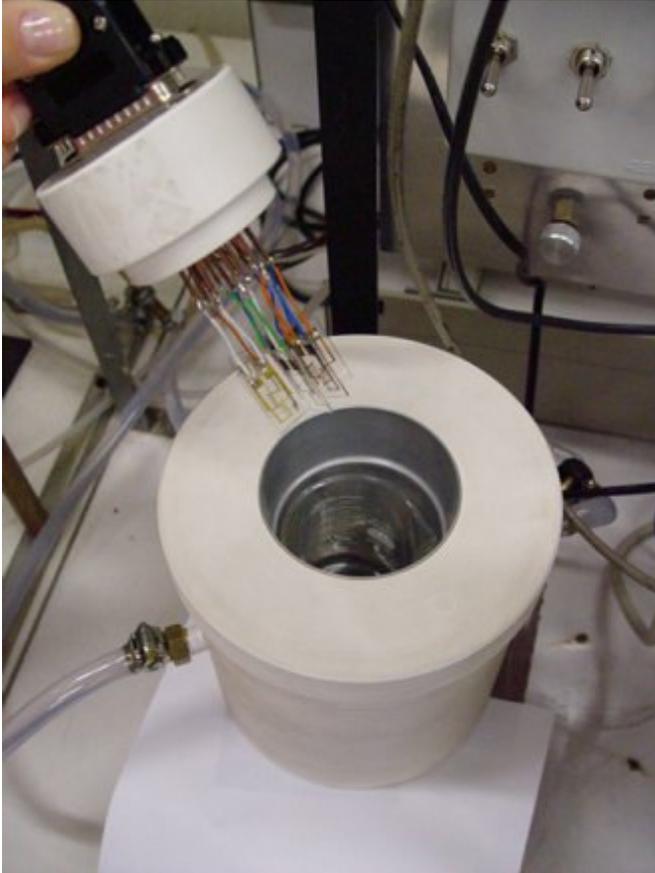


Applications

- ✓ Food
- ✓ Quality Control
- ✓ Environmental
- ✓ Chemistry
- ✓ Terrorism prevention

Flavour Identification / Classification, Adulteration, Contamination, Validity Time, etc..

Nariz e Língua Eletrônicas



Project:
Auxílio à Pesquisa - FAPESP

Applications

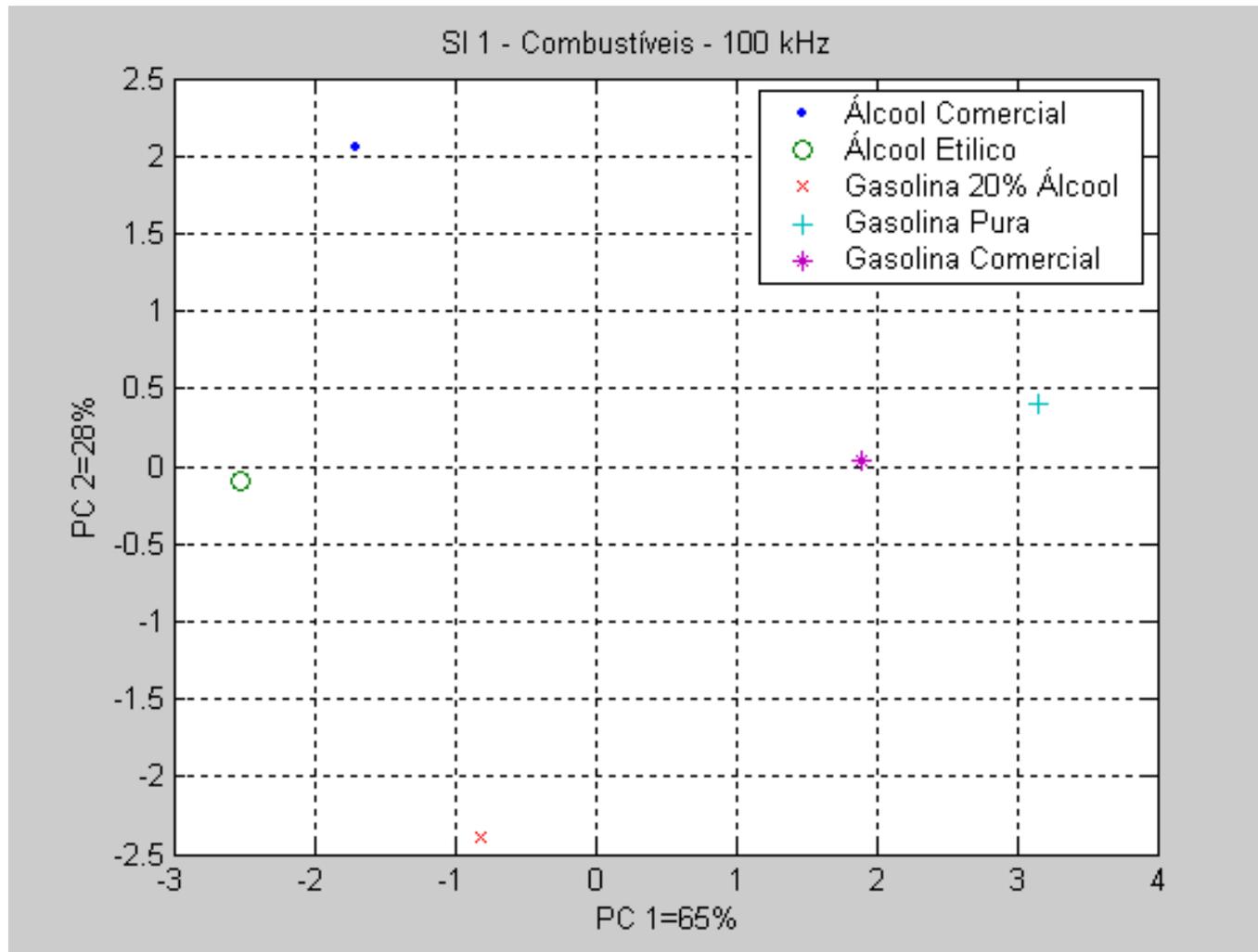
✓ Quality Control (Fuel)

Quality evaluation of alcohol and gasoline in the distribution location

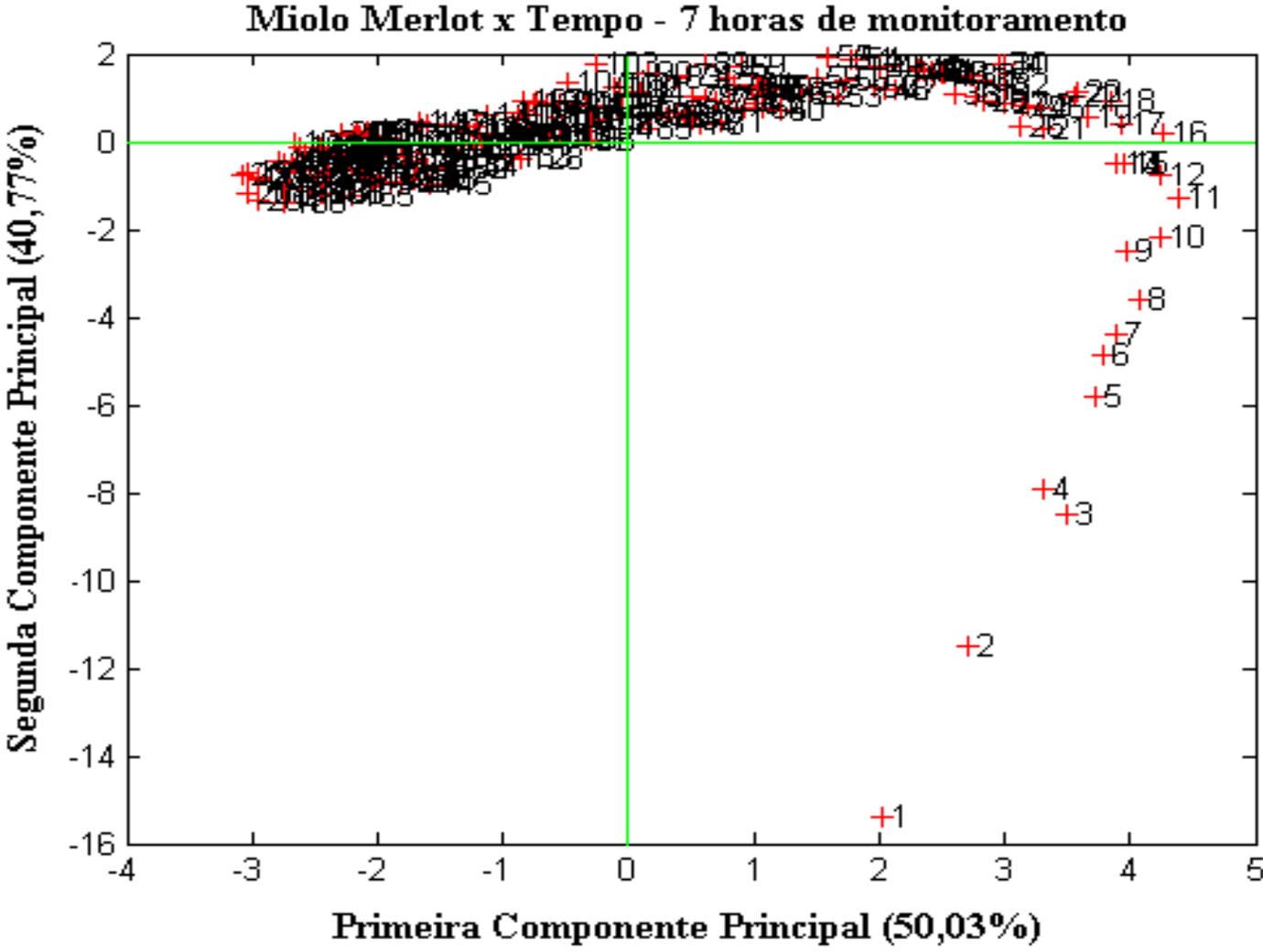
- Quick test *in locu*
- Data transmission in long distances
 - Low cost
- Integrated system EN+ET

Drawbacks:
Sensors life-time
Friendly system

SI-1 – Discriminação de combustíveis



Monitoramento de qualidade de alimentos



Célula solar orgânica de heterojunção em volume (“bulk heterojunction”)

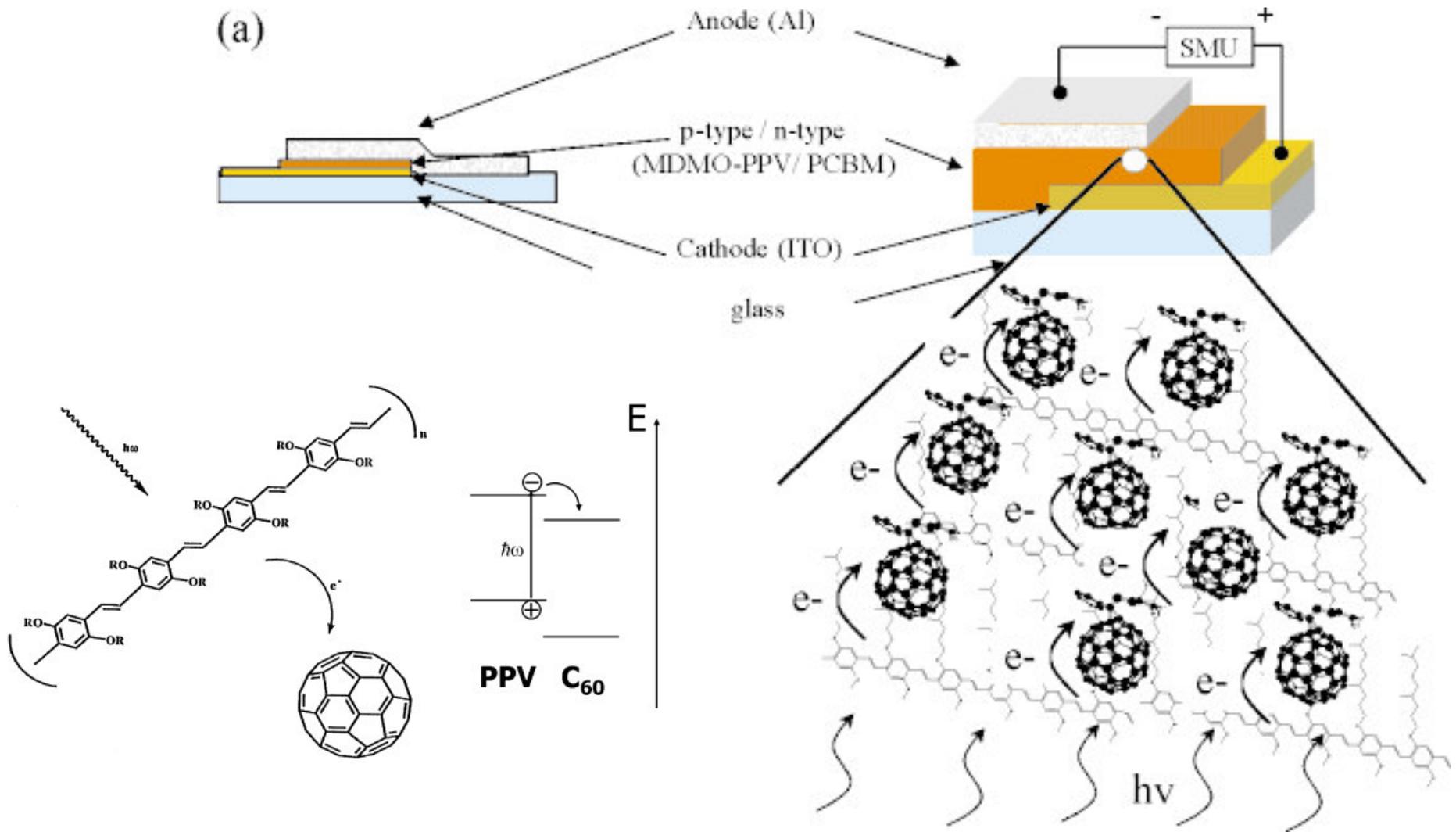
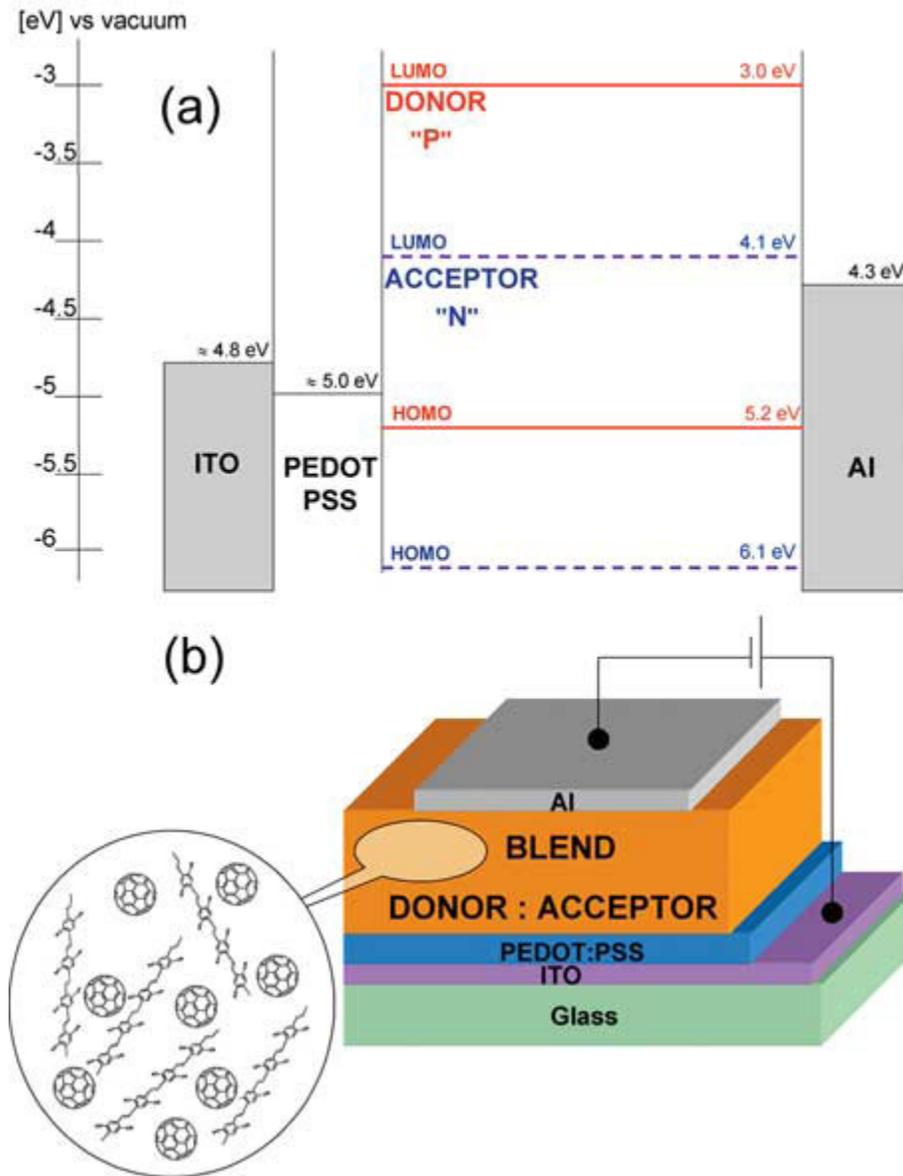
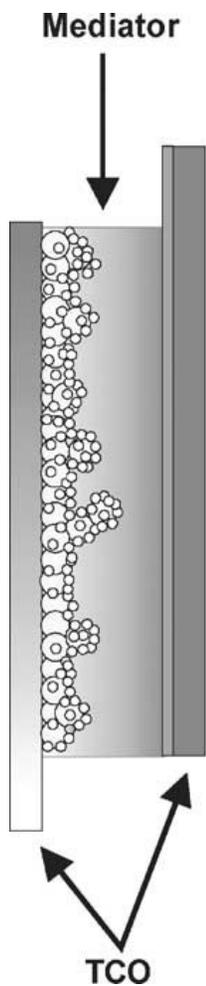


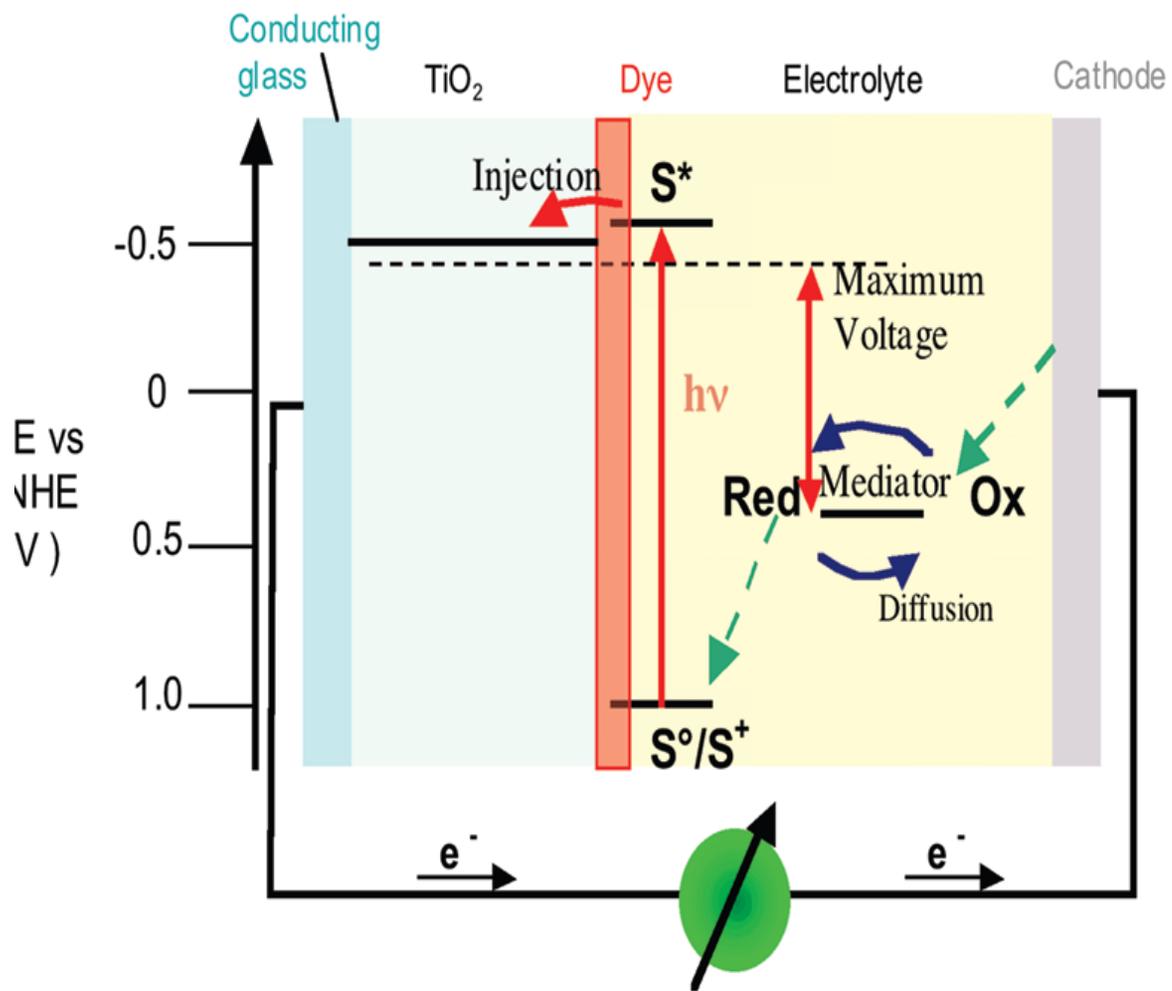
Diagrama dos níveis de energia na célula orgânica de heterojunção em volume (MDMO-PPV)/PCBM



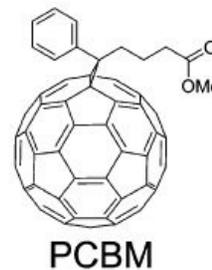
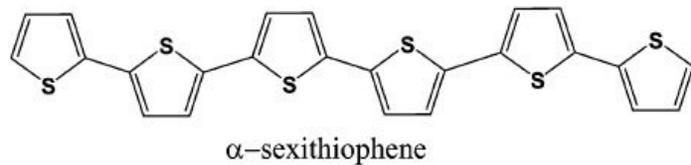
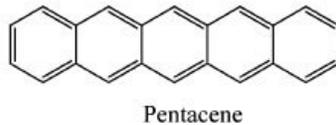
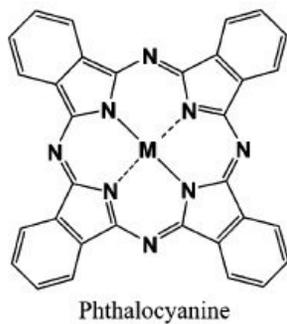
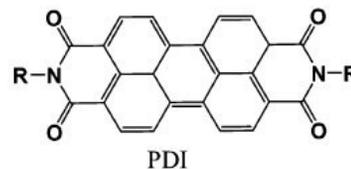
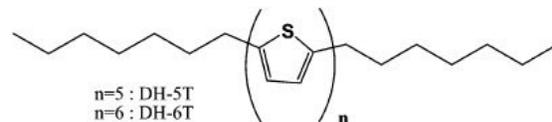
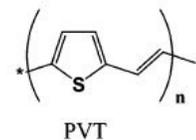
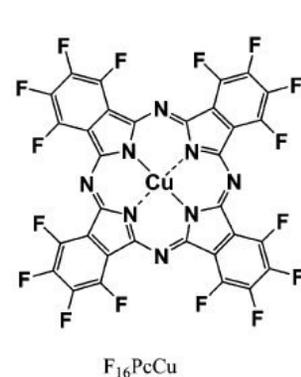
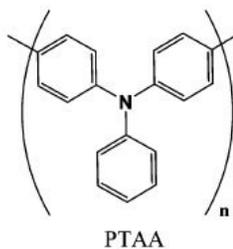
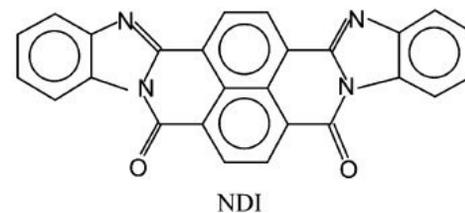
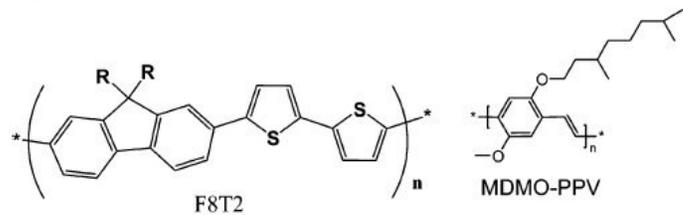
Célula solar sensibilizada por corante (“dye-sensitized solar cell”)

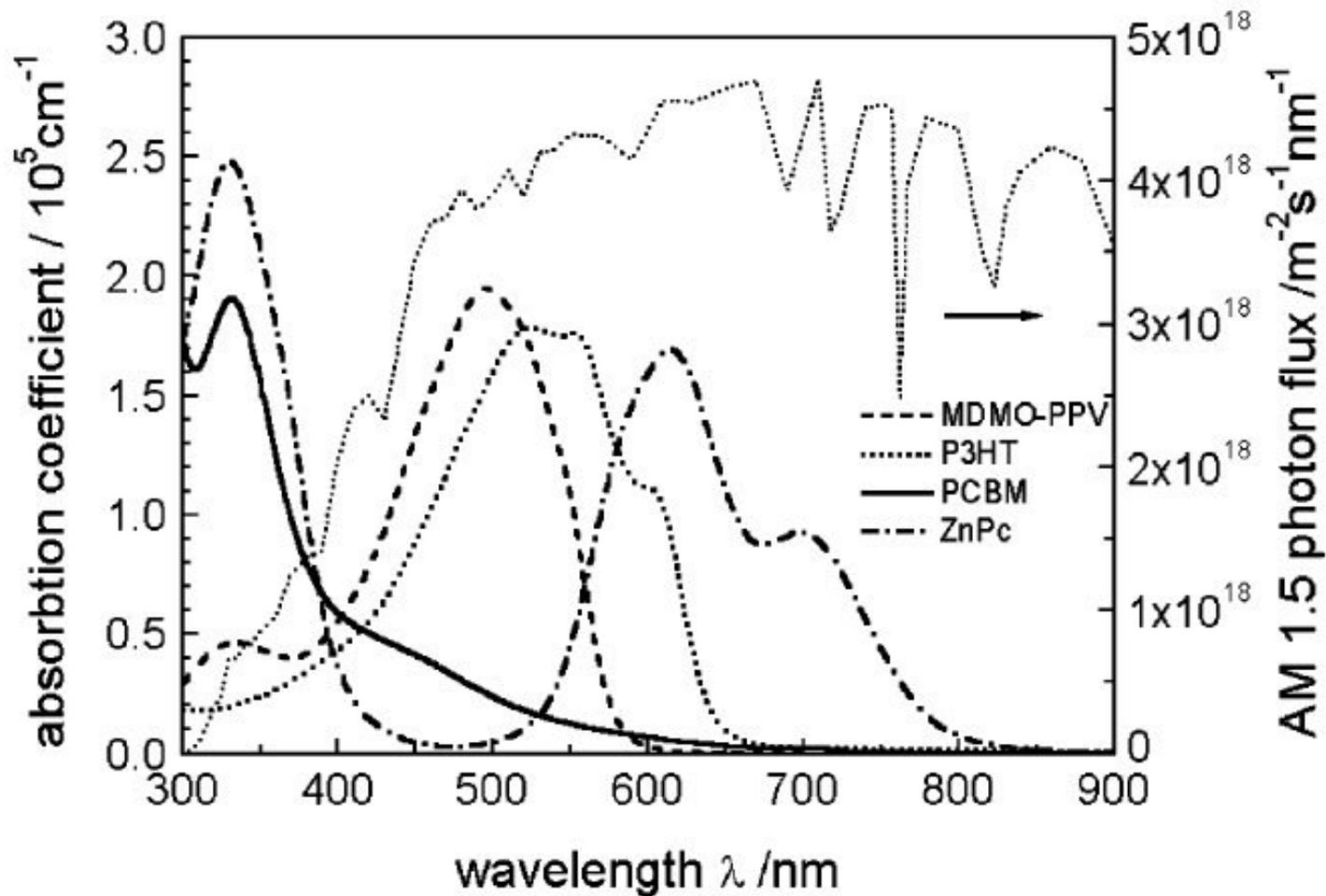


- TiO_2 film
- Adsorbed dye
- ▬ Catalyst



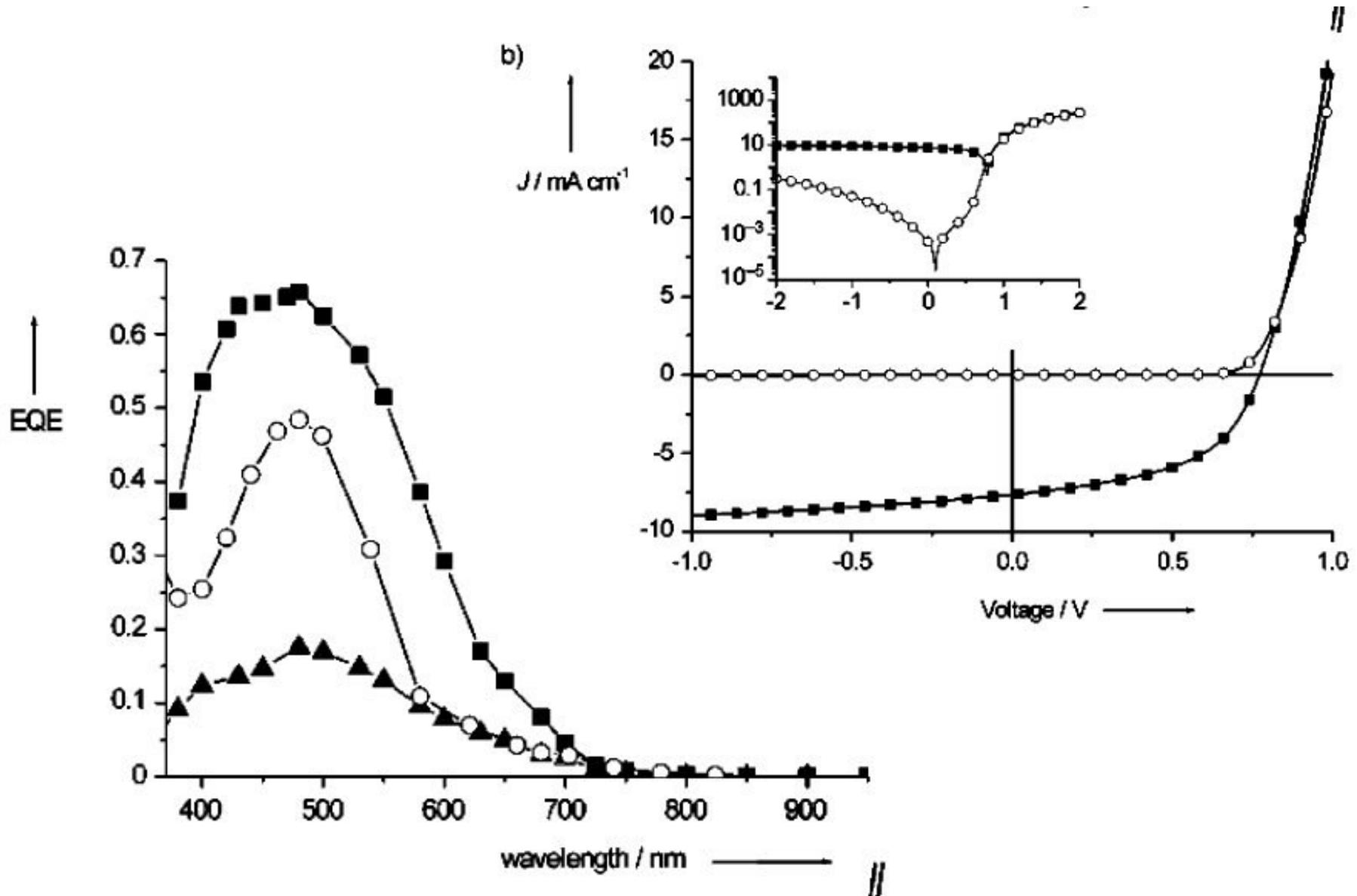
Materials

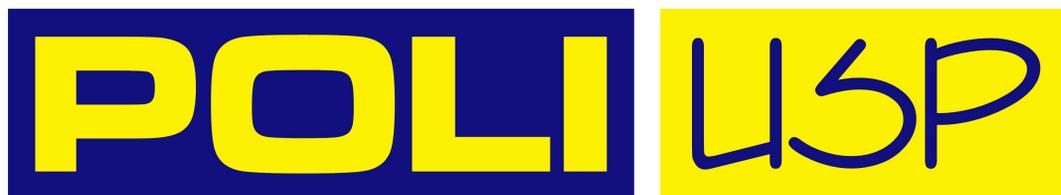




Coeficiente absorção de filmes de materiais comumente usados em CSO são apresentados comparativamente com o padrão AM 1.5 do espectro solar terrestre.

Características eléctricas





Grupo de Eletrônica Orgânica

Interessados em trabalhar conosco
podem escrever para:

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fernando.fonseca@poli.usp.br
Fone 3091-5256 r218

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Escola Politécnica da USP