PHAS0058

Physics of Advanced Materials

Lecture 4: Organic Field Effect Transistors (OFETs)

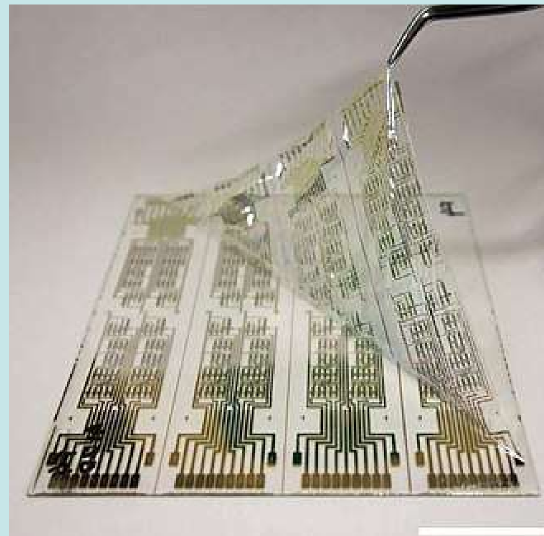
In this lecture…

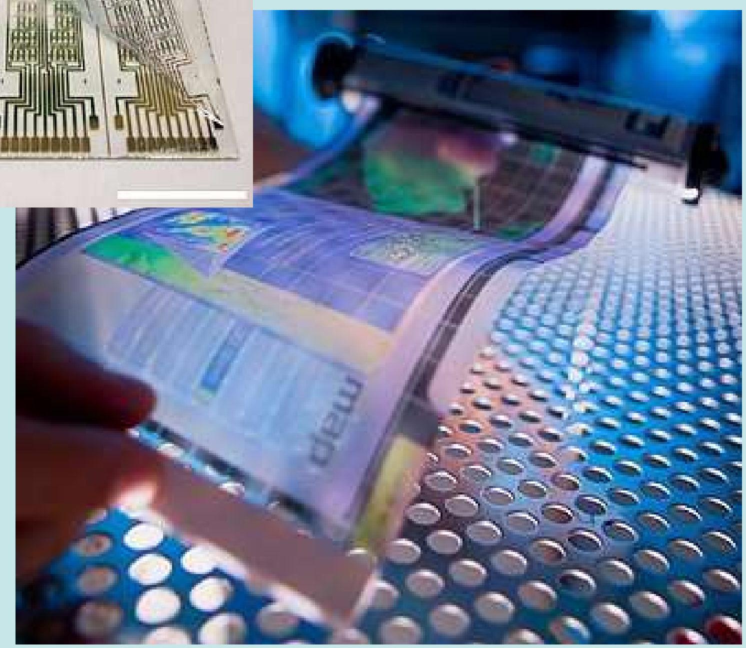
- what are OFETs
- basic physics
- characterisation of OFETs
- materials
- optimisation
- Organic Thermoelectrics (OTEs)

What are OFETs?

Motivation for OFETs

- low performance logic
  - RFID tags
  - chip cards
  - e-paper
- high performance logic
  - driving stages for polymer displays





Field Effect Transistor

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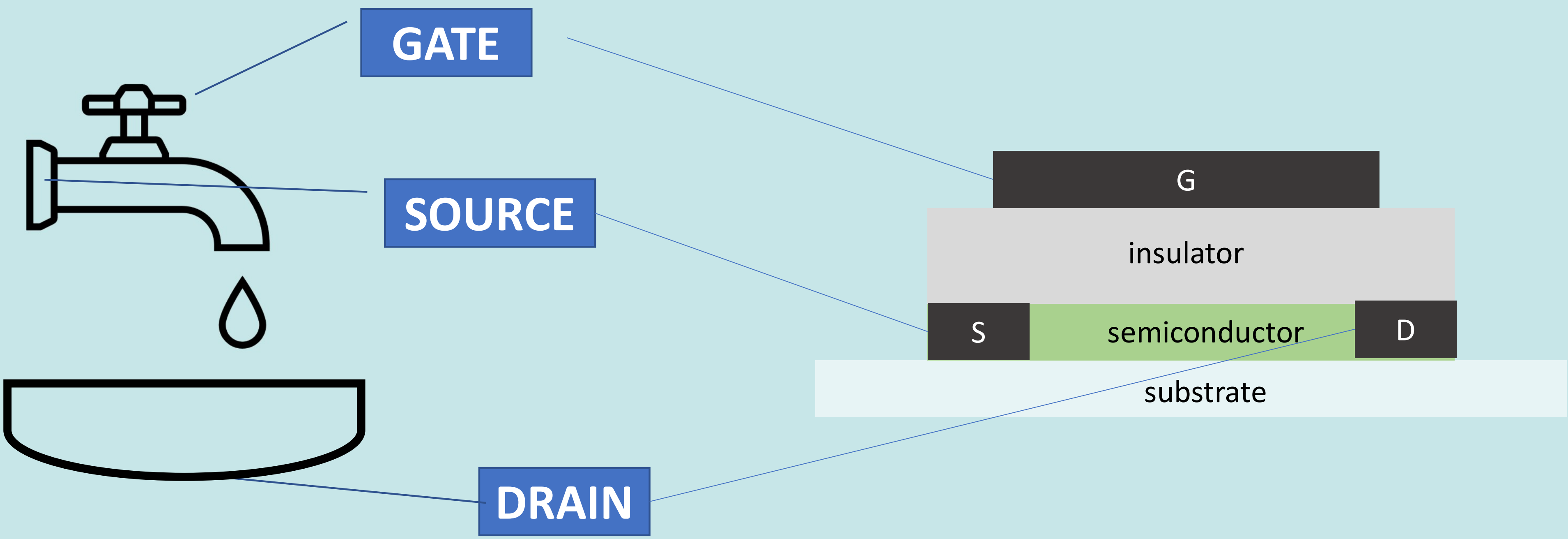

OFET architectures (OTFTs)

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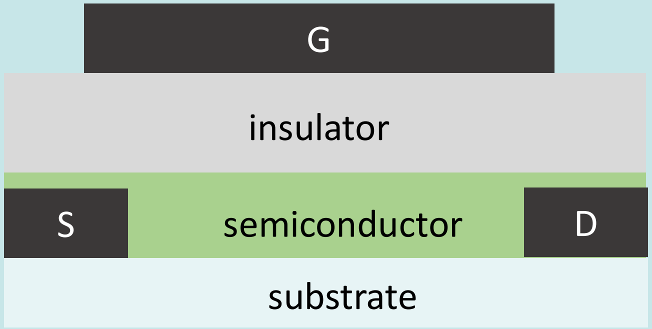
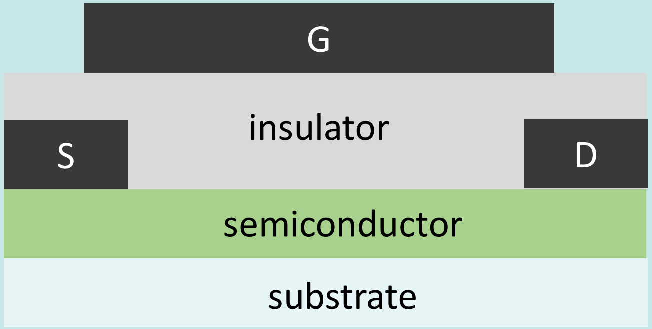
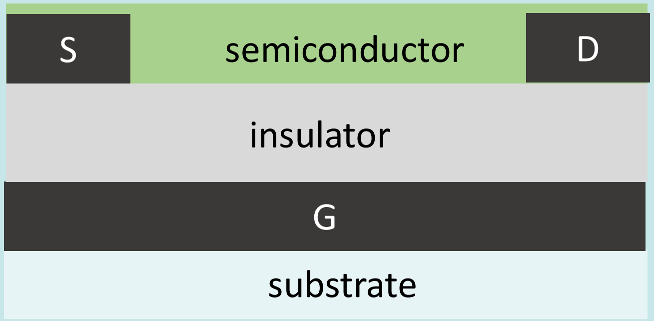


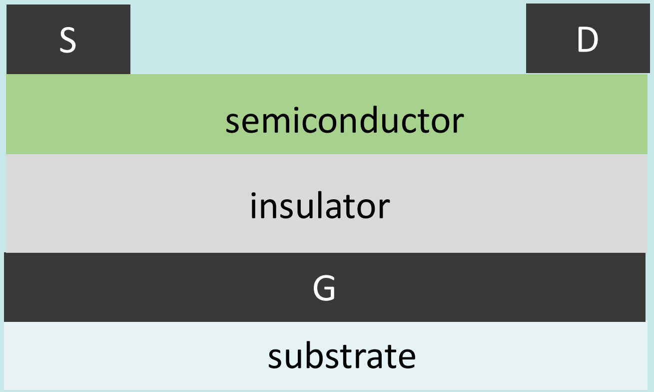
top gate, bottom contact



top gate, top contact

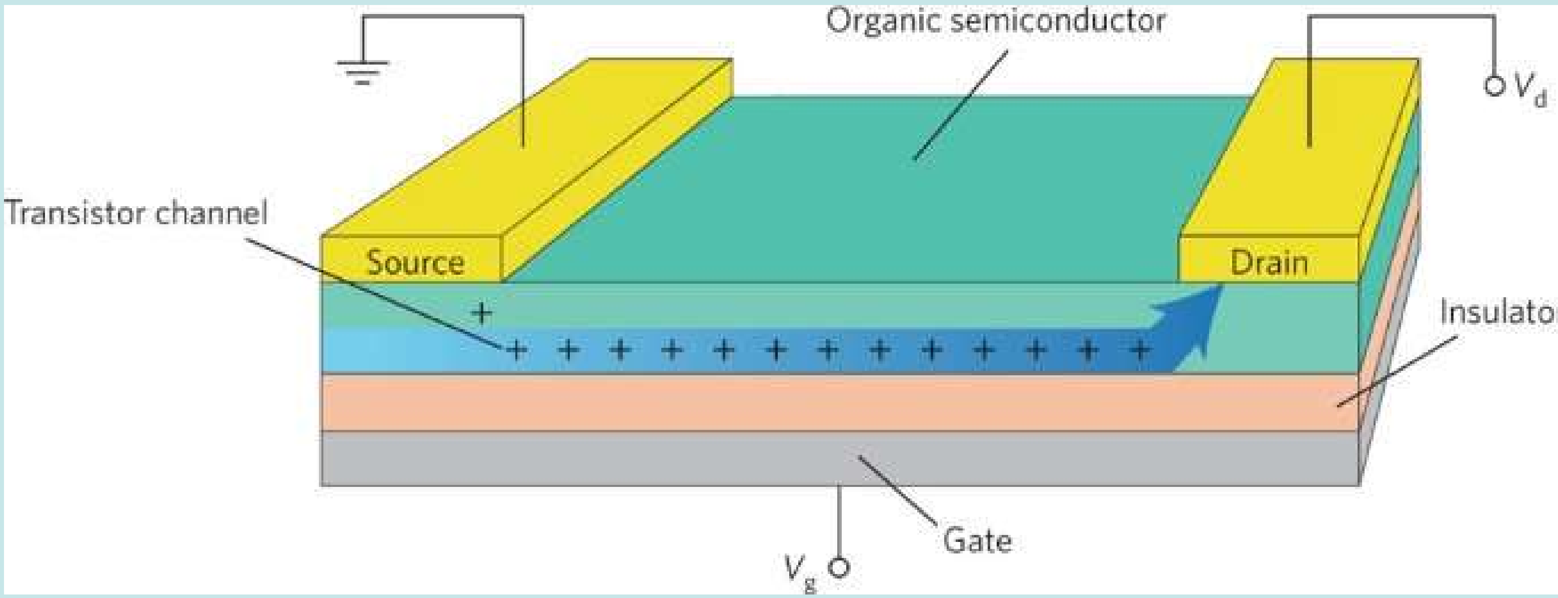


bottom gate, bottom contact



bottom gate, top contact

Transistor channel



- gate voltage causes charge accumulation in semiconductor by polarisation of the dielectric
- charge density modulated by gate field ("field effect")
- reverse polarity by reversing gate voltage
- p-type, n-type or ambipolar – depending on the semiconductor

Characterisation of OFETs

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Gradual channel approximation

assumptions:

- $\frac{L}{d} \geq 10$
- $V_G >> V_{SD}$
- μ independent of applied E field

$$Q = -C_{diel} V_{total}(x)$$

$$V_{total} = V_G - V(x)$$

L – channel length

d – thickness of the dielectric

Q – density of charge in the channel

C_{diel} – dielectric capacitance per unit area

x – distance between S and D

V_{Th} – minimal voltage required for opening a channel

μ – charge mobility

add threshold voltage to fill charge traps:

$$Q_{mobile} = -C_{diel}(V_{GS} - V(x) - V_{Th})$$

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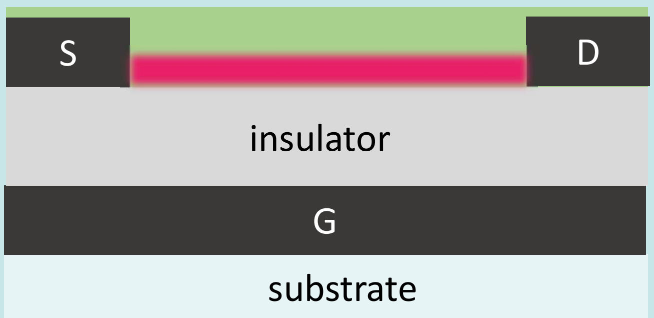
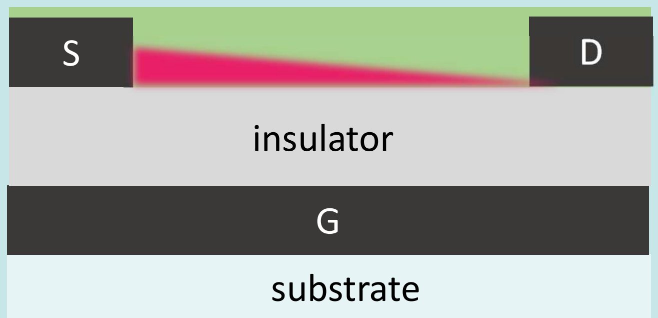
Current in an OFET

$$V_{DS} < |V_G - V_{Th}|$$



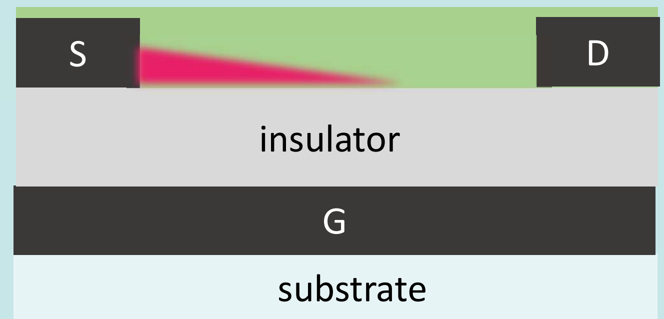
LINEAR REGIME
- free carriers available everywhere in the channel
- I_D increases with V_{DS}

$$V_{DS} = |V_G - V_{Th}|$$



PINCH-OFF
- depletion of free carriers at D
- I_D starts to saturate

$$V_{DS} > |V_G - V_{Th}|$$



SATURATION REGIME
- depletion region grows
- I_D saturated (constant)

$$I_D = \mu W Q E_x = -\mu Q W \frac{dV}{dx}$$

$$I_D dx = \mu W C_{diel}(V_G - V(x) - V_{Th})dV$$

W-channel width
Ex – electric field in the direction of current flow
μ – charge-carrier mobility

Characterisation equations for OFETs

$$I_D = \frac{W}{L}\mu C_{diel}\left[(V_G - V_{Th})V_{DS} - \frac{1}{2}V_{DS}^2\right]$$

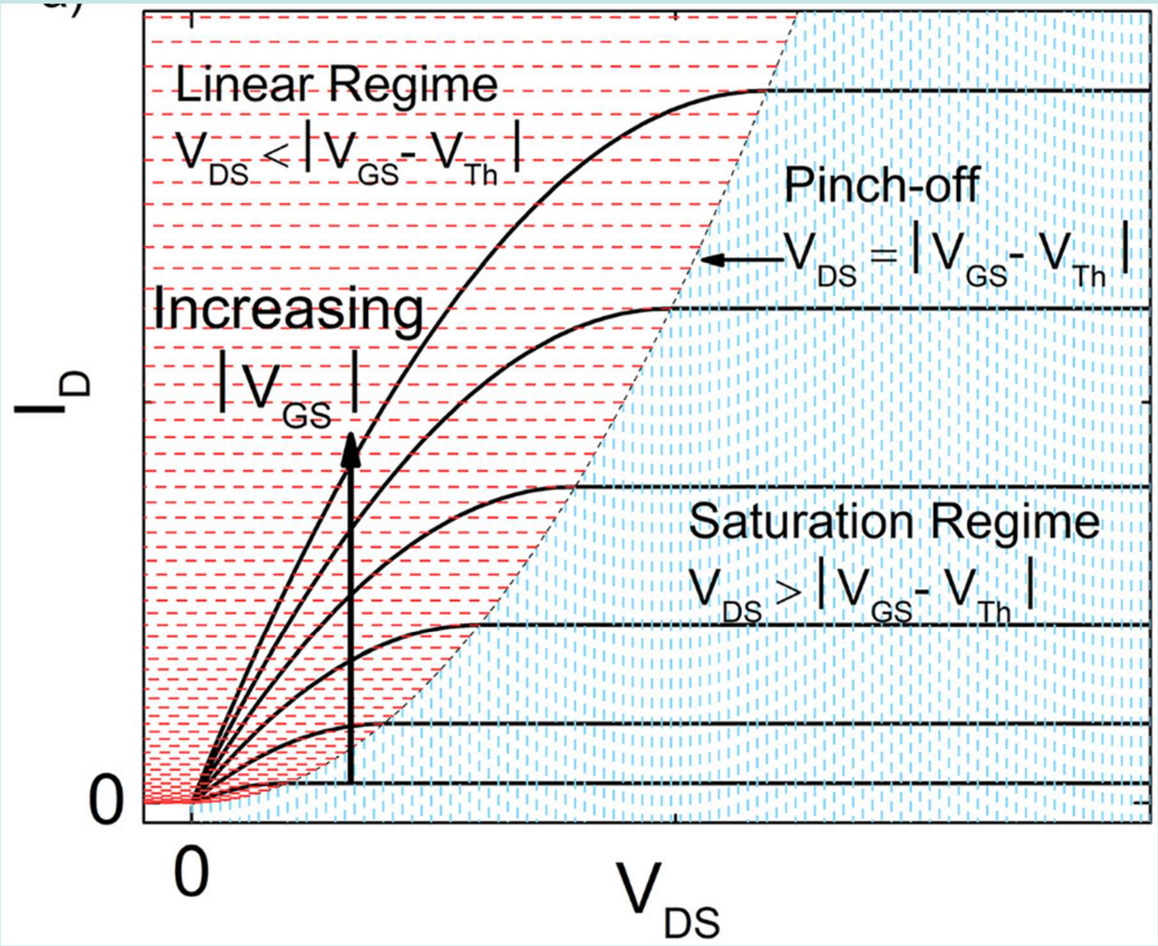
linear regime

once channel depletion starts, V_{DS}=V_G-V_{Th} is the max effective voltage, so by substituting we get:

$$I_{D,sat} = \frac{W}{2L}\mu C_{diel}(V_G - V_{Th})^2$$

saturation regime

Output curves



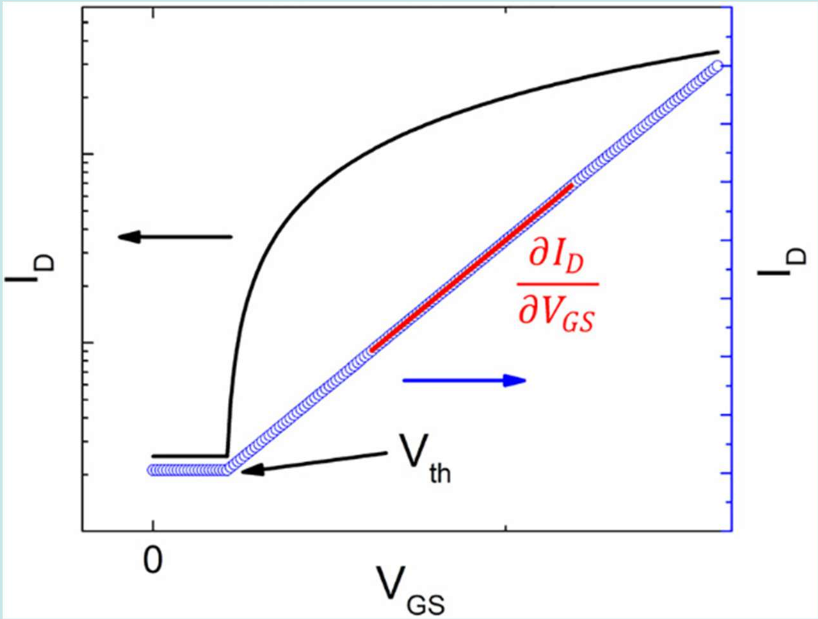
$$I_{D,lin} = \frac{W}{L}\mu C_{diel}\left[(V_G - V_{Th})V_{DS} - \frac{1}{2}V_{DS}^2\right]$$

$$I_{D,sat} = \frac{W}{2L}\mu C_{diel}(V_G - V_{Th})^2$$

Image from:Phys JA, Jurchescu OD (2019). J Appl Phys 124:071101

Transfer curves

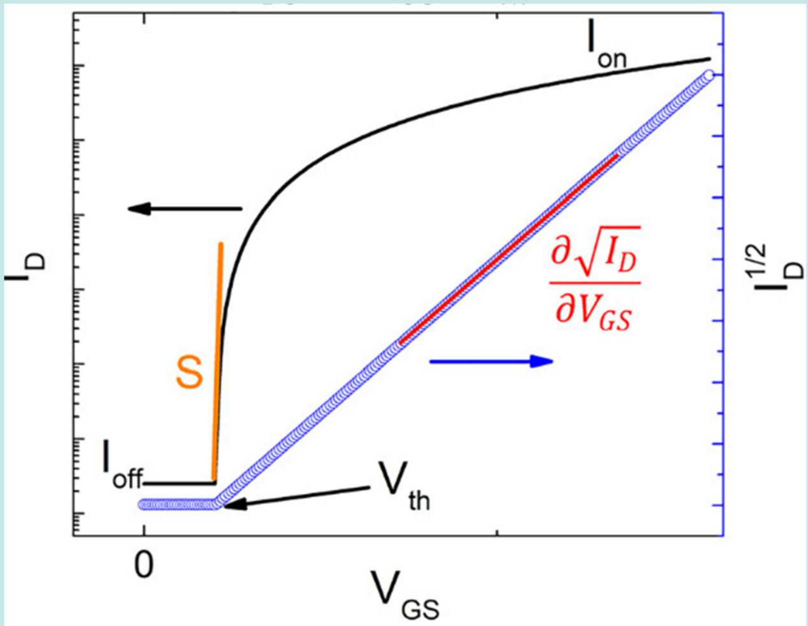
$$V_{DS} < |V_G - V_{Th}|$$



LINEAR REGIME

$$I_{D,lin} = \frac{W}{L}\mu C_{diel}\left[(V_G - V_{Th})V_{DS} - \frac{1}{2}V_{DS}^2\right]$$

$$V_{DS} > |V_G - V_{Th}|$$



SATURATION REGIME

$$I_{D,sat} = \frac{W}{2L}\mu C_{diel}(V_G - V_{Th})^2$$

Image from:Phys JA, Jurchescu OD (2019). J Appl Phys 124:071101

Extracting charge mobility

LINEAR REGIME

$$I_{D,lin} = \frac{W}{L}\mu C_{diel}\left[(V_G - V_{Th})V_{DS} - \frac{1}{2}V_{DS}^2\right]$$

$$\mu_{lin} = \frac{L}{C_{diel}WV_{DS}}\frac{\partial I_D}{\partial V_G}$$

SATURATION REGIME

$$I_{D,sat} = \frac{W}{L}\mu C_{diel}(V_G - V_{Th})^2$$

$$\mu_{sat} = \frac{2L}{WC_{diel}}\left(\frac{\partial\sqrt{I_D}}{\partial V_G}\right)$$

in theory: $\mu_{lin} = \mu_{sat}$

in practice: $\mu_{lin} < \mu_{sat}$

Horowitz, G. Organic thin film transistors: From theory to real devices. *Journal of Materials Research* **19**, 1946–1962 (2004)

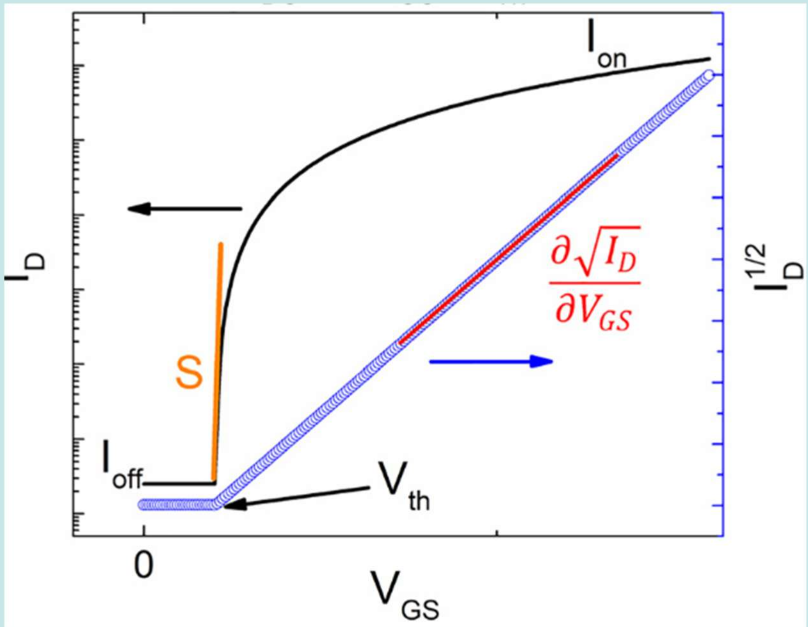
Other characteristics of OFETs

- **density of interfacial traps**
  - from threshold voltage change with temperature:

$$N_{it} = \frac{C_{diel}}{k_B T}\frac{\partial V_{Th}}{\partial T}$$

  - from **subthreshold swing** (orange line)
    - proportional to density of traps
    - high subthreshold slope (low swing) = fast switching
    - ideal value: < 1 V/dec

$$S = \frac{\partial V_G}{\partial(\log_{10} I_D)}$$



- **on/off ratio**
  - defines switching capabilities
  - I_{off} determined by dielectric material and semiconductor processing
  - I_{on} determined by mobility, operating voltages, gate capacitance, trap density
  - ideal value: 10^6

Organic materials for FETs

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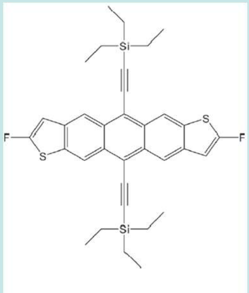
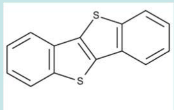
Materials for OFETs

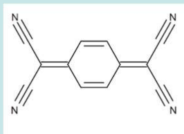
small molecules



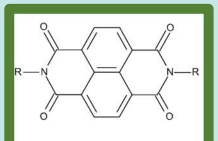
diF TES ADT



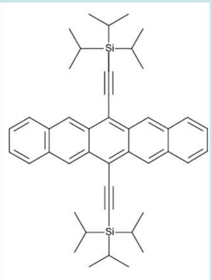
BTBT



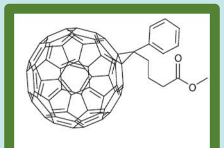
TCNQ



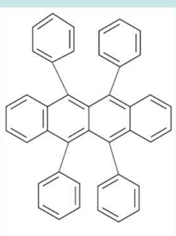
NTCDI



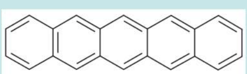
TIPS-pentacene



PCBM

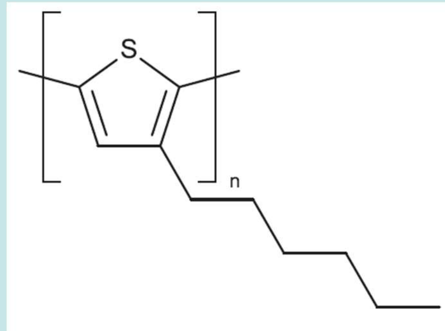


Rubrene

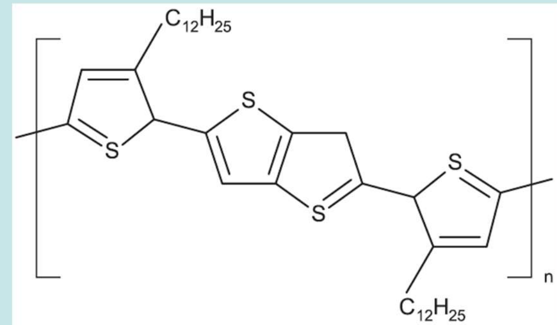


Pentacene

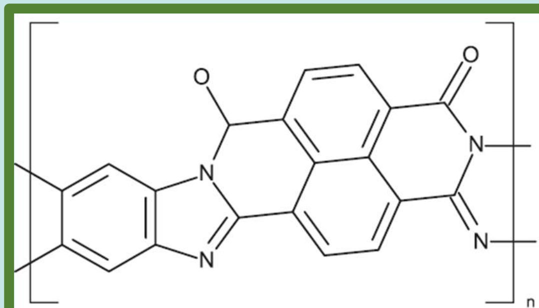
polymers



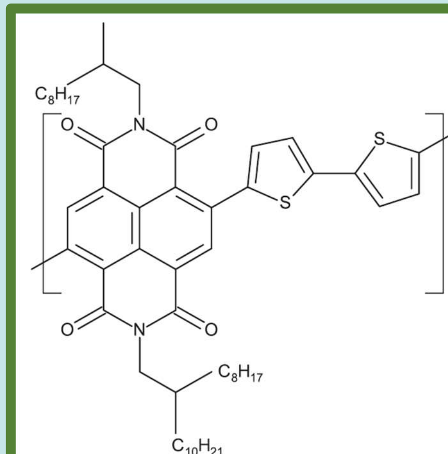
P3HT



PBTTT



BBL



P(NDI2OD-T2)

Rubrene single crystals

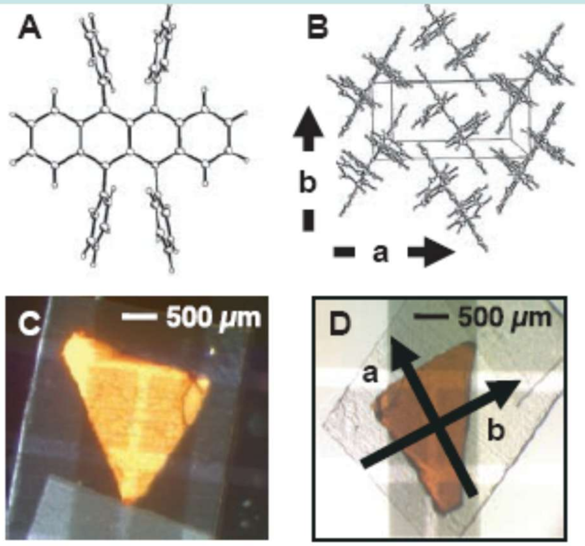


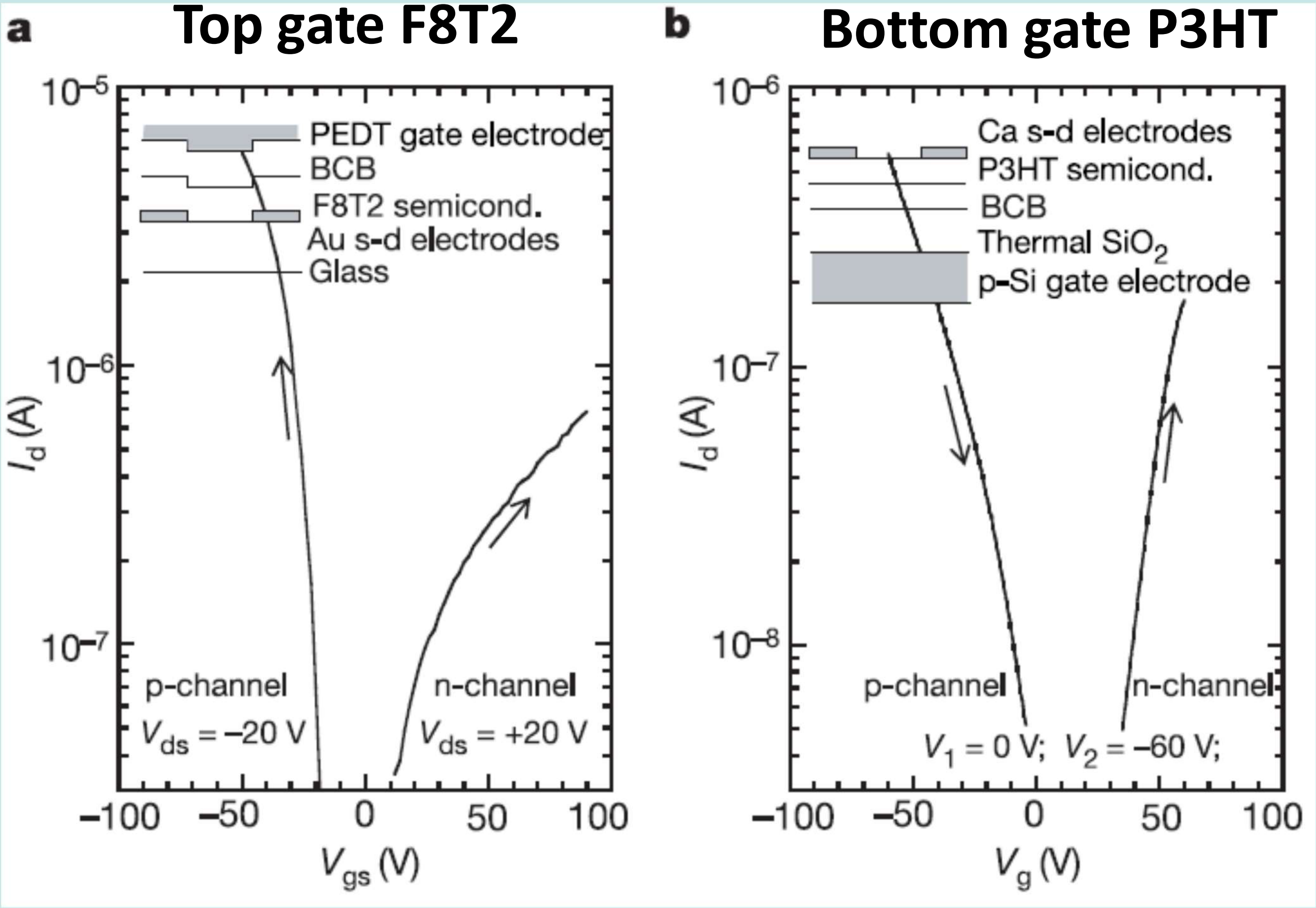
Fig. 2. (**A**) Molecular structure of rubrene. (**B**) Orthorhombic, crystallographic structure of a single crystal of rubrene shows the enhanced π-π overlap along the *b* direction and reduced overlap along the *a* direction. (**C**) Optical micrograph of a sample viewed through crossed polarizers. (**D**) Natural facets on the crystal surface correspond well to the crystallographic data and enable easy identification of the *a* and *b* axes confirmed by Laue diffraction.

Sundar et al. Science 303, 1644 (2004).

- mobilities of 15 cm2/Vs
- substituents allow favourable packing

- disadvantages:
  - rather fragile
  - requires PDMS stamping

Ambipolar OFETs



LL Chuah et al. Nature 434, 194 (2005)

P3HT

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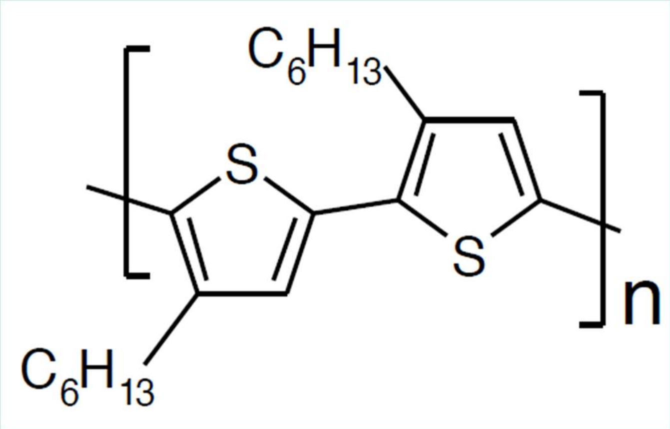
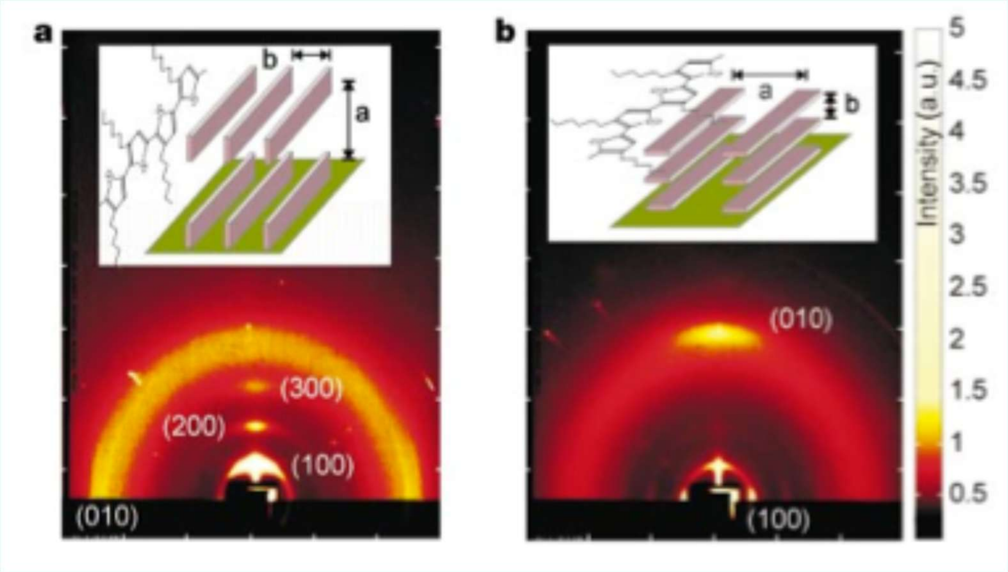
Regioregular Head-to-tail Poly(3-hexylthiophene),



mobilities of 0.1 cm2/Vs
sufficient to drive an organic LED



Z. Bao, et al. Appl. Phys. Lett. 69, 4108 (1996)
H. Sirringhaus, et al. Science 280, 1741 (1998)

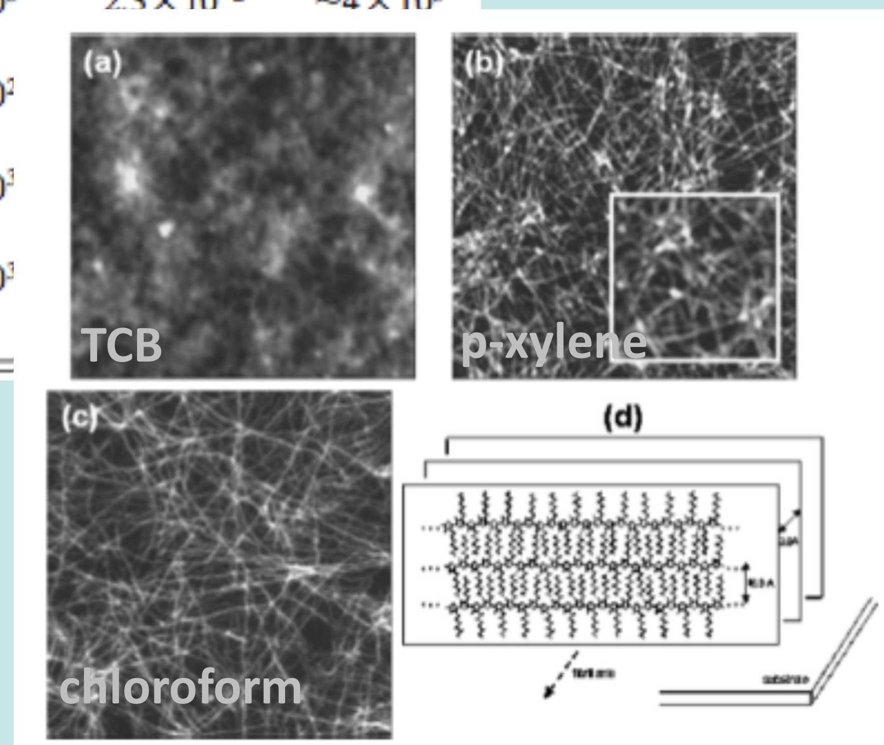
Optimisation of OFETs

Strategies for better performance

1) material design
   a) side chain engineering:
      i. solubility
      ii. molecular packing
      iii. polarity
      iv. film forming properties
   b) HOMO/LUMO design
   c) electrode materials
   d) improved conjugation (polymers)
2) interface engineering
   a) charge injection layers
3) fabrication
   1) deposition from solution:
      a) spin-coating
      b) drop-casting
      c) printing
   2) alignment
      a) friction transfer
      b) nanoimprinting
      c) E/B field alignment
      d) rubbing
      e) dip-coating, zone-casting
      f) …

Fabrication parameters

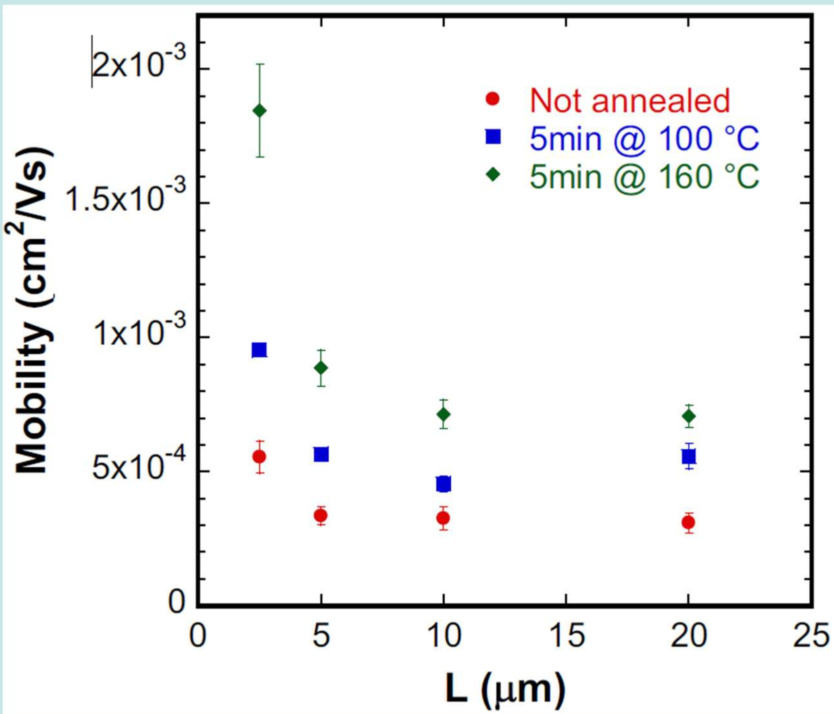
Solvent/Process	Dip coating		Drop casting		Spin coating	
	μ	I on/off	μ	I on/off	μ	I on/off
TCB (b.p. 213 °C)	2.4×10^{-3} $(\pm0.7\times10^{-3})$	$\sim10^{6}$	1.5×10^{-4} $(\pm1\times10^{-4})$	$\sim10^{3}$	2.3×10^{-2}	$\sim4\times10^{3}$
p-xylene (b.p. 138 °C)	1.5×10^{-2} $(\pm0.4\times10^{-2})$	$\sim10^{4}$	1.4×10^{-3} $(\pm0.5\times10^{-3})$	$\sim10^{2}$		
Chloroform (b.p. 61 °C)	8.5×10^{-2} $(\pm2\times10^{-2})$	$\sim5\times10^{4}$	2.1×10^{-2} $(\pm0.3\times10^{-2})$	$\sim10^{3}$		
Chloroform on HMDS-treated SiO_2	1.5×10^{-1} $(\pm0.2\times10^{-1})$	$\sim2\times10^{5}$	2.3×10^{-3} $(\pm0.2\times10^{-3})$	$\sim10^{3}$		

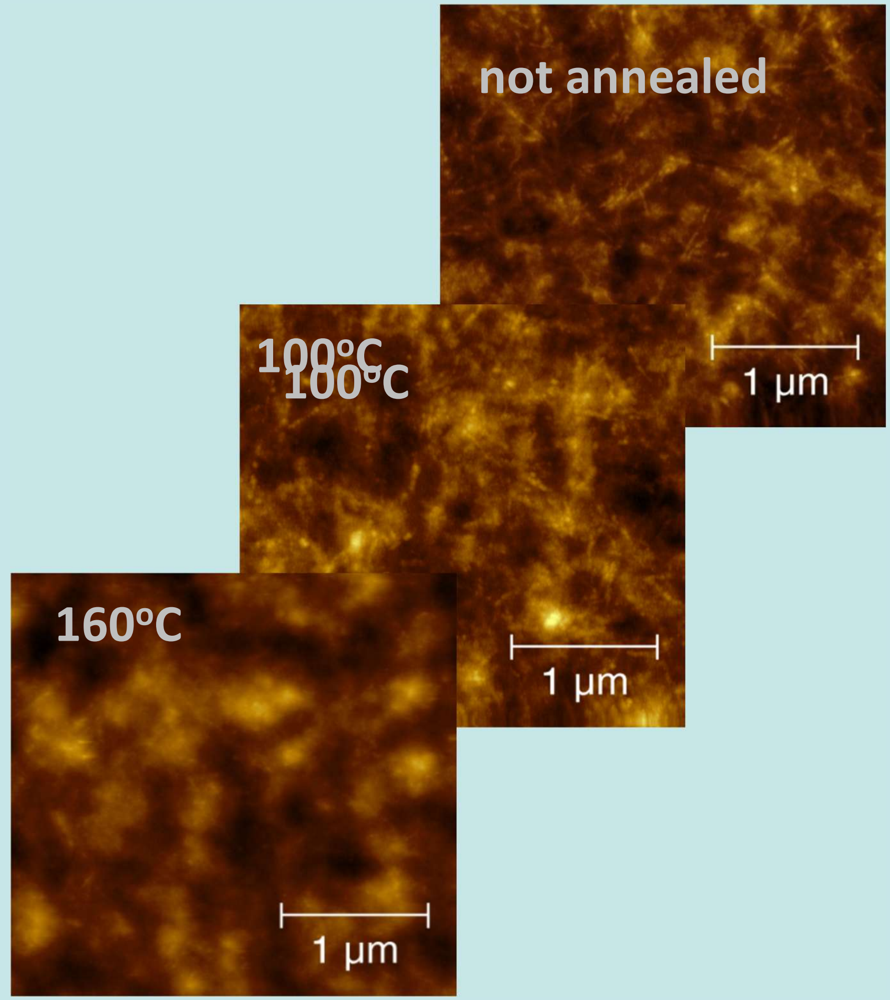


Surin, M et al., Journal of Applied Physics, AIP, 2006, 100, 033712

Annealing

PPy3T

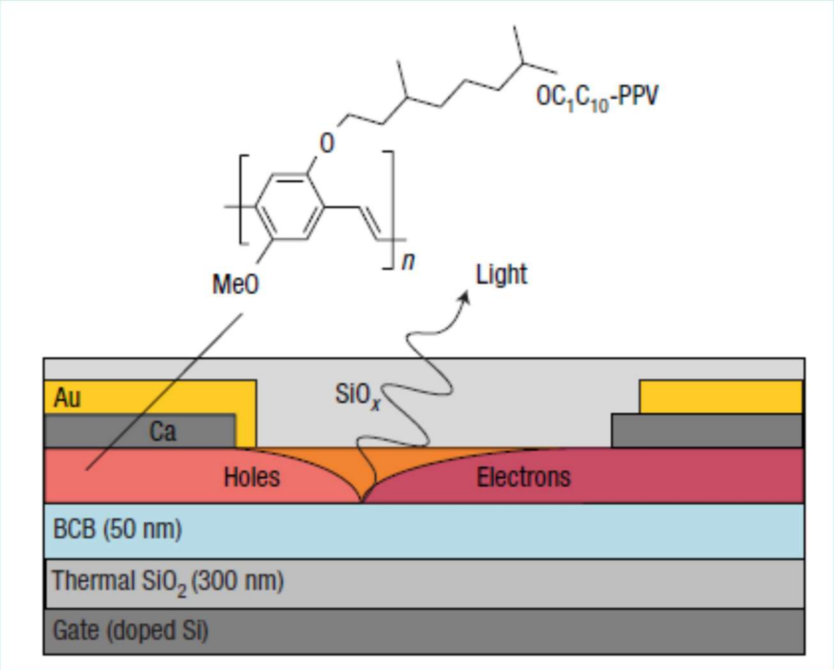


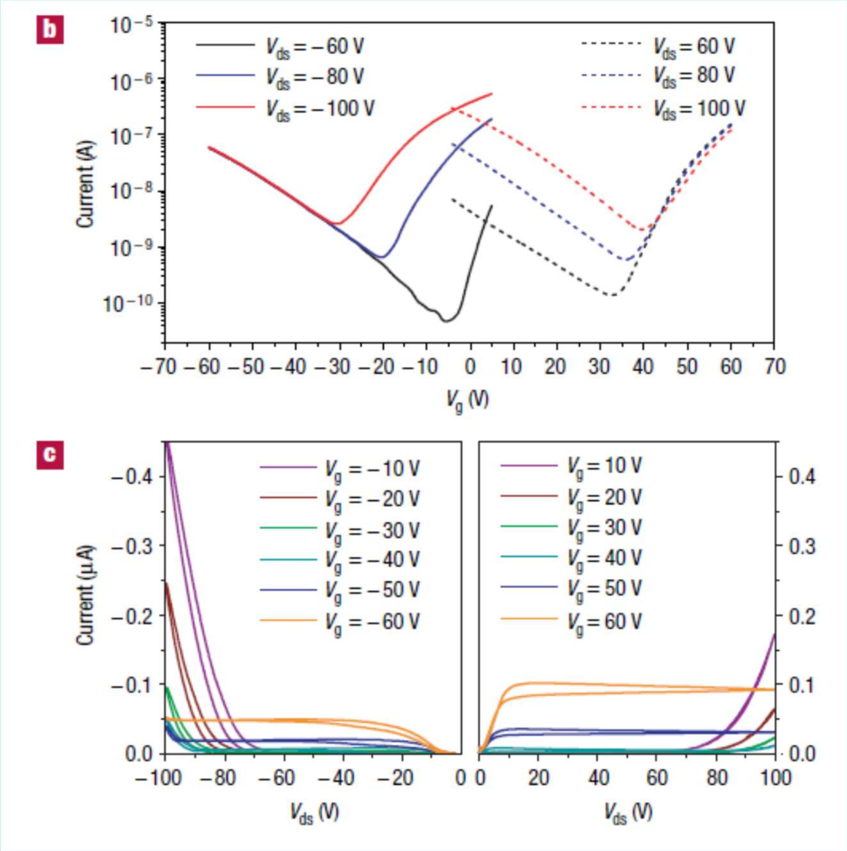


Li, Penglei et al. (2011) Chemical communications (Cambridge, England). 47. 8820-2. 10.1039/c1cc12752g.

OLETs

Organic Light Emitting Transistors





J Zaumseil et al,Nat. Mat. 5, 69 (2006)

OLETs

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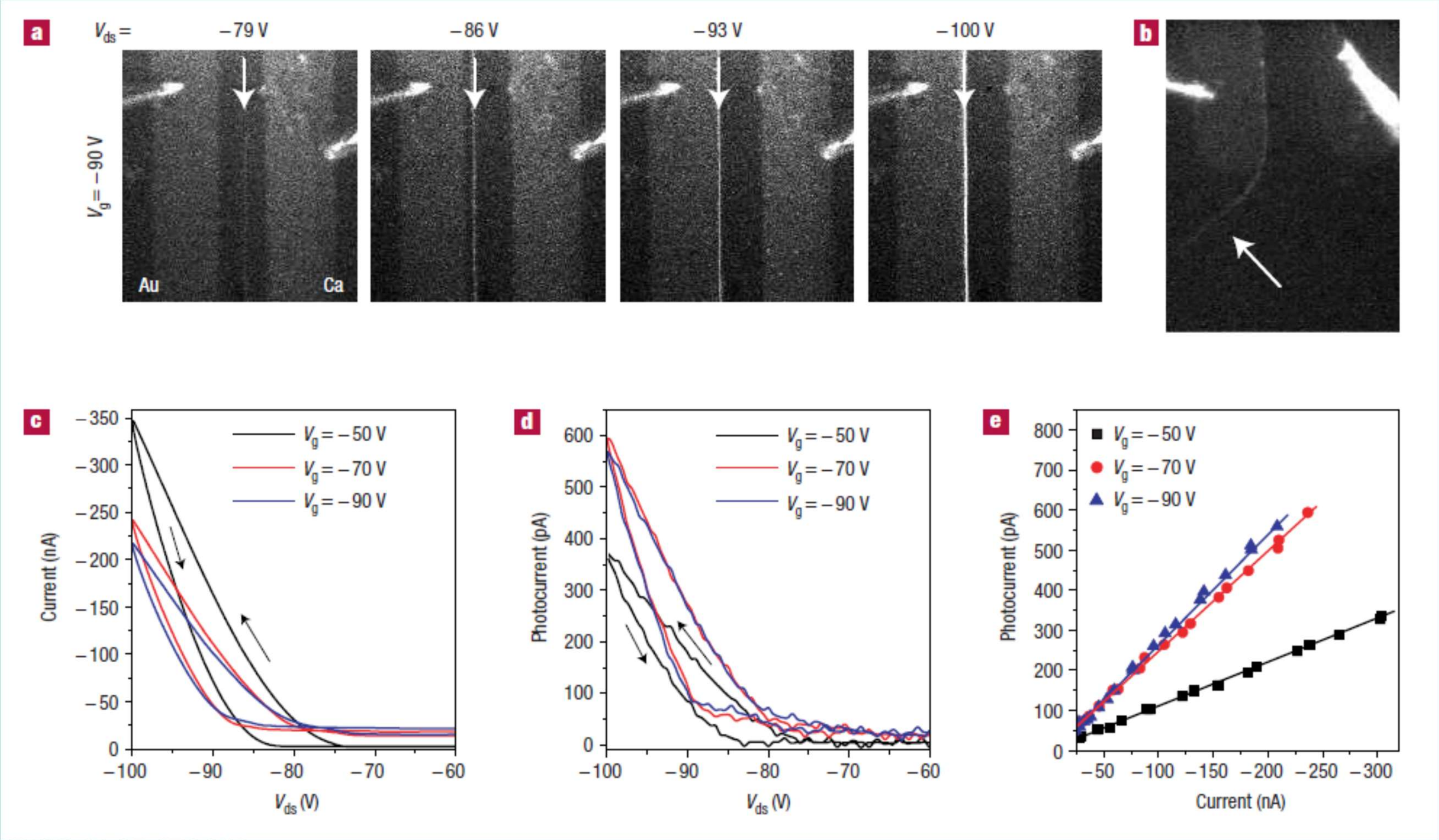
Organic



J Zaumseil et al,Nat. Mater. 5, 69 (2006)

Summary

- Challenges:
  - stability of devices
  - active layer films with uniform morphology
  - fabrication methods suitable for large scale applications

Next week:

2D materials

Organic thermoelectrics

Motivation

70% of primary energy consumption wasted as heat

current inorganic materials:

- toxic
- not abundant
- costly processing (melt-spinning, hot pressing, ball milling)
- heavy and brittle

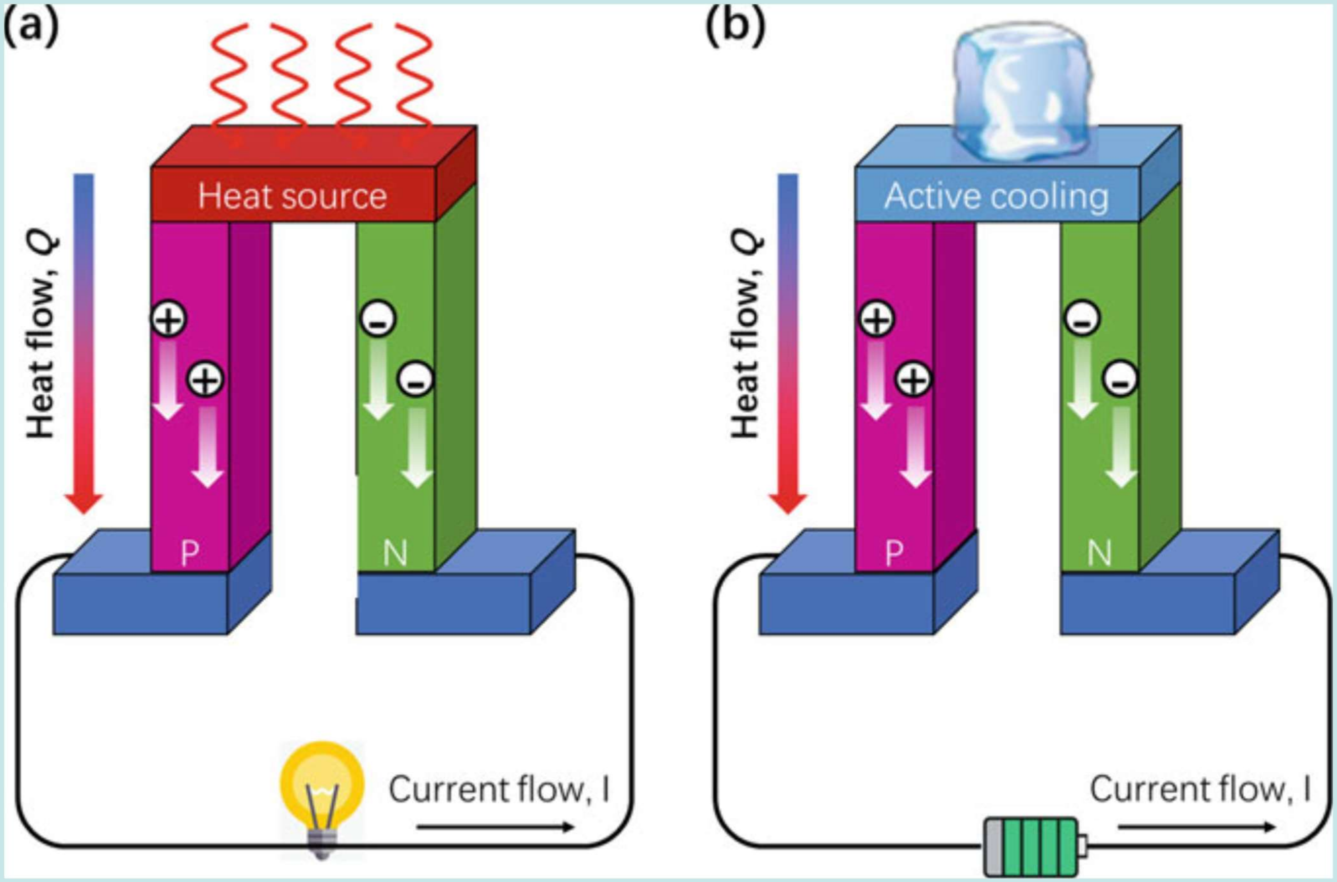
organic materials:

- none of the above
- additionally intrinsically low thermal conductivity

Forman, C. et al. (2016) Renew. Sustain. Energy Rev. 57:1568-1579

Seebeck and Peltier effect

Seebeck effect **Peltier effect**



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Characterisation of thermoelectrics

Seebeck equation

$$S_{12} = \frac{V_1 - V_2}{T_1 - T_2}$$

Peltier effect

$$Q = (\pi_1 - \pi_2)I$$

Thomson effect

$$Q = \beta I\ \Delta T$$

Figure of merit

$$ZT = \frac{S^2 \sigma T}{\kappa}$$

TEG efficiency

$$\eta = \frac{T_{hot} - T_{cold}}{T_{hot}} \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + \frac{T_{cold}}{T_{hot}}}$$

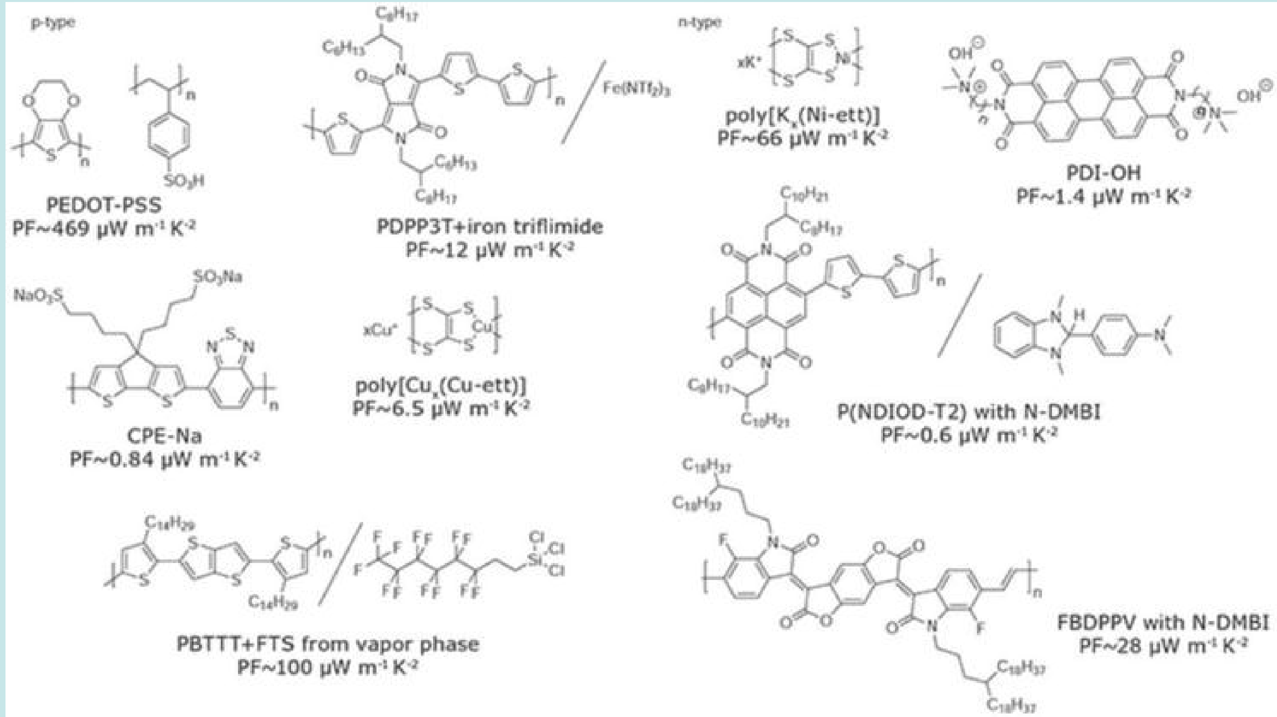
$$PF = S^2 \sigma$$

- *S* - Seebeck coefficient (thermopower)
- *T* – temperature
- *V* – voltage
- *Q* – heat
- *π* - Peltier coefficient
- *I* - current from 1 to 2
- β – Thomson coefficient
- *ZT* – figure of merit
- σ – electrical conductivity
- κ – thermal conductivity
- *PF* – power factor

Organic thermoelectrics

Opportunities:

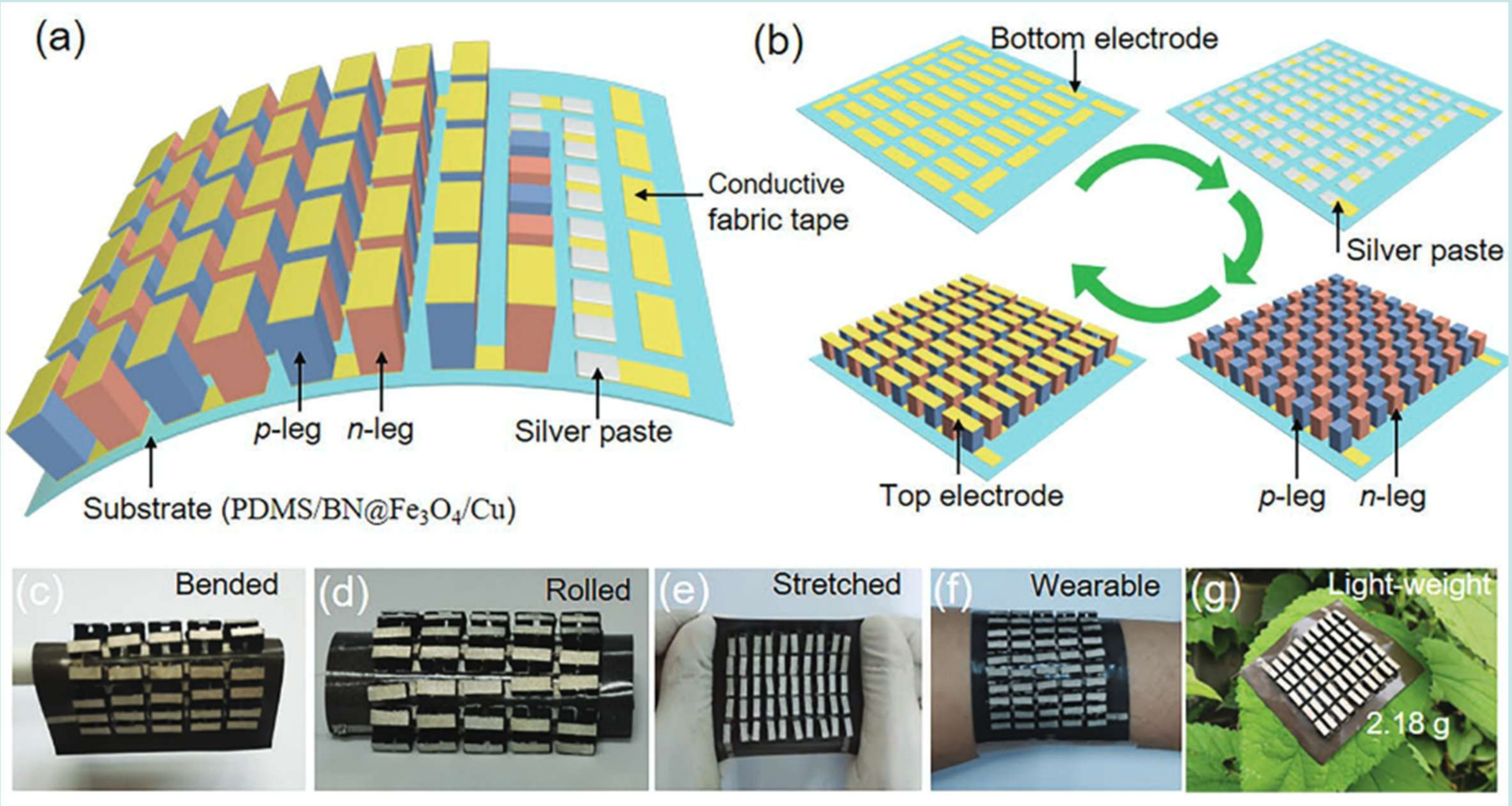
- anisotropic transport
- mW power extracted at 10K temperature difference
- flexibility
- body compatibility (non-toxic)



Challenges:

- low charge mobilities
- inferior Seebeck coefficients
- best materials usually organic-inorganic hybrids

Body heat application



Wang, Y., Zhou, Z., Zhou, J., Shao, L., Wang, Y., Deng, Y.,. *Adv. Energy Mater.* 2022, 12, 2102835.
https://doi.org/10.1002/aenm.202102835