Organic semiconductors - From a lab curiosity to serious applications

Karl Leo

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Technische Universität Dresden, 01062 Dresden, Germany
www.iapp.de

Dresden Integrated Center for Applied Physics and Photonic Materials (IAPP)

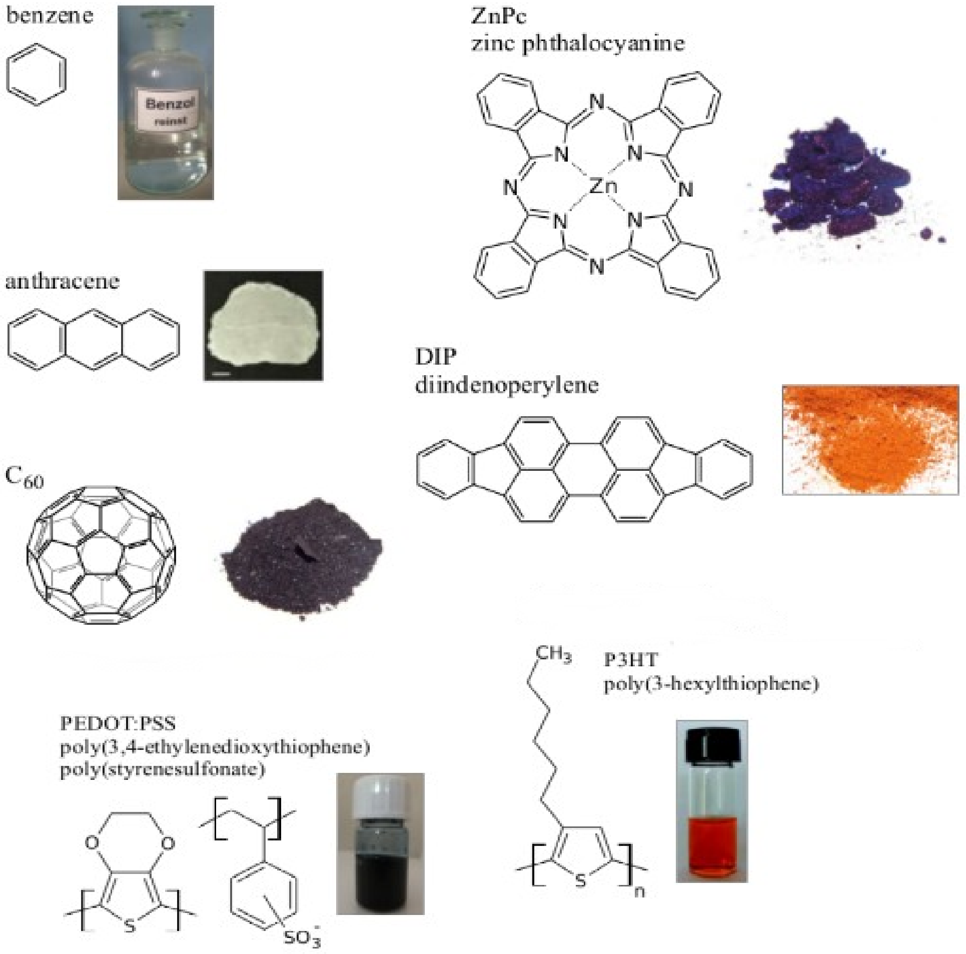
- Founded 1908 with endowed chair
- Work on Photography till 1990
- Today:
- Organic Semiconductors
- Novel devices
- Ca. 120 employees

Roland Moser, Michael Halbe
Heinle, Wischer & Partner

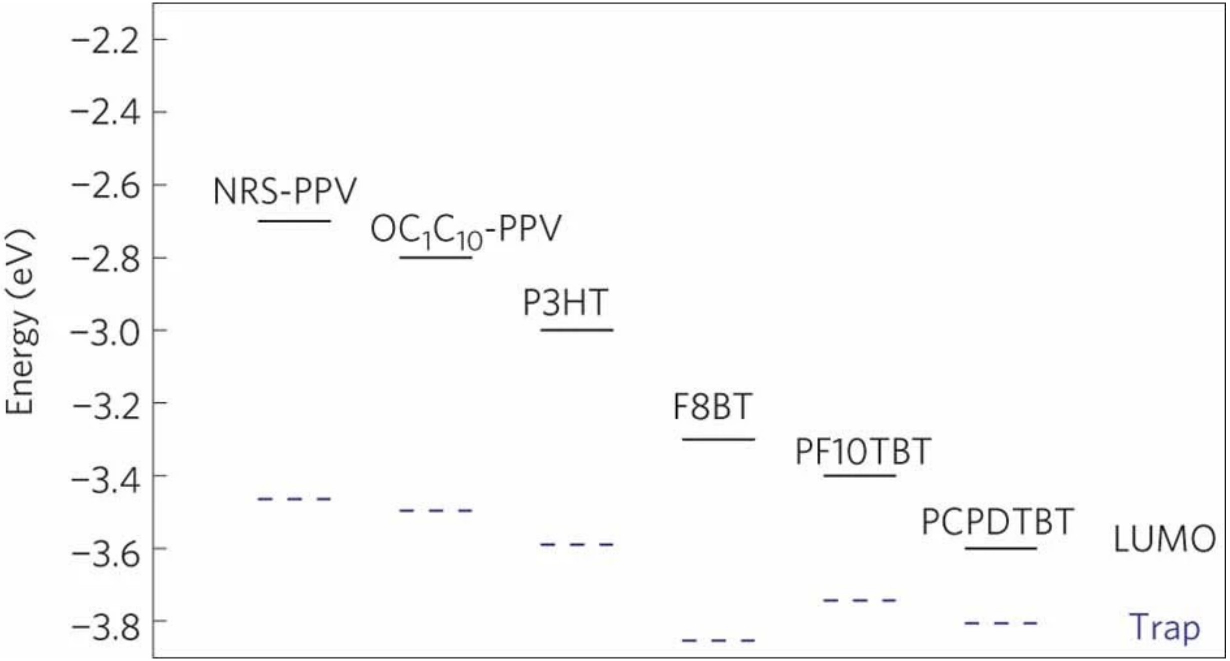
Web: www.iapp.de

Hermann Krone 1858

Organic semiconductors



Electron traps due to hydrated oxygen



Unification of trap-limited electron transport in semiconducting polymers

H. T. Nicolai, M. Kuik, G. A. H. Wetzelaer, B. de Boer, C. Campbell, C. Risko, J. L. Brédas & P. W. M. Blom

Nature Materials **11**, 882–887 (2012) | Cite this article

Dark spots due to electrode delamination

RESEARCH ARTICLE | MARCH 12 2012

Dependence of dark spot growth on cathode/organic interfacial adhesion in organic light emitting devices

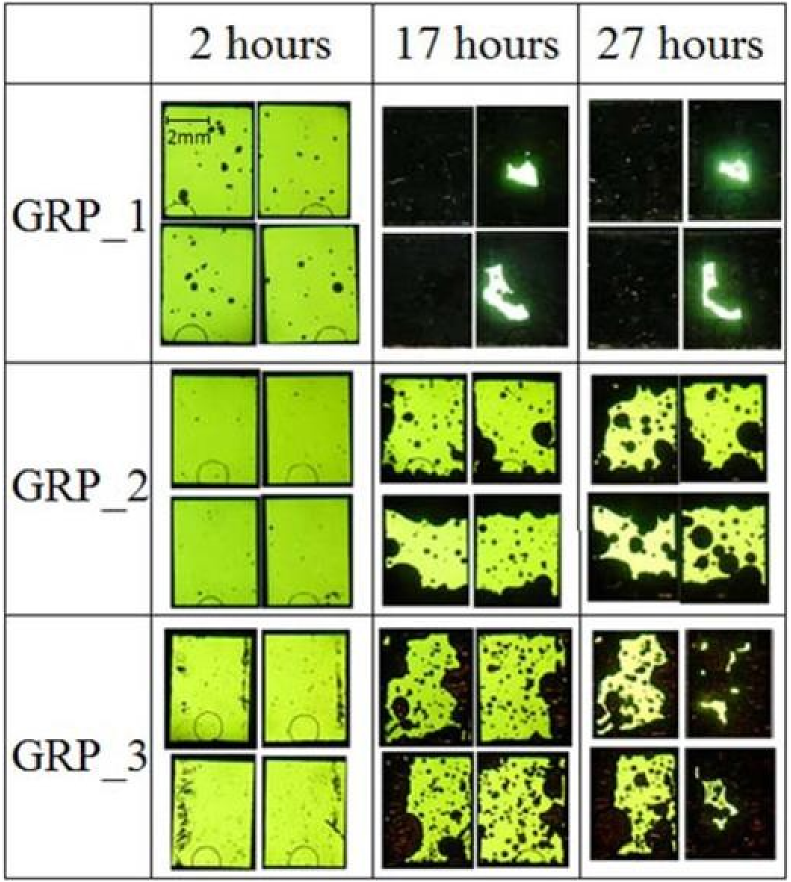
R. Phatak; T. Y. Tsui; H. Aziz

Check for updates

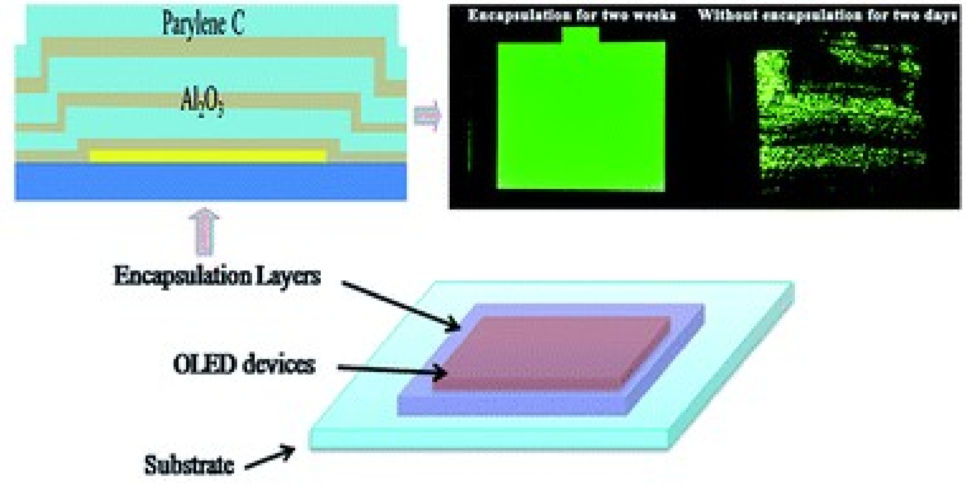
+ Author & Article Information

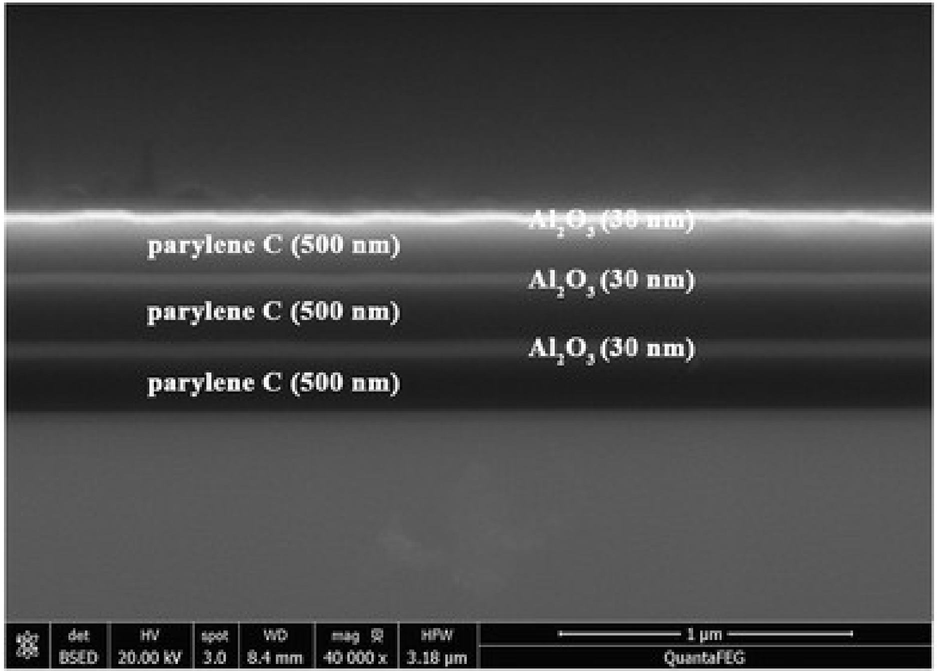
Journal of Applied Physics 111, 054512 (2012)

https://doi.org/10.1063/1.3692390 **Article history**



Multilayer thin-film encapsulation





From the journal:
RSC Advances

Efficient multi-barrier thin film encapsulation of OLED using alternating Al_2O_3 and polymer layers†

Check for updates

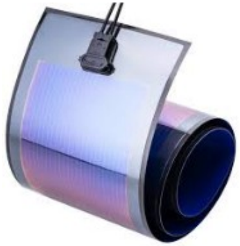
Jie Wu,‡[ab] Fei Fei,‡[a] Changting Wei,[ac] Xiaolian Chen,[a] Shuhong Nie,[a] Dongyu Zhang,[a] Wenming Su *[a] and Zheng Cui *[a]

Rollable OLED TV (LG)

The future of organic products

5. wave: Organic Transistors

4. wave: OPV



3. wave: OLED lighting

2. wave: OLED TV

1. wave: small display OLED

Time

Images: Samsung, Philips, Novaled, Heliatek, Plastic Logic

OLED Television

Xiaomi

Novel lighting concepts

LG, Osram

OPV Testbed at IAPP

This talk made from 100% organic electrons

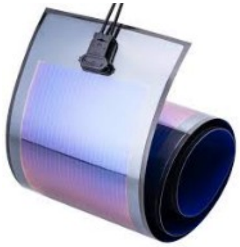
The future of organic products

1. wave: small display OLED

2. wave: OLED TV

3. wave: OLED lighting

4. wave: OPV



5. wave: Organic Transistors

Time

Images: Samsung, Philips, Novaled, Heliatek, Plastic Logic

Where silicon transistors stand

SCIENCE AND TECHNOLOGY

Silicon-Germanium Chip Sets New Speed Record

Posted February 18, 2014 | Atlanta, GA

A research collaboration consisting of IHP-Innovations for High Performance Microelectronics in Germany and the Georgia Institute of Technology has demonstrated the world's fastest silicon-based device to date. The investigators operated a silicon-germanium (SiGe) transistor at 798 gigahertz (GHz) fMAX, exceeding the previous speed record for silicon-germanium chips by about 200 GHz.

=469 GHz/Volt

Although these operating speeds were achieved at extremely cold temperatures, the research suggests that record speeds at room temperature aren't far off, said professor John D. Cressler, who led the research for Georgia Tech. Information about the research was published in February 2014, by *IEEE Electron Device Letters*.

Transit frequency record values for organic transistors

- Silicon record: **469 Ghz/V**
- Organics record: **7 Mhz/V** (Borchert et al., Science Advances 6(21):eaaz5156 (2020))

Reference	Substrate	Device	Voltage (V)	f_T/V (MHz V^{-1})
Brown, Science, vol. 270, p. 972, 1995	Rigid	RO*	20	$1.25 \cdot 10^{-4}$
Crone, J. Appl. Phys., vol. 89, p. 5125, 2001	Rigid	RO*	100	$5 \cdot 10^{-4}$
Baude, Appl. Phys. Lett., vol. 82, p. 3964, 2003	Rigid	RO*	50	$6.67 \cdot 10^{-4}$
Sheraw, Int'l Electr. Dev. Meeting 2000	Flexible	RO*	20	0.00125
Fix, Appl. Phys. Lett., vol. 81, p. 1735, 2002	Flexible	RO*	80	0.0092
Wagner, Appl. Phys. Lett., vol. 89, p. 243515, 2006	Rigid	RO*	10	0.2
Heremans, Int'l Electr. Dev. Meeting 2009	Flexible	RO*	20	0.2
Zschieschang, Org. Electronics, vol. 14, p. 1516, 2013	Flexible	RO*	4	0.42
Kitamura, Appl. Phys. Lett., vol. 95, p. 023503, 2009	Rigid	TFT[a]	25	0.8
Kitamura, Jpn. J. Appl. Phys., vol. 50, p. 01BC01, 2011	Rigid	TFT[a]	25	1.11
Zaki, Org. Electronics, vol. 14, p. 1318, 2013	Rigid	TFT[b]	3	1.37
Nakayama, Adv. Mater. Interfaces, vol. 1, p. 1300124, 2014	Rigid	TFT[a]	10	1.9
Yamamura, Sci. Adv., vol. 4, p. eaao5758, 2018	Rigid	TFT[a]	10	2
Perinot, Adv. Sci., vol. 6, p. 1801566, 2019	Flexible	TFT[a]	14	2.06
Borchert, Int'l Electr. Dev. Meeting 2018	Flexible	TFT[b]	3	2.23
Kheradmand-Boroujeni, Sci. Rep., vol. 8, p. 7643, 2018	Rigid	TFT[c]	8.6	4.65
This work	Flexible	TFT[b]	3	7

4 A. Perinot et al., Adv. Sci. 8, 2001098 (2021)

Transit frequency record values for organic transistors

- Silicon record: 469 GHz/V
- Best organics value: Borchert et al., Science Advances 6(21):eaaz5156 (2020): 7MHz/V

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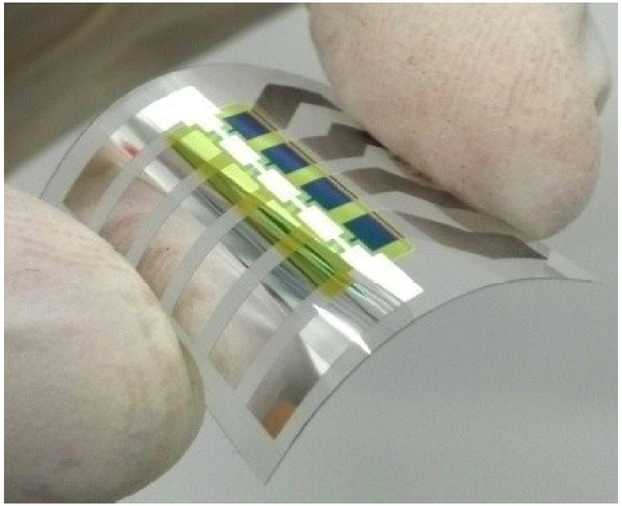
4 A. Perinot et al., Adv. Sci. 8, 2001098 (2021)

Mobility ratio silicon:organics: ~**10**

Transistor speed ratio: ~ **67,000**

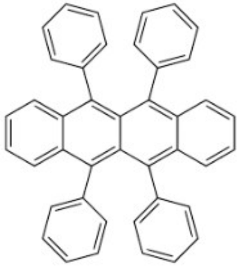
Outline

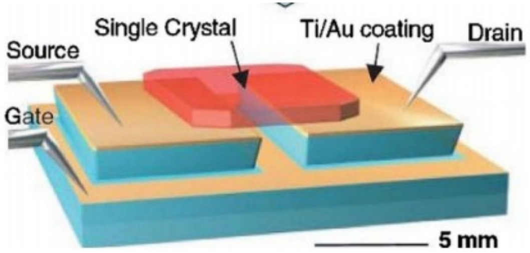
- Organic Bipolar Transistors
- Organics for Neuromorphics
- Resorbable Organics

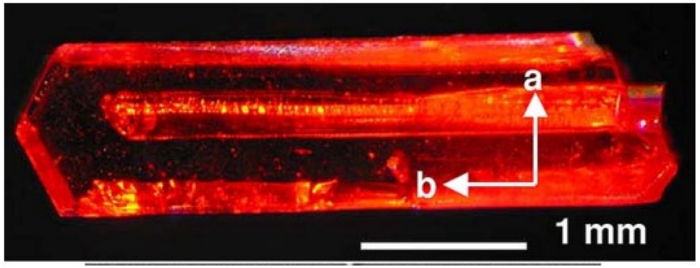


Rubrene single crystal results

- Grows in large single crystals
- Excellent mobilities reported: 40 cm^2/Vs (Hasegawa&Takeya 2007)







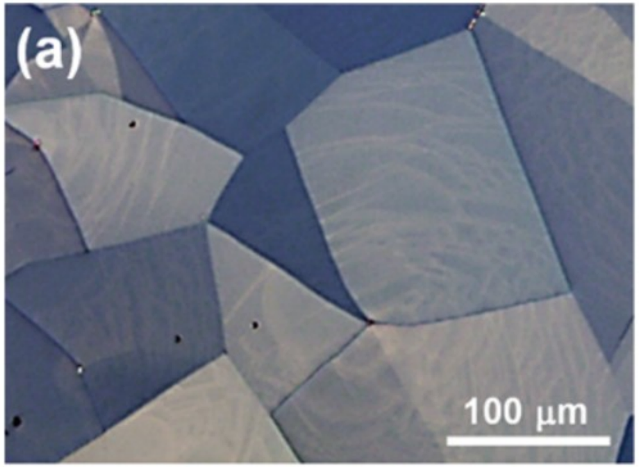
Gershenson, Podzorov &Morpurgo, Rev. Mod. Phys. 78, 973 (2006)

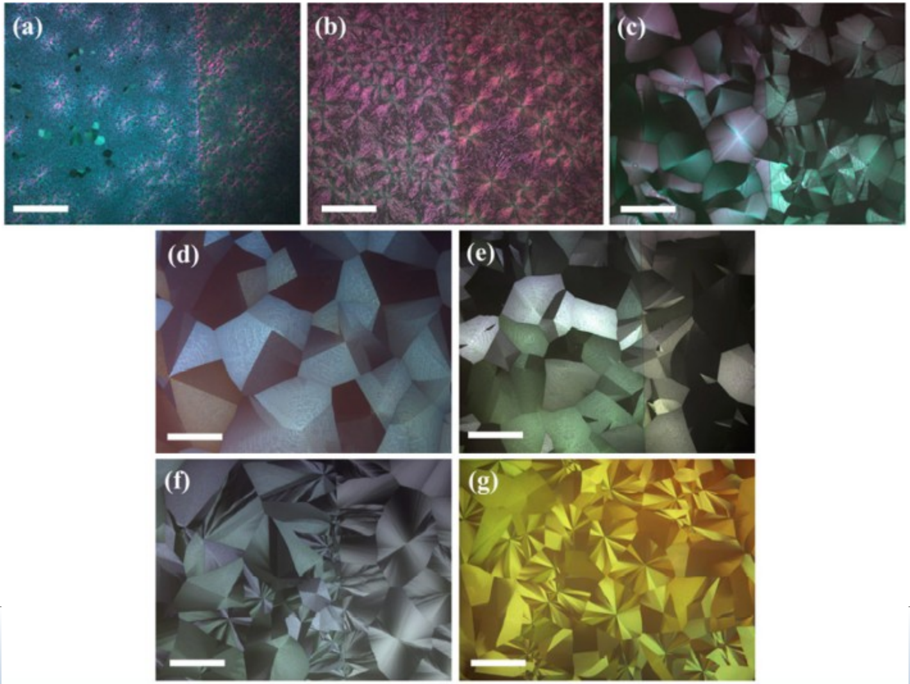
V. Podzorov et al., Appl. Phys. Lett. 82, 1739 (2003)
V. Podzorov et al., Appl. Phys. Lett. 83, 3504 (2003)
V. C. Sundar et al., Science 303, 1644 (2004)
V. Podzorov et al., Phys. Rev. Lett. 93, 086602 (2004)
O.D. Jurchescu et al., Acta Cryst. B62, 330 (2006)
J. Takeya et al., Appl. Phys. Lett. 90, 102120 (2007)
T. Hasegawa and J. Takeya, Science and Technology of Advanced Materials 10, 024314 (2009)

Highly ordered rubrene films

- Rubrene evaporated as thin film
- Heating to 130-170^{0}C forms large crystals
- Organic underlayer allows morphology control

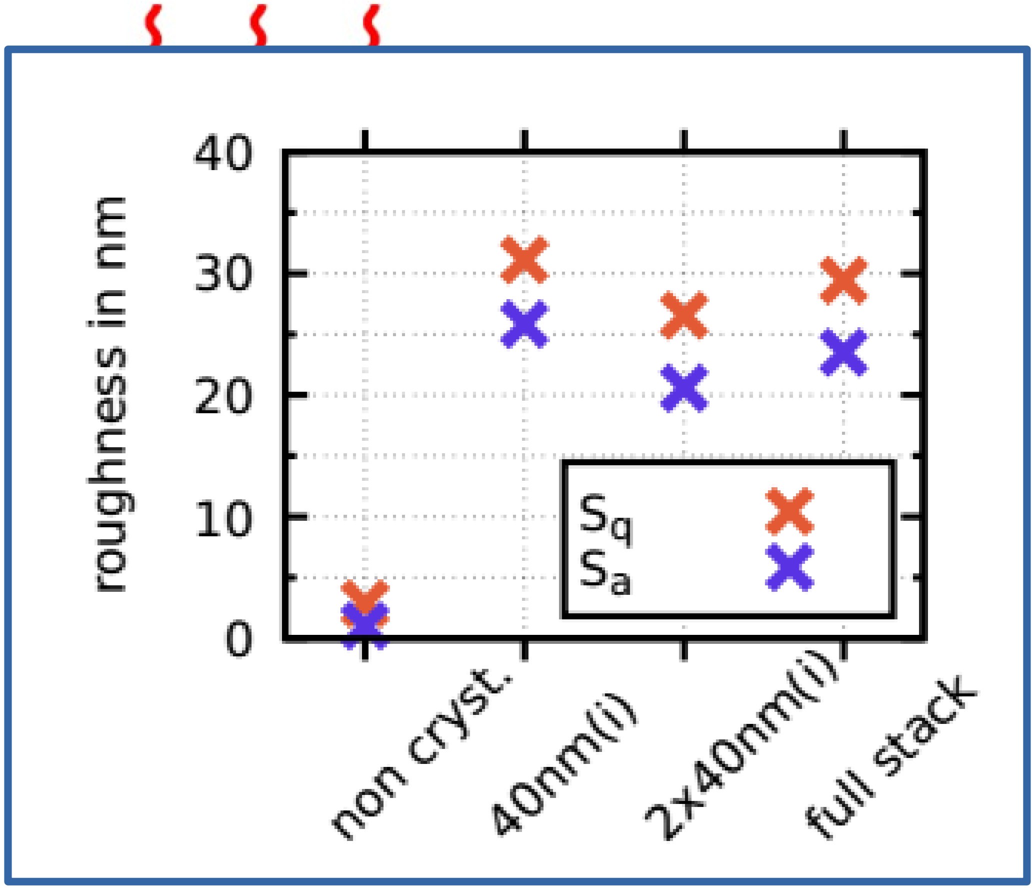
S.-W. Park et al., Appl. Phys. Lett. **90**, 153512 (2007)
H. M. Lee et al., ACS Nano **5**, 8352 (2011)
M.A. Fusella et al., Chem. of Mater. 29, 6666 (2017)





Epitaxial growth is possible!

- Evaporation of amorphous film
- Annealing In glove box
- Triclinic and orthorombic structure

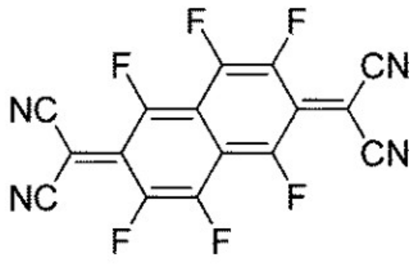


Further layers grow epitaxially!

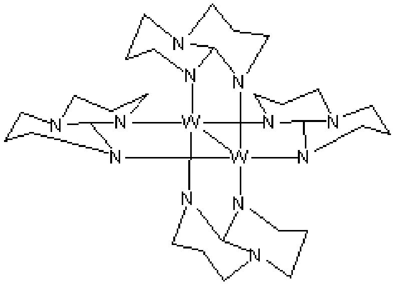
M. Sawatzki, PhD thesis, TU Dresden

Highly ordered rubrene films: Doping

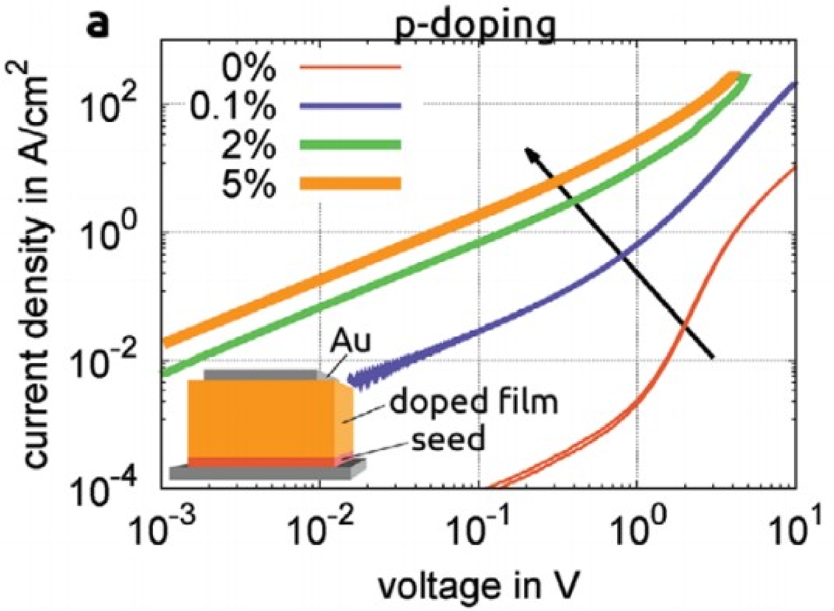
- Layers can be reasonably well p- and n-type doped
- Doping efficiency in the 1...5% range: expected due to reserve regime



F6-TCNNQ



$W_2(hpp)_4$



M. Sawatzki et al., Adv. Sci. 2003519 (2021)

Bipolar Organic Transistor

nature

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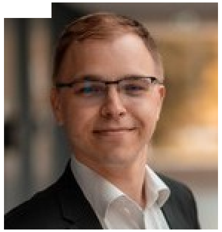
Article | Open Access | Published: 22 June 2022

Organic bipolar transistors

Shu-Jen Wang, Michael Sawatzki, Ghader Darbandy, Felix Talnack, Jörn Vahland, Marc Malfois, Alexander Kloes, Stefan Mannsfeld, Hans Kleemann & Karl Leo

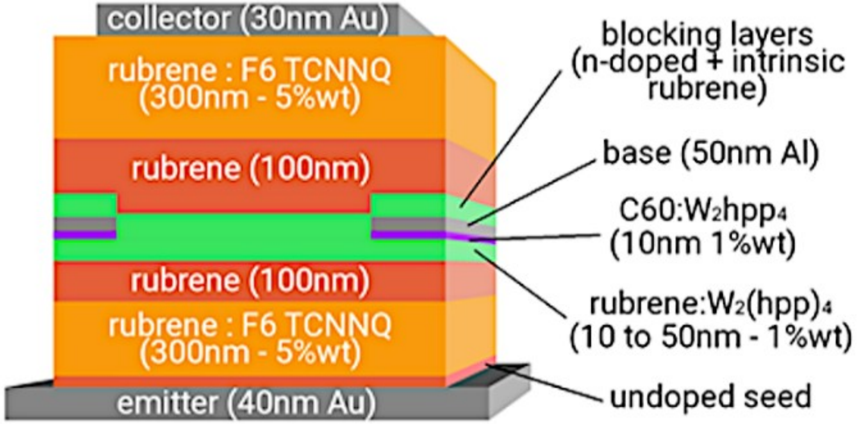
Nature **606**, 700–705 (2022) | Cite this article

S-J. Wang, M. Sawatzki et al., Nature **606**, 700-705 (2022)



Bipolar Organic Transistor

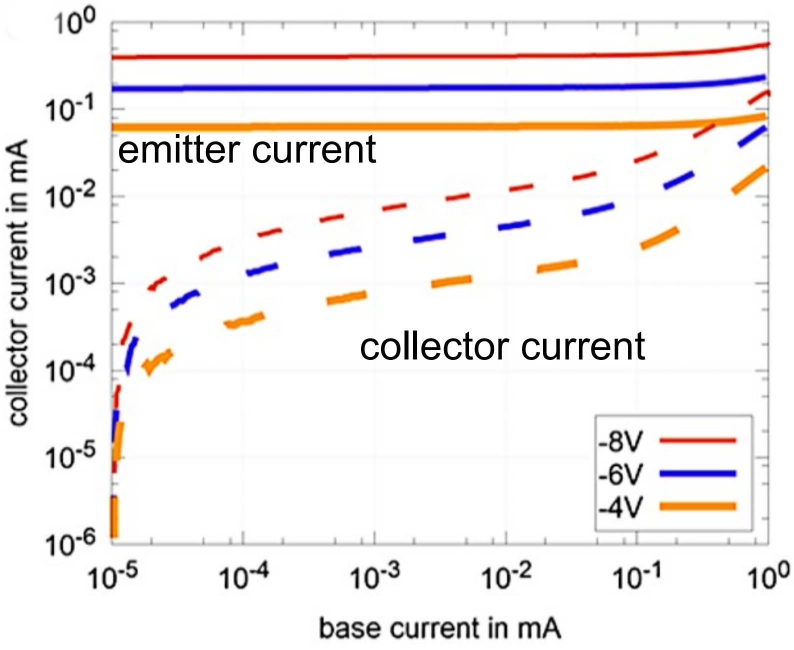
- Rubrene vertical pnp structure
- Pin diodes for reasonable blocking
- Challenge: Keep uniform potential in base: hit the right doping range!

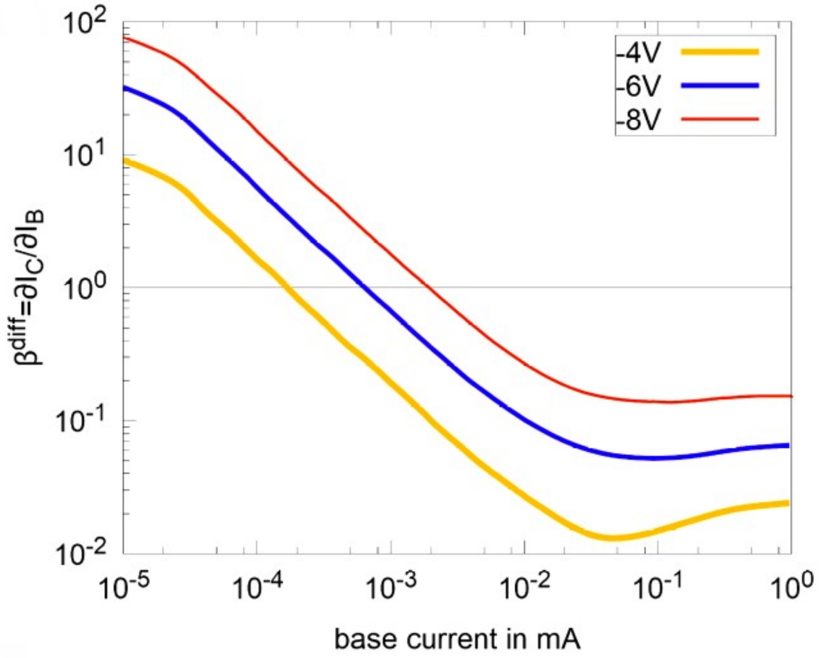


S-J. Wang, M. Sawatzki et al., Nature **606**, 700-705 (2022)

Bipolar Organic Transistor

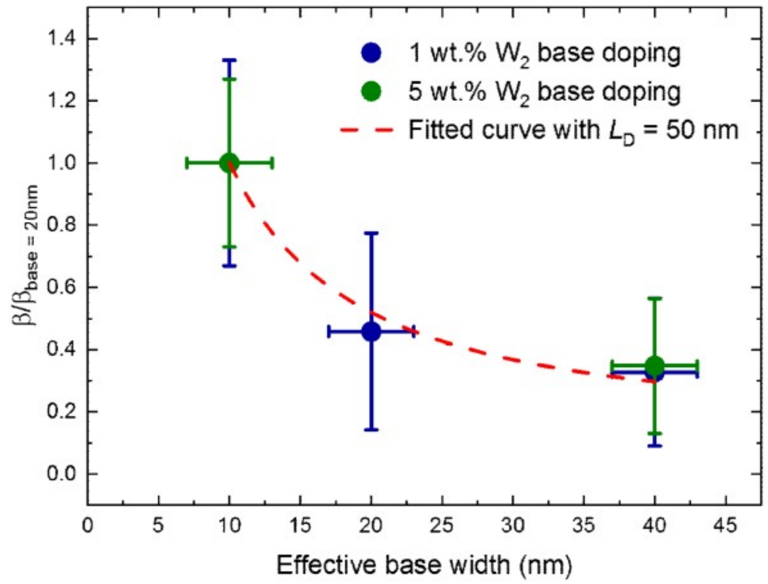
- Devices show clearly control of collector current with base current
- Comparatively high leakage current
- High differential gain





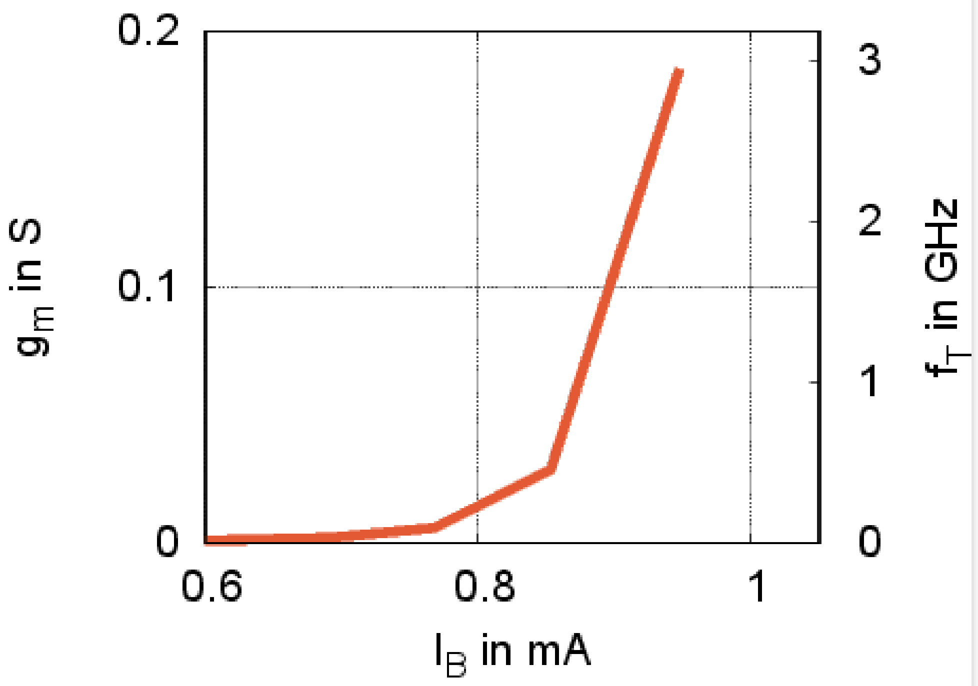
Minority carrier diffusion length

- Differential gain can be related to diffusion length $\beta \propto \coth\left(\frac{W}{L_D}\right)$
- Different doping concentrations
- Compatible with $\tau = \frac{1}{\gamma n_0}$ law
- Best fit: $L_D \sim 50$nm



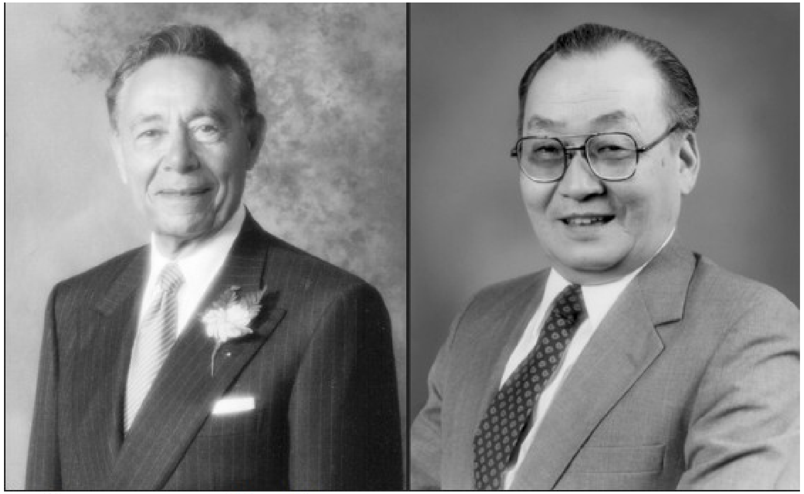
Transistor speed estimation

- Transition frequency: $f_T = \frac{g_m}{2\pi C}$
- with $g_m = \frac{\partial I_c}{\partial V_{BE}} = \beta \frac{\partial I_B}{\partial V_{BE}}$
- g_m ~0.1 S and C~10 pF
- Speed estimate: **1.6 GHz**



History of transistors

John Bardeen William Shockley Walter Brattain



Source: www.wikipedia.com

Martin Atalla Dawon Kahng

Inorganics: Bipolar transistor: 1947 Field-effect transistor: 1960

Organics: Bipolar transistor: 2022 Field-effect transistor: 1986

Outline

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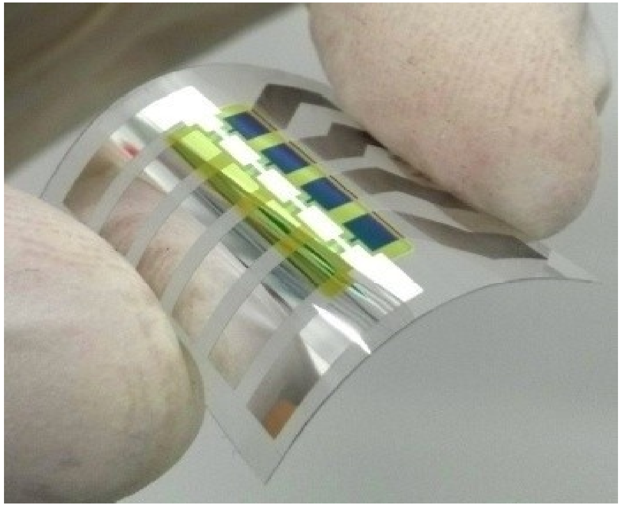
- Organics for Neuromorphics
- Resorbable Organics



Why Bioelectronics?

Information processing in Nature und Technology:
Materials and functions are very different!

soft (<10kPa), water based (>70%), neuromorphic

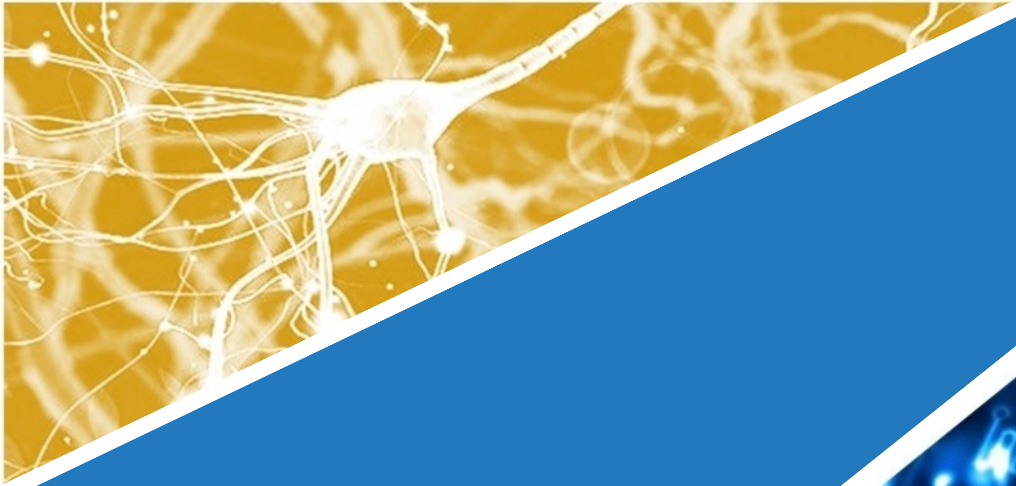
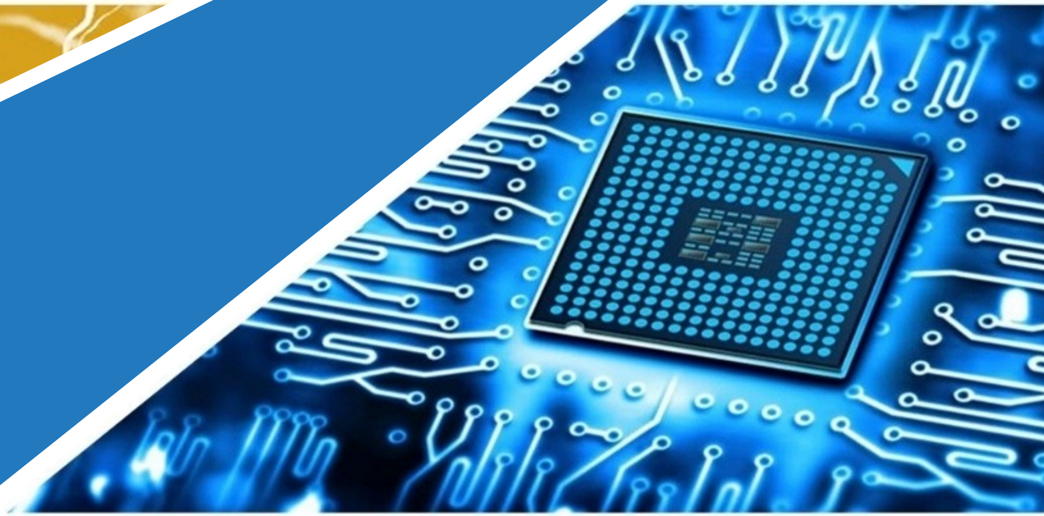
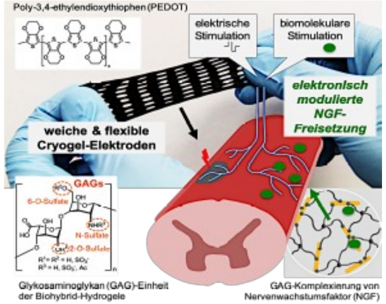


Figure: Carsten Werner

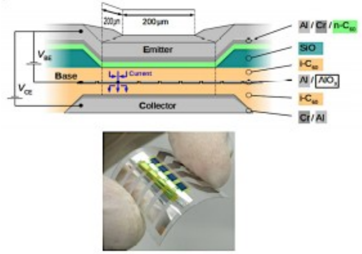


rigid (GPa), dry, von Neumann

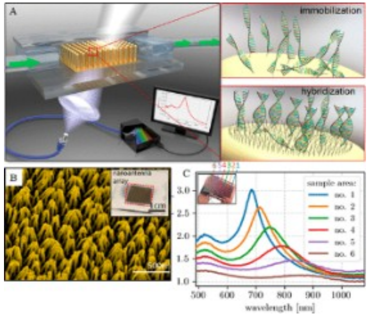
Smart Electronics for Humans



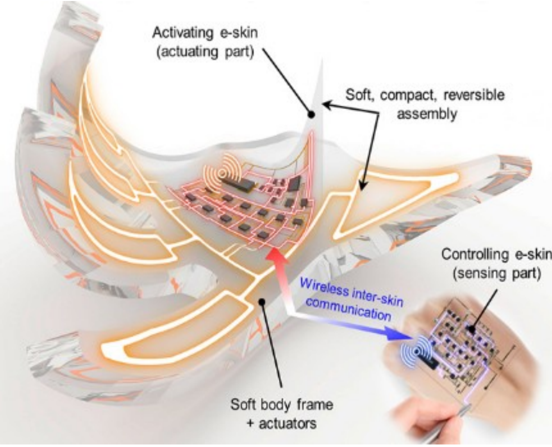
Drug release



Logic



Sensory

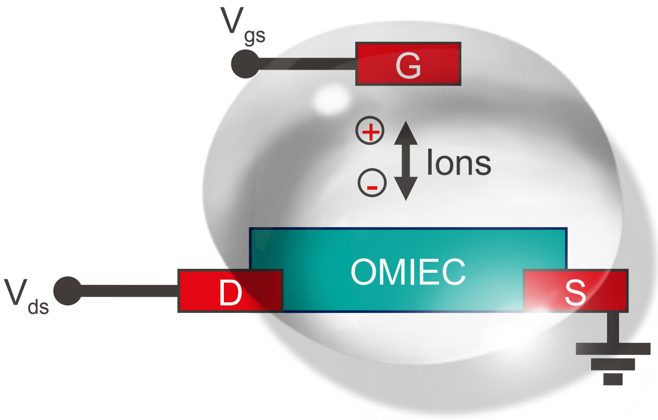


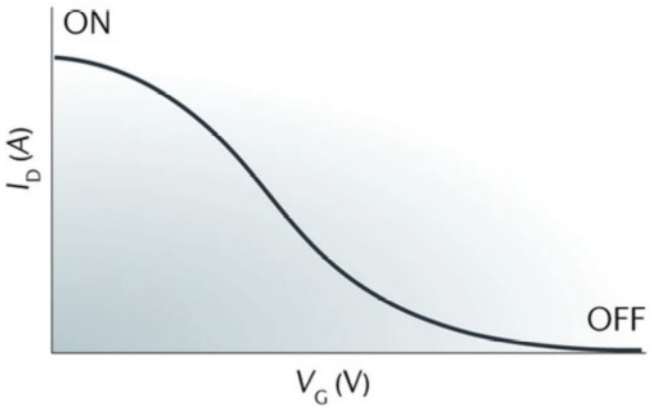
Complex Systems

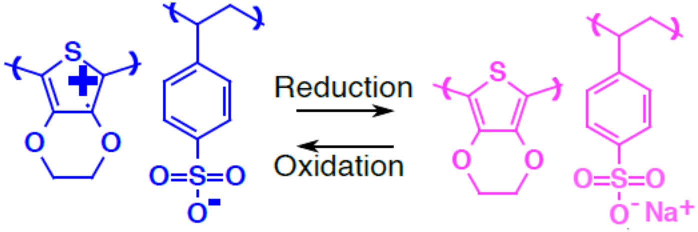
⋮

Additional Fuctionality

Organic electrochemical transistors





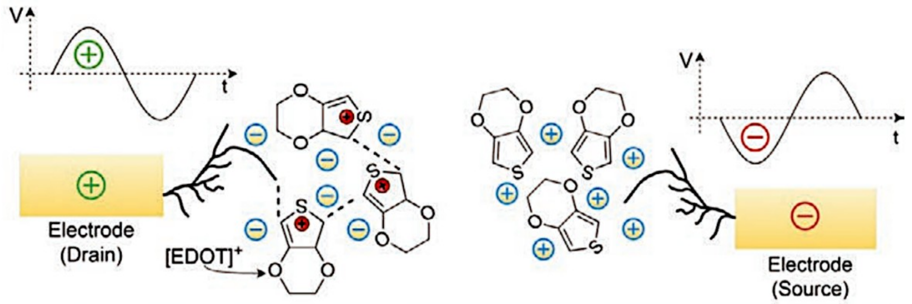


$PEDOT^+$ PSS^- $PEDOT^0$ PSS^- Na^+

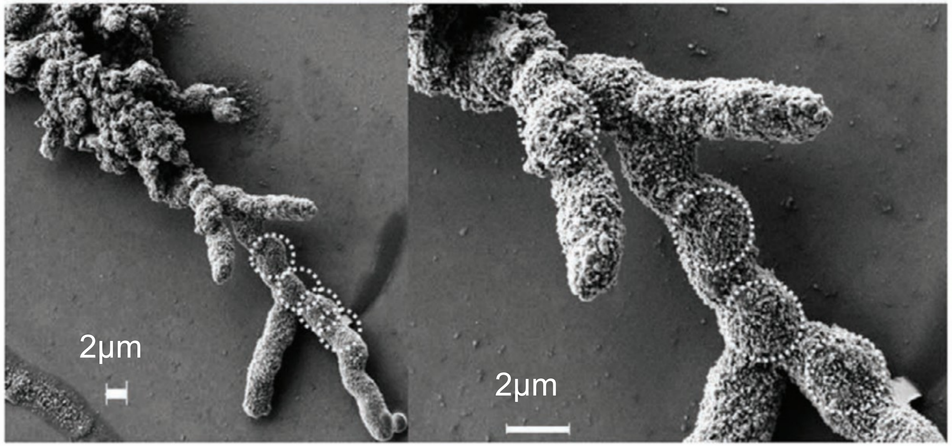
- Biocompatible
- Soft
- Water-stable
- Low-power
- …

Rivnay et al., *Nature review materials*, **3**: 17086 (2018)

Polymer network by field directed electropolymerisation



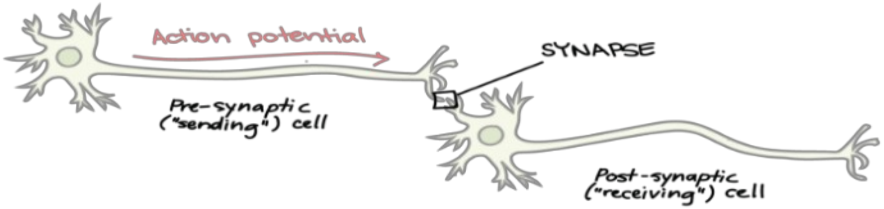
- EDOT with NaCl in Water
- Potential and frequency tune directionality and branching of fibers
- Fibers work as organic electrochemical transistors (OECT)



Matteo Cucchi

M Cucchi, H Kleemann, H Tseng, G Ciccone, A Lee, D Pohl, K Leo, Advanced Electronic Materials 7, 2100586 (2021)
M. Cucchi, PhD thesis, TU Dresden 2021

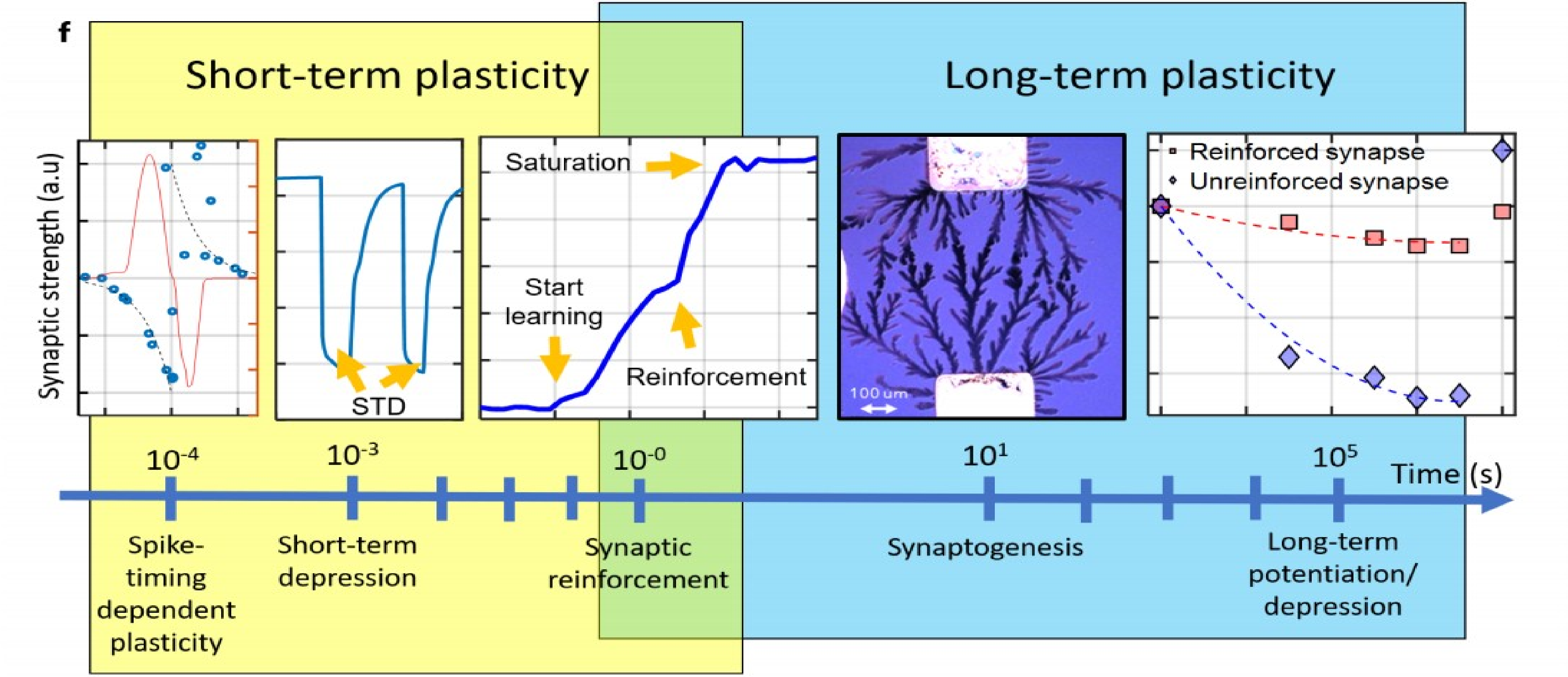
Polymer fibers: Neuromorphic function



- Network resembles the geometry and function of synapses
- Artificial Neuronal Networks
- Pavlovian conditioning and pattern recognition shown

M Cucchi, H Kleemann, H Tseng, G Ciccone, A Lee, D Pohl, K Leo, Advanced Electronic Materials 7, 2100586 (2021)

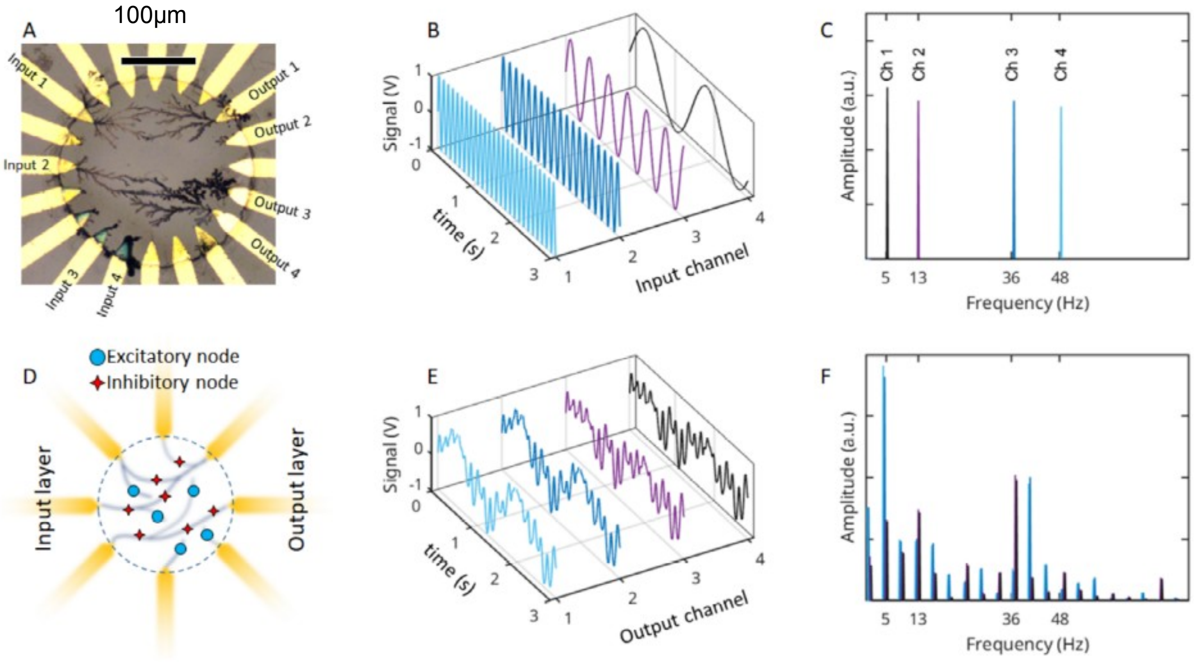
Short- and Long-term Plasticity



M Cucchi et al., Advanced Electronic Materials 7, 2100586 (2021)

Reservoir Computing: Nonlinearity

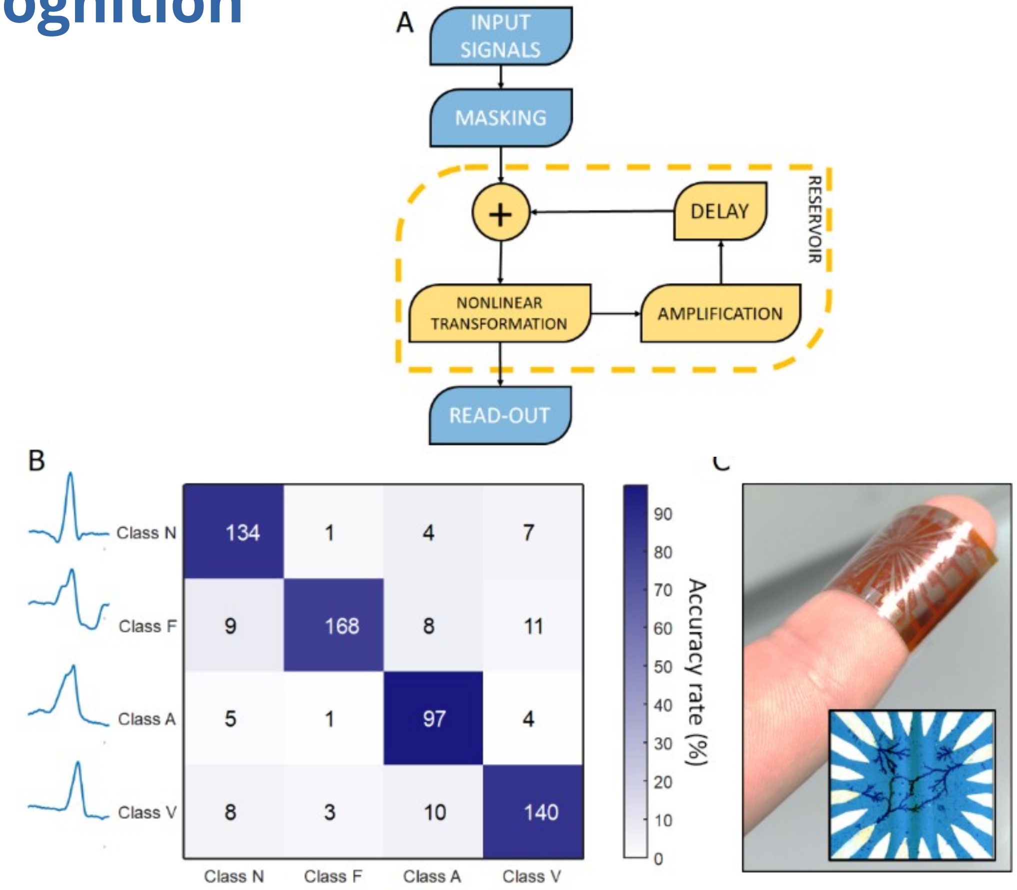
- Polymer fibers form nonlinear network
- Sum and difference frequencies in output channels



M. Cucchi et al., Science Advances 7, eabh0693 (2021)

Reservoir Computing: Pattern Recognition

- Reservoir employed for heartbeat pattern recognition
- Feedback loop improves results
- Competitive recognition rates
- Low power: 200nW



M. Cucchi et al., Science Advances 7, eabh0693 (2021)

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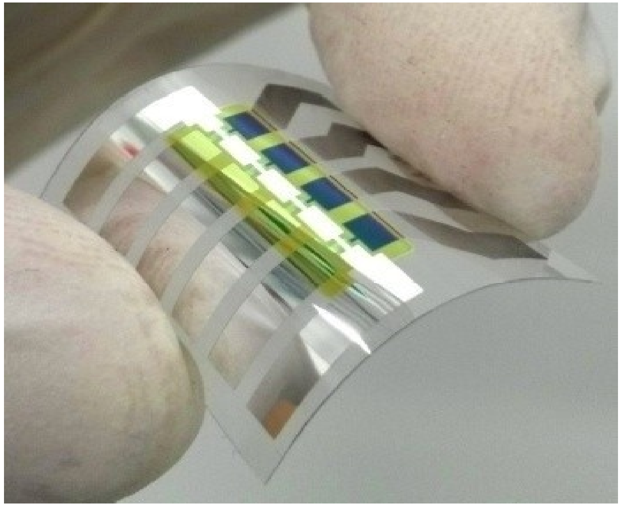

Pressure sensor in the middle ear

EKFZ Digital Health

frontiers

Bio-compatible sensor for middle ear pressure monitoring on a bio-degradable substrate

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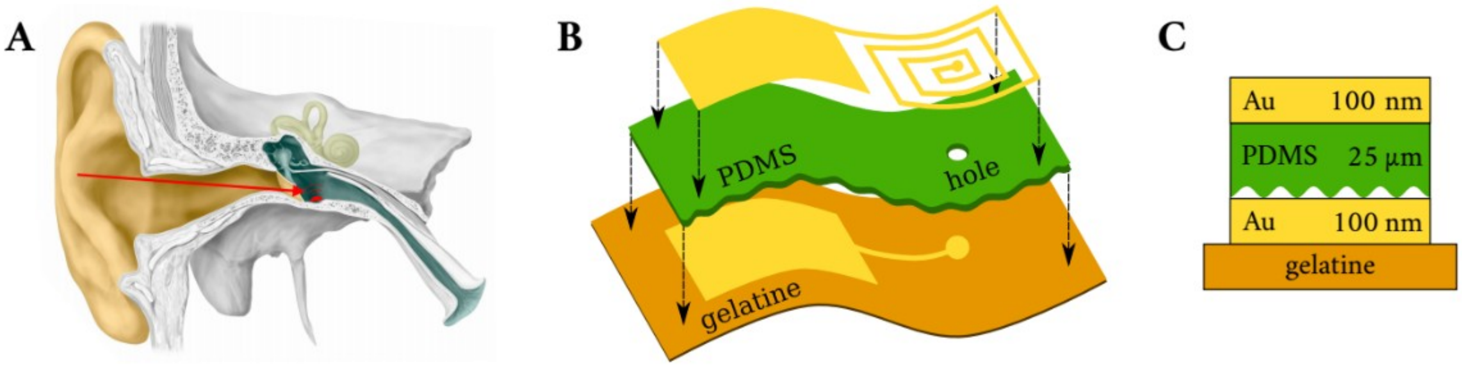
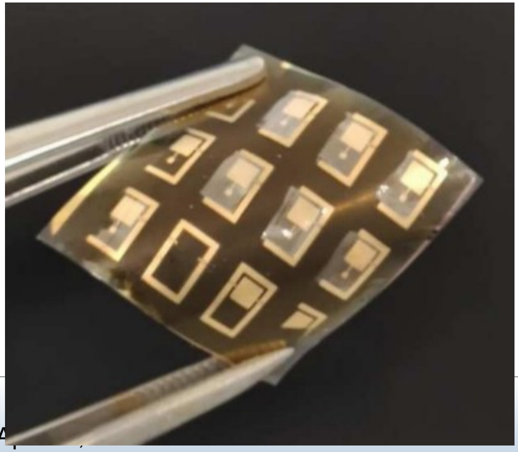
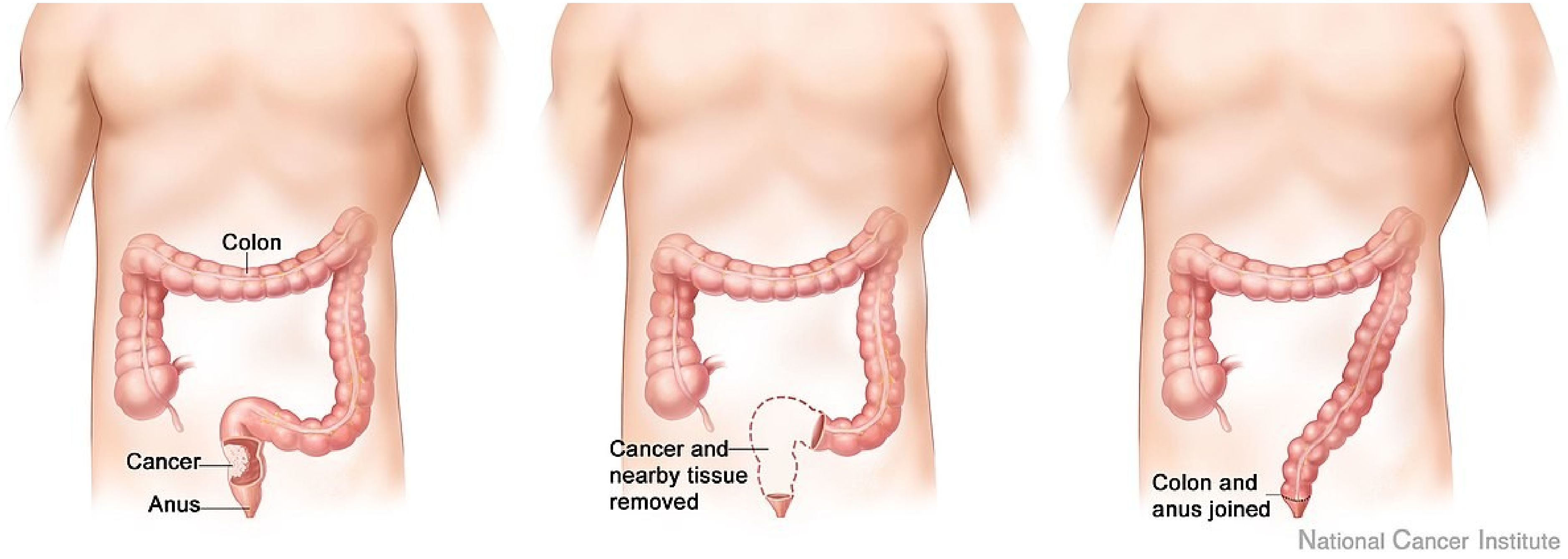


Figure 1. **(A)** Scheme of a human ear. The red arrow indicates the position of the pressure sensor within the middle ear (adapted from [22]). **(B)** Schematic illustration of the sensor structure on a flexible gelatine substrate. **(C)** Cross-section of sensor structure.

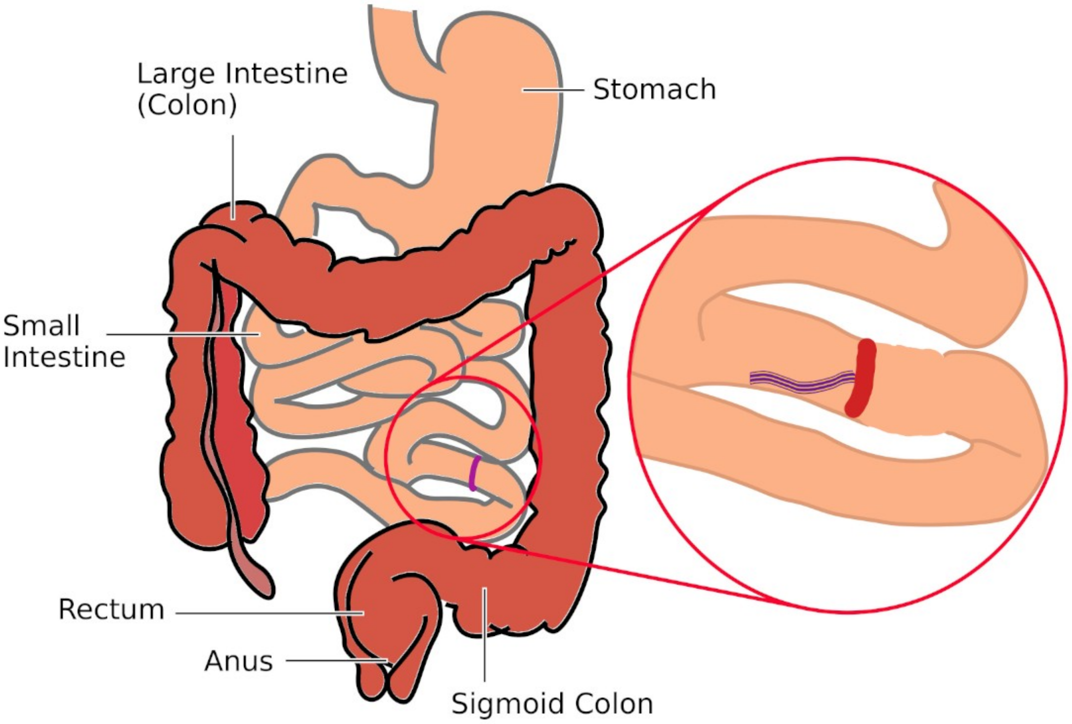


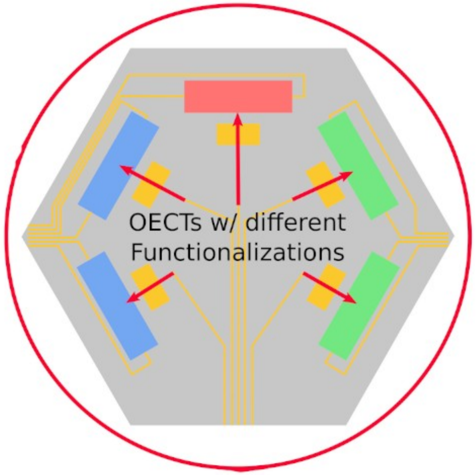
Anastemosis

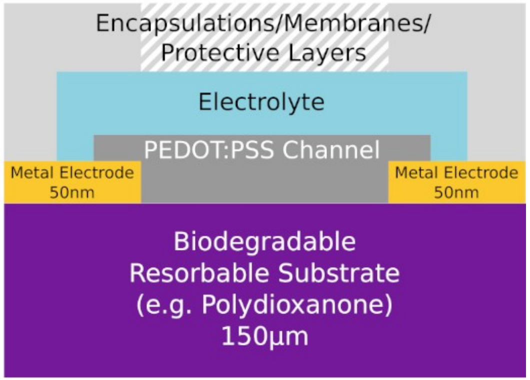


- High Risk of leakage
- Very dangerous for patient
- Difficult to detect

Sensor for Anastemosis-Leakage







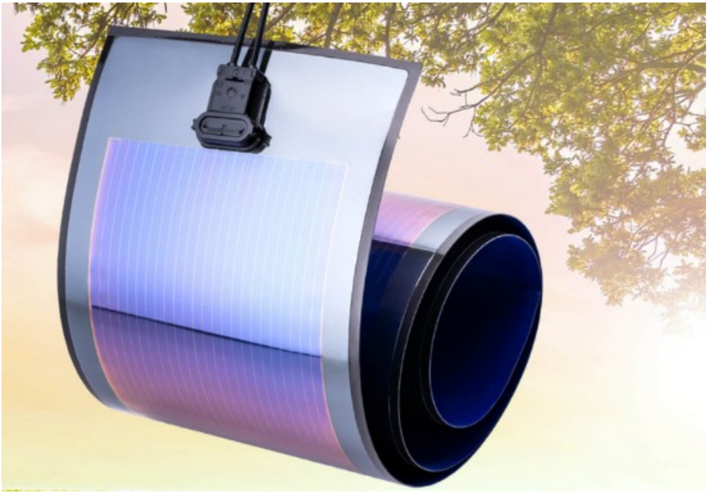
With C. Schafmayer et al. Univ. Rostock

Test on pigs

- Sensor implemented
- After 14 days covered by body
- Next step: sensor functions

Heliatek

INDEPENDENT. GREEN. FUTURE.



- Founded in 2006
- Production of Small-Molecule Organic Solar Cells
- 4 investment rounds: BASF, Bosch, RWE, Engie, VC
- 13.2% @ $1 cm^2$ efficiency reached
- **www.heliatek.com**


Heliatek
Dresden Mass Manufacturing Line
5,000 m² floor space
~1 million m²/year capacity

Carbon Dioxide Budget

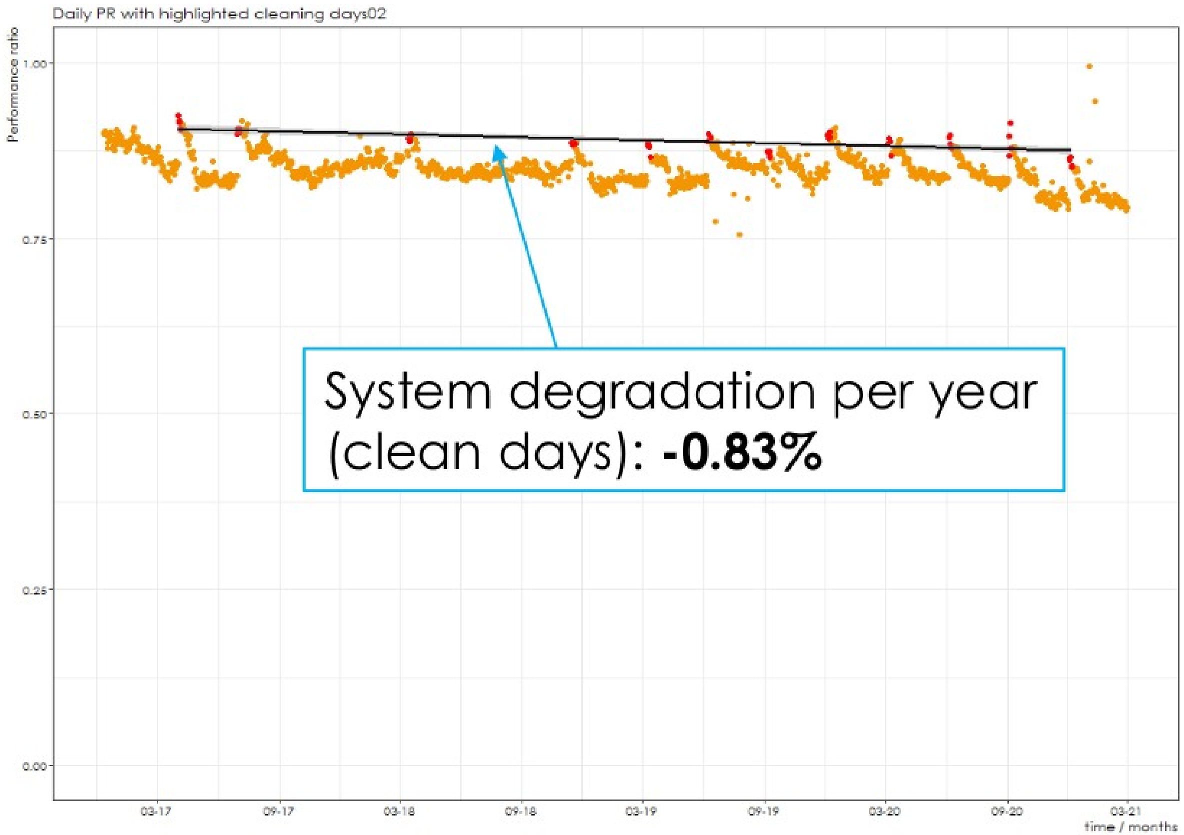
- Manufacturing: 16 kg CO_2 per m^2
- Results in 7-9g CO_2 per kWh
  (in central Europe, better in southern locations)
- Energy fed back after 3 months operation:
  4-10x better than crystalline silicon
- Lowest CO_2 footprint of any energy generating technology!

Lifetime >20 years expected in outdoor environment

Seris Outdoor Module Testing in Singapore

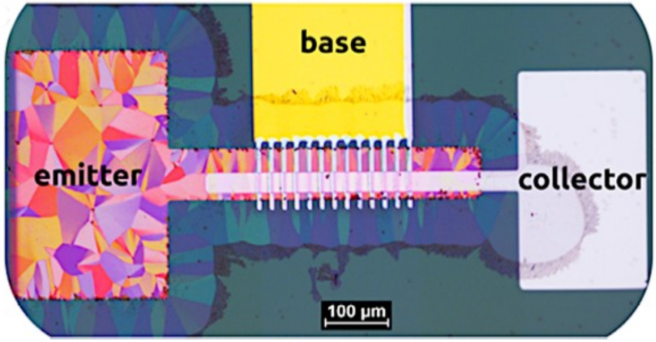
Heliatek
The future is light

- **Test:**
  - Nominal module power: 22 Wp
  - Test period: From Dec 2016 onwards (ongoing)
  - Data saved daily
- **Finding:**
  - Performance ratio decreases only **< 1 % per year**



Conclusions

- Organic semiconductors: a success story
- Highly crystalline doped rubrene layers: the age of GHz organic electronics has begun
- Organic Bioelectronics: breakthrough potential
- Stability for mass application is there!



Acknowledgments

Hans Kleemann
Björn Lüssem
Sebastian Reineke
Moritz Riede
Martin Schwarze
Matteo Cucchi
Peter Birkholz
Stefan Mannsfeld
Jochen Hampe
Carsten Werner

Martin Pfeiffer
Jan Blochwitz-Nimoth
Ronny Timmreck

And many, many more I cannot personally mention!

ICSM 24

International Conference on the Science and Technology of Synthetic Metals

23–28 June 2024
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ICSM is the largest conference on organic electronics and has covered the most important developments in this field for over 40 years

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