Organic Materials for Energy and Optoelectronics

Organic Field-Effect Transistors

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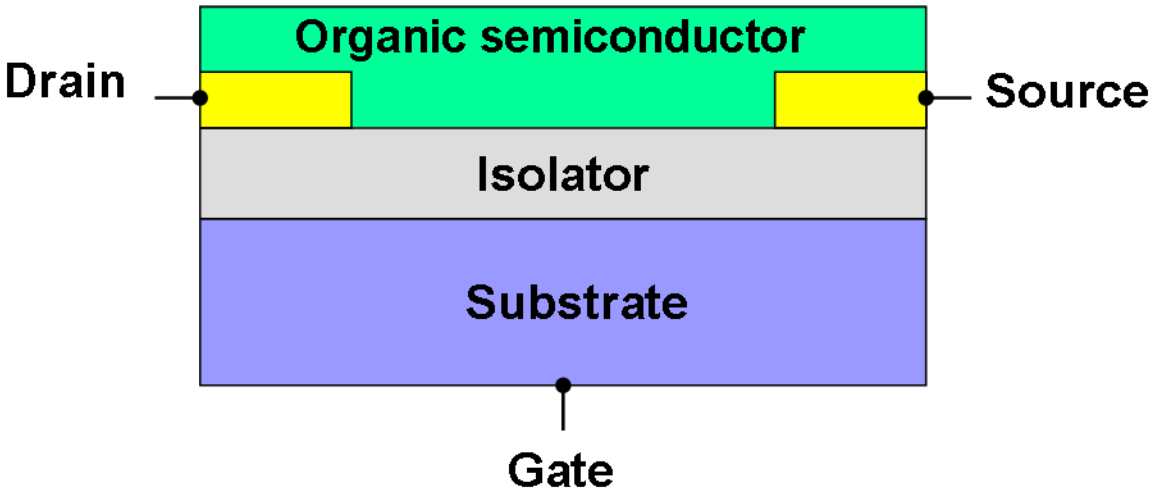
Outline

- Why OFET
- Principles of operation, parameters
- Charge transport in organic semiconductors
- Materials, structure-property relationships

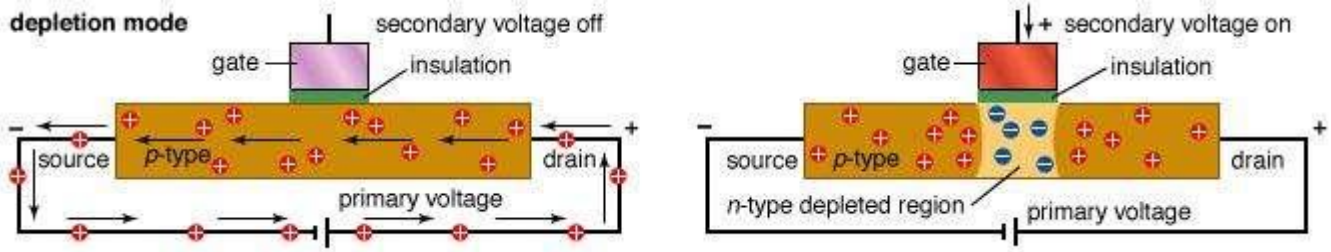
Why OFET

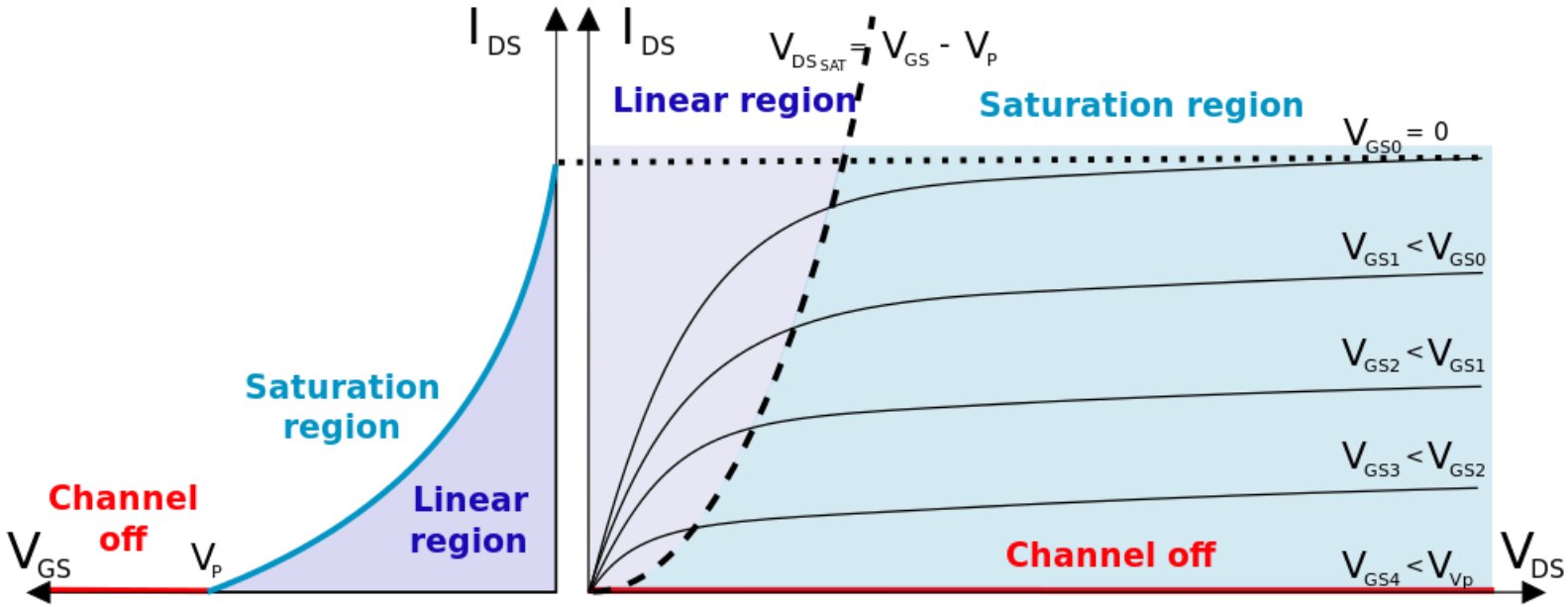
Field-effect transistor is probably the most commonly used device to determine key properties of a semiconductor including its ability to transport charge carriers in a controlled way:

- Simple setup
- Plenty of information – $J(V_{source\text{-}drain}, V_{gate})$
- Top side exposed for extra control



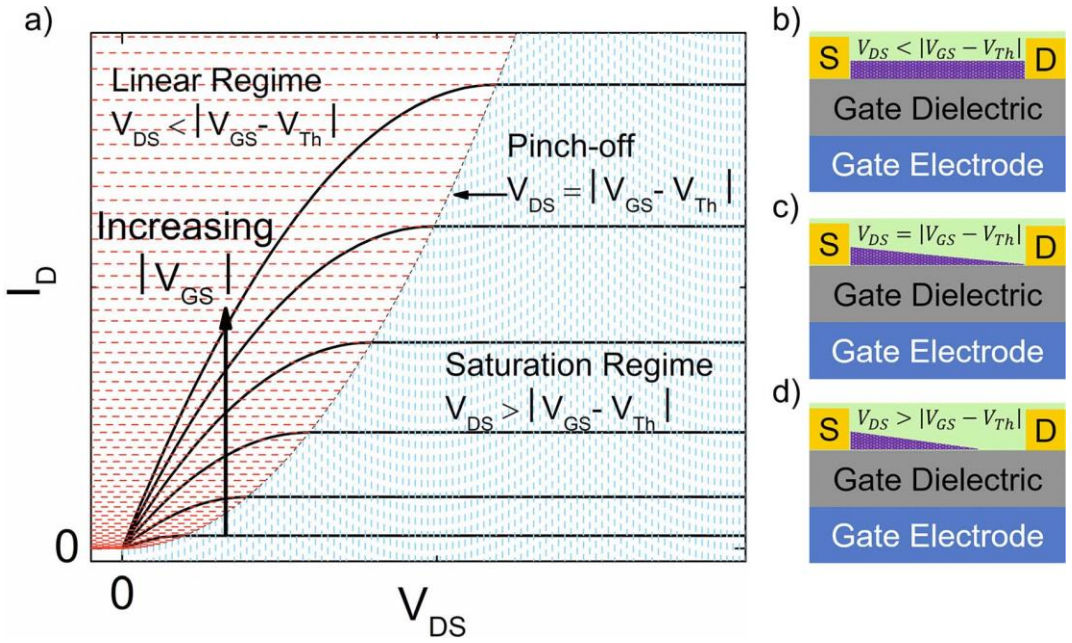
Principles of operation

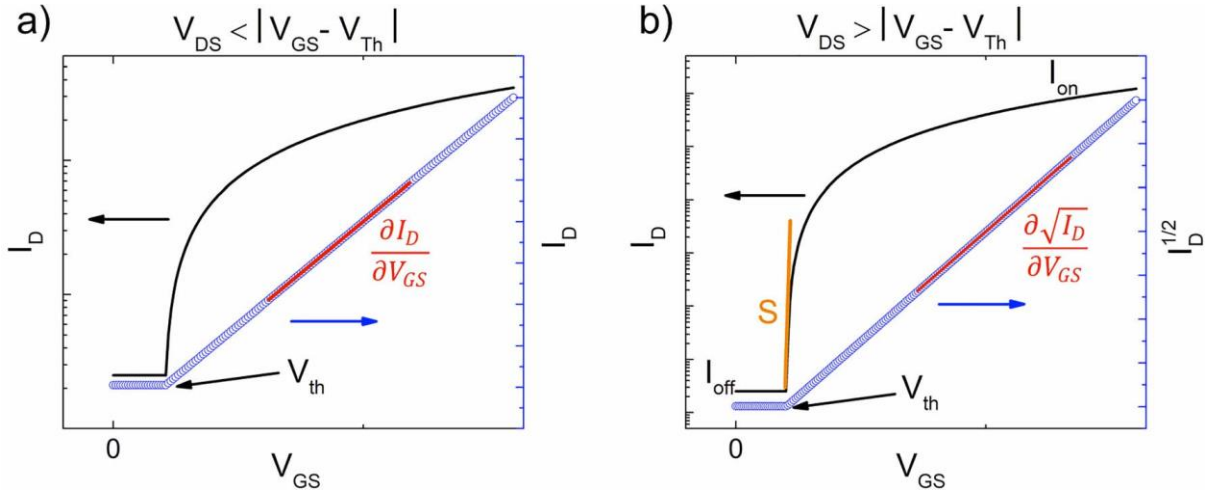




OFET-related parameters

- Charge carrier mobility (at least 0.1 cm^2/Vs)
- Saturation velocity (the higher the better)
- On/off current ratio (at least 10^4)
- Threshold voltage (the lower the better)
- Subthreshold swing (less than 1 V/dec)

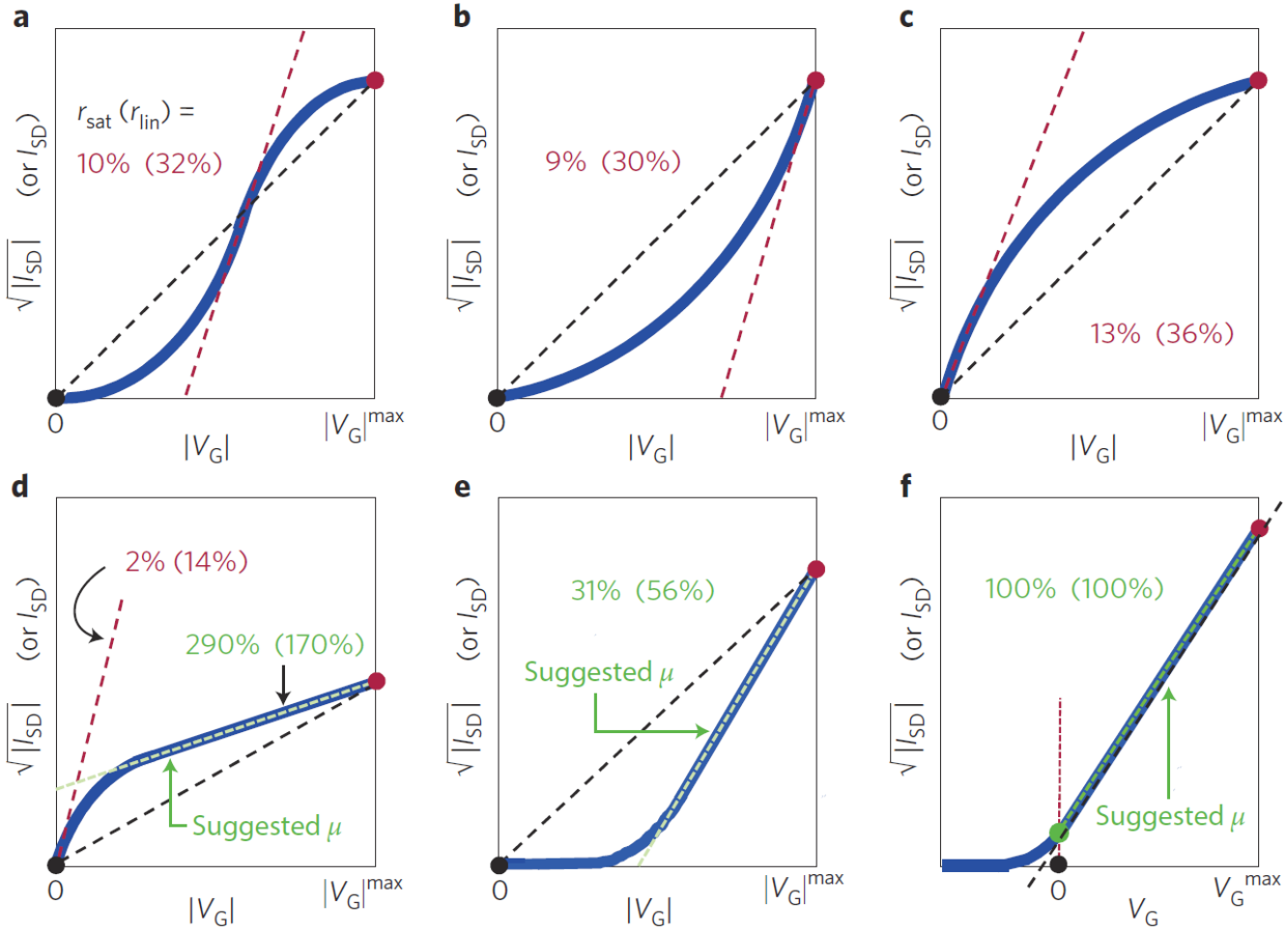




J Appl Phys 124, 071101 (2018)

Mobility from OFET measurements

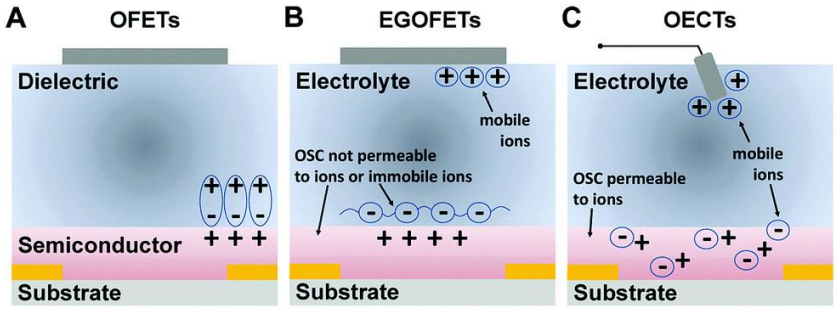
H H Choi, K Cho, C D Frisbie, H Sirringhaus, V Podzorov, Nat Mater 17, 2 (2018)



In linear regime $\mu = \frac{L/W}{CV_{SD}} \frac{dI_{SD}}{dV_G}$, where L/W is channel form-factor (length/width) and C is gate-channel capacitance per unit area[1]

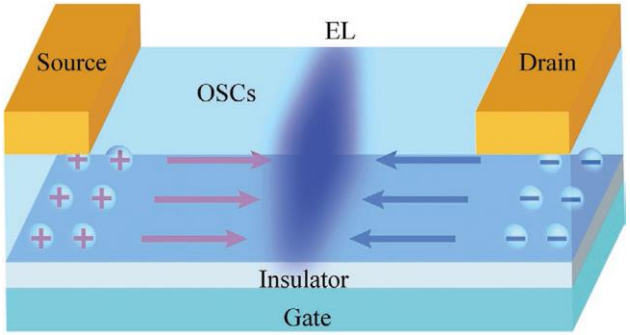
[1]Should be measured, if not possible, estimate as $\epsilon\epsilon_0/d$

Extensions of OFET



Electrochemical transistors

J Mater Chem C 6, 11778 (2018)
Nat Rev Mater 3, 17086 (2018)



Light emitting transistor

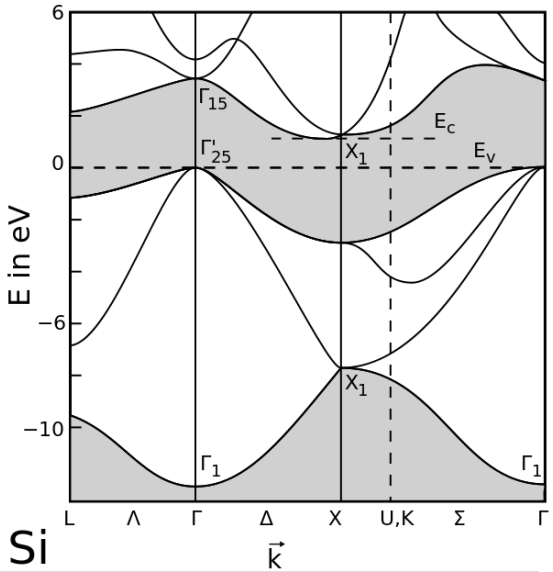
Adv Mater 33, 2007149 (2021)

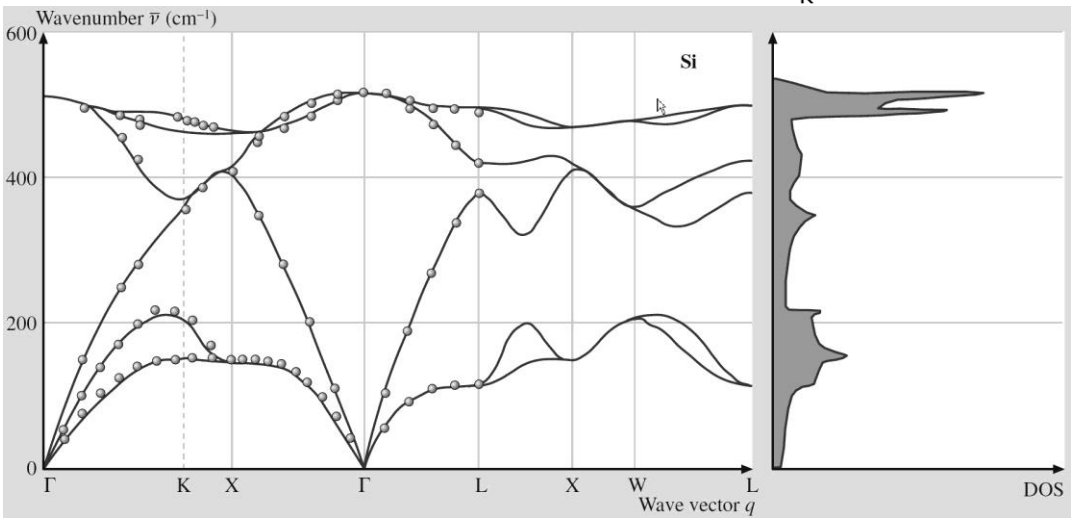
- chemical sensors [Chem Soc Rev 44, 2087 (2015)]
- mechanical sensors [Adv Funct Mater 30, 2004700 (2020)]
- photochromic molecules [Mater Chem Front 5, 1060 (2021)]

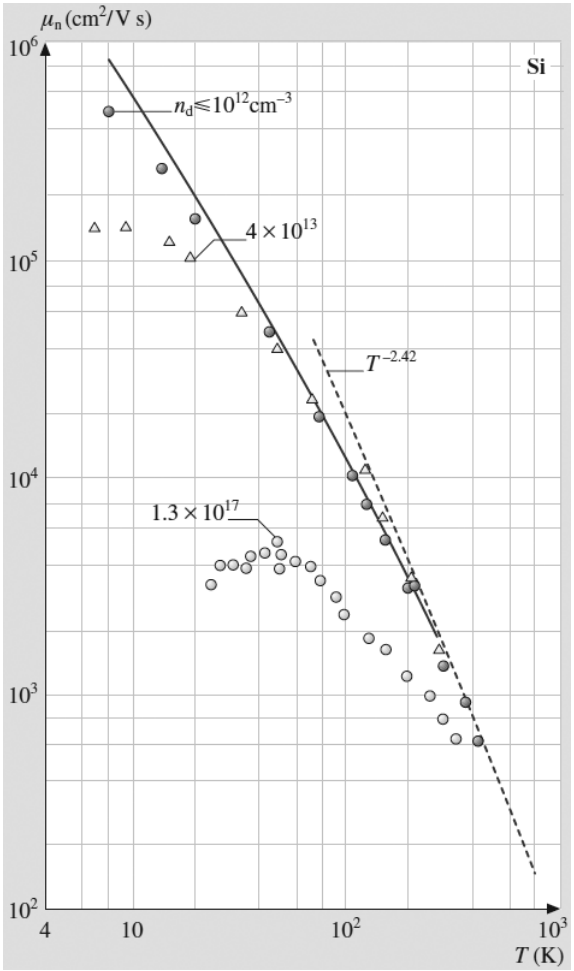
Charge transport in organic semiconductors

Very different from charge transport in “classic” inorganic semiconductors (free motion of electrons and holes scattered by phonons and defects)

* In this section we exclude from consideration fully connected rigid frameworks such as graphene, MOF, COF







Definitions: charge carrier mobility

Basic equations in homogeneous medium

Current density $j = \mu \cdot n \cdot e\mathcal{E}$

Free charge carriers Drude formula	**Localized charge carriers** Hopping
$\mu = \frac{e\,\tau_{\text{scattering}}}{m_{\text{effective}}}$	$\mu = \frac{2\pi e}{\hbar} f \cdot (aV)^2 \frac{J}{T}$

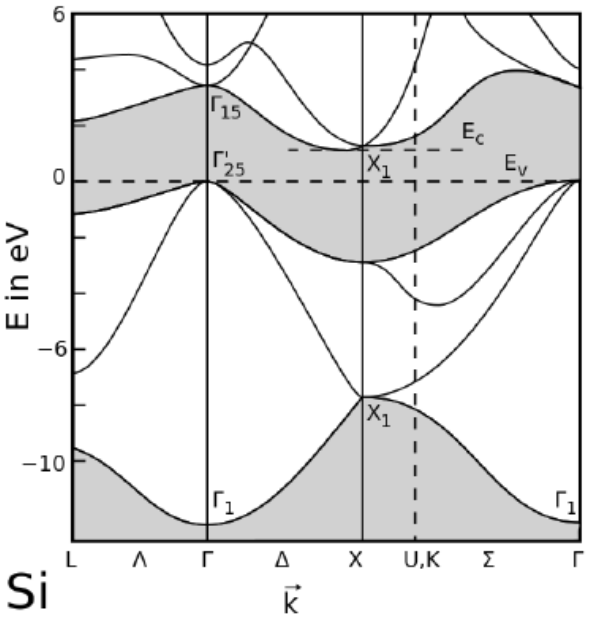
* Purely electronic and electron-phonon interaction terms are factorized

Scattering (or localization) mechanisms:

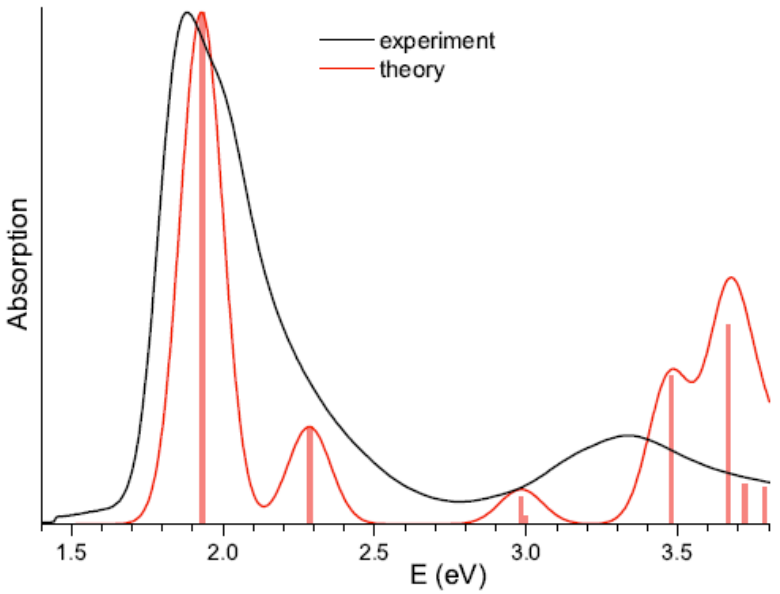
- dynamic lattice defects (phonons, intramolecular vibrations)
- extrinsic disorder: from lattice defects to mesoscopic nonhomogeneity (grain boundaries, interfaces, composites)
- carrier-carrier interaction

f = lattice form-factor, a = lattice spacing, V = electronic inter-site coupling, J = spectral overlap, mobility definition $v = \mu\mathcal{E}$, zero-field mobility = eD/T, exciton diffusion length = $\sqrt{D \cdot \text{lifetime}}$

Definitions: electronic and vibronic bandwidth



Electronic bandwidth



Vibronic bandwidth

$$W_{\text{el}}^2 = \langle \Delta\varepsilon^2 \rangle + \langle \Delta\varepsilon^2 \rangle_T$$

$$W_{\text{vib}}^2 = \sum_\alpha g_\alpha^2 \hbar^2 \omega_\alpha^2 \coth \frac{\hbar\omega_\alpha}{2T}$$

For bandwidth W, correlation function decreases as $\mathrm{e}^{-W^2 t^2/2\hbar^2}$ at small t

Electron-phonon coupling: organic vs inorganic

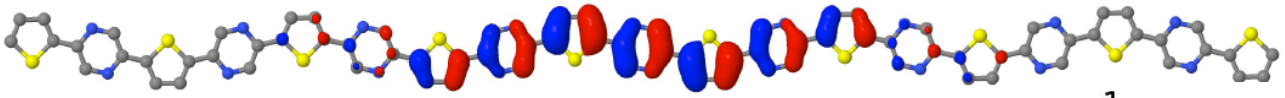
Electron-phonon couplings are always large for bonding electrons, with W_{vib} of the order of tenths of eV. The difference is in W_{el}:

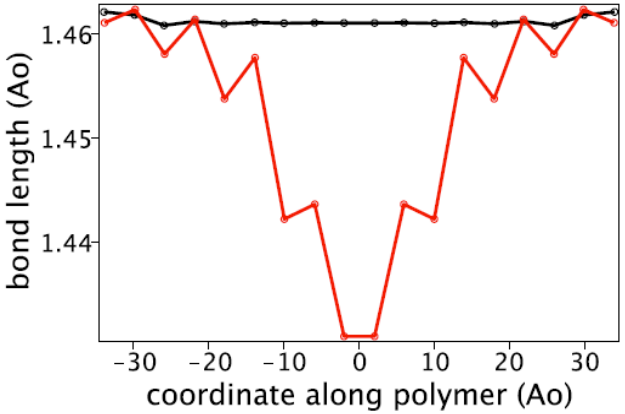
"Inorganic electronics"	"Organic electronics"
$W_{\text{el}} \gg W_{\text{vib}}$	$W_{\text{el}} \sim W_{\text{vib}}$
(weak el-ph correlations)	(strong el-ph correlations)
$\Longrightarrow$ model of free charge carriers scattered by phonons	$\Longrightarrow$ more complicated models

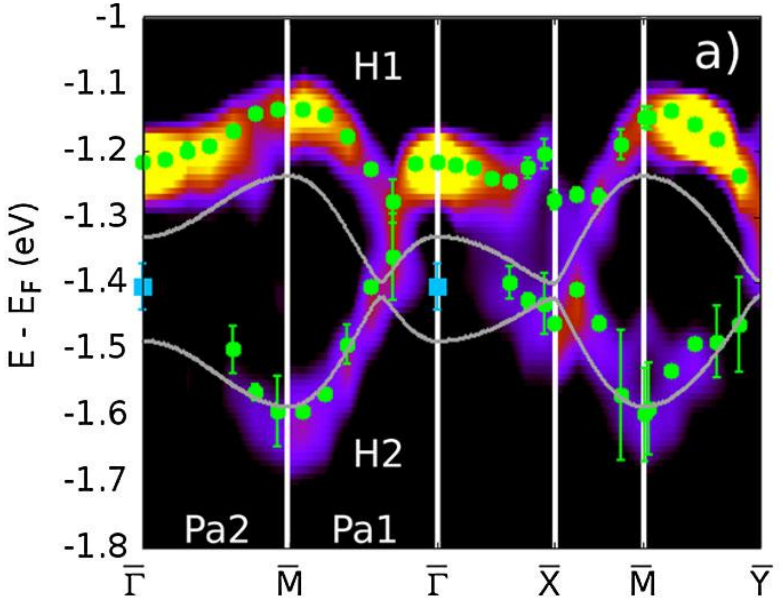
Additional complication: soft lattice (no rigid framework, flexible dihedrals, intermolecular motions) $\Longrightarrow$ doping and intercalation challenges (also chalcogenides, transition metal oxides)

Charge transport in organic semiconductors

- Polarons, not free electrons/holes
- Hopping for amorphous structures or at elevated temperatures
- Bandlike motion of polarons in crystals at low temperatures
- Ballistic motion only at single-molecule scale (STM experiment)







Phys Rev Lett 108, 256401 (2012)

Classes of materials

Can be classified by type of ppπ electronic connectivity, noting that:

- coupling is about 1 eV for bonded atoms (intramolecular)
- coupling is about 0.1 eV for vdW contacts (intermolecular)
- electronic bandwidth and mobility are proportional to coupling strength and number of contacts

→ Several classes:

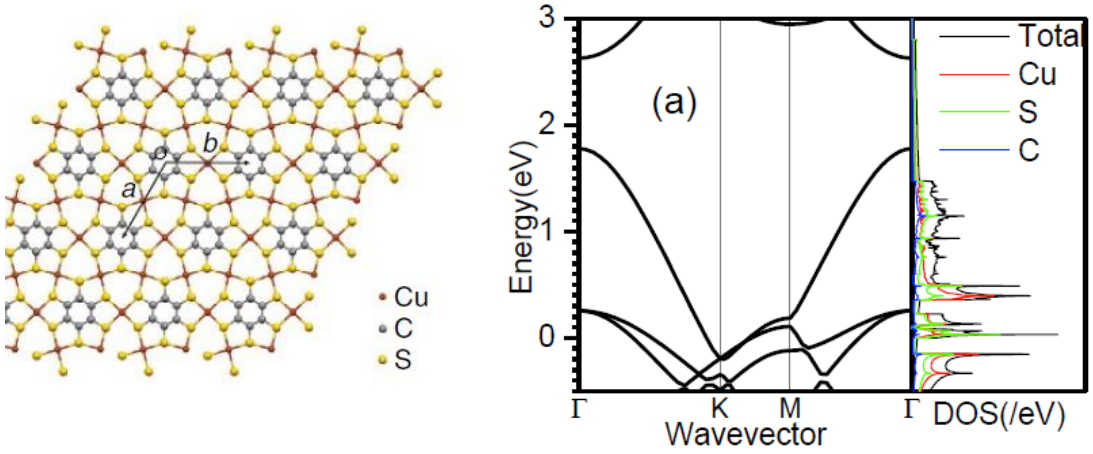
- Fully connected rigid frameworks such as graphene, MOF, COF
- Molecular solids
- Conjugated polymers
- Biopolymers

Fully connected rigid frameworks

Electronic bandwidth is a few eV and larger

→ free charge carriers scattered by phonons

→ high mobility comparable to inorganic semiconductors



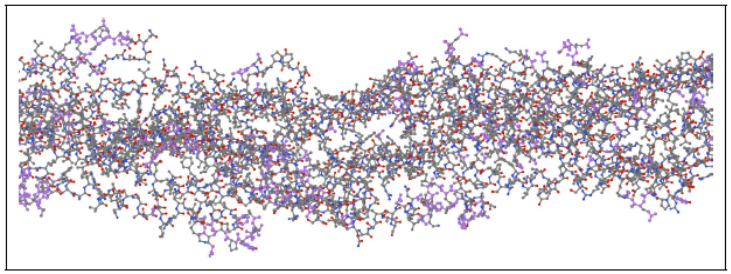
Nat Commun 6, 7408 (2015)

Biopolymers

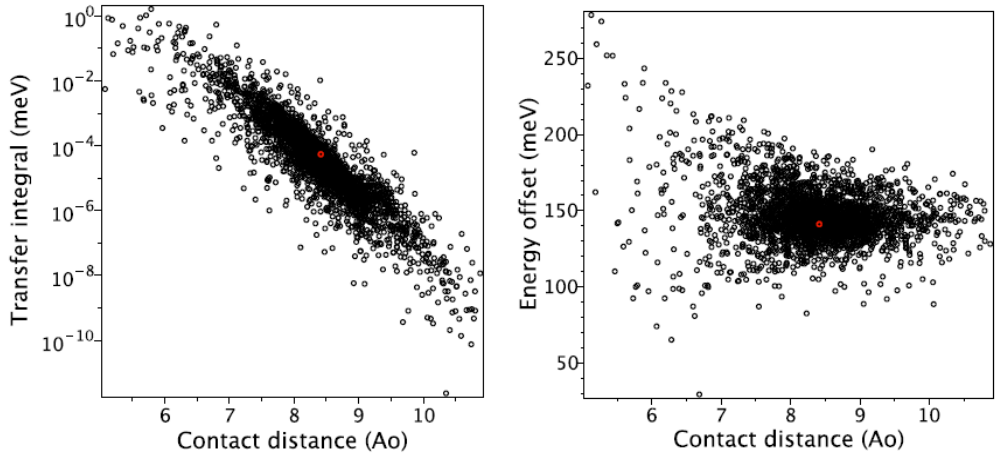
Poor connectivity

→ hopping in fluctuation regime

→ negligible transport via π-conjugated system compared to other charge transport channels (e.g. ion diffusion)



$B(Å^2)$	$\lg\langle V^2\rangle$	$-\lg\langle V^{-2}\rangle$
2.5	-4.1	-5.0
12	-3.4	-6.2
23	-2.8	-7.0
34	-1.4	-8.5

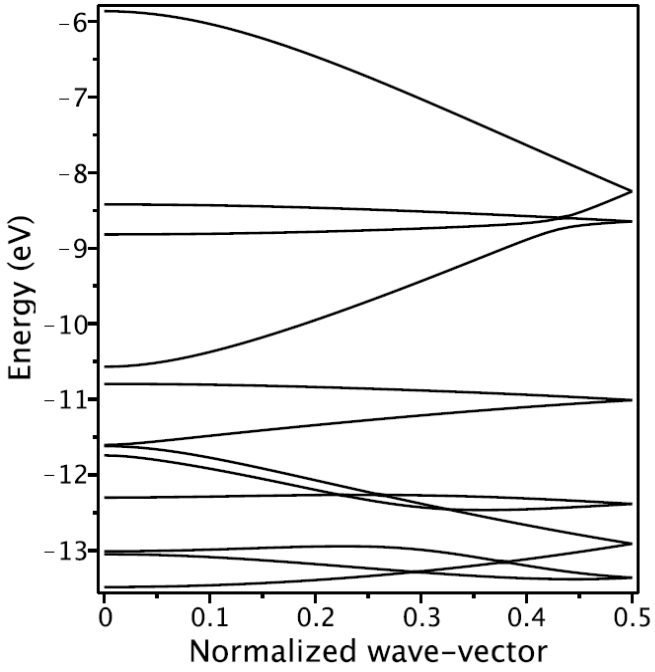


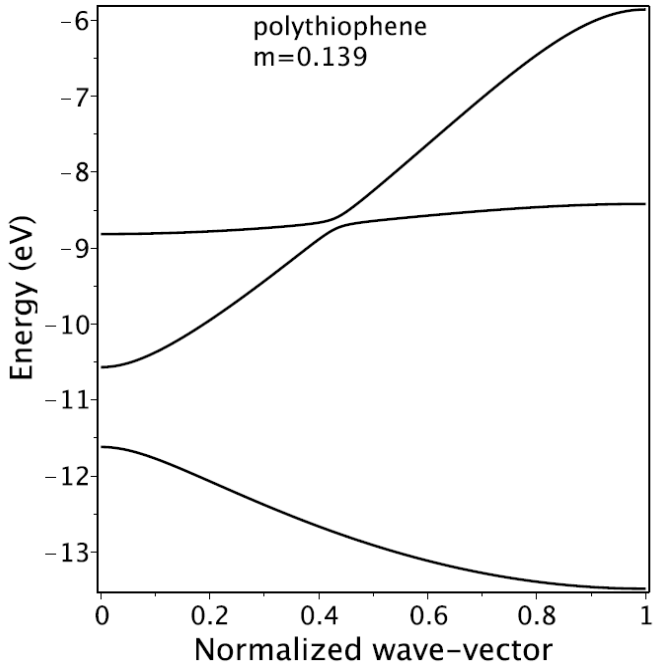
H Yan, C Chuang, A.Z., S Tretiak, F W Dahlquist, G C Bazan, Adv Mater 27, 1908 (2015)

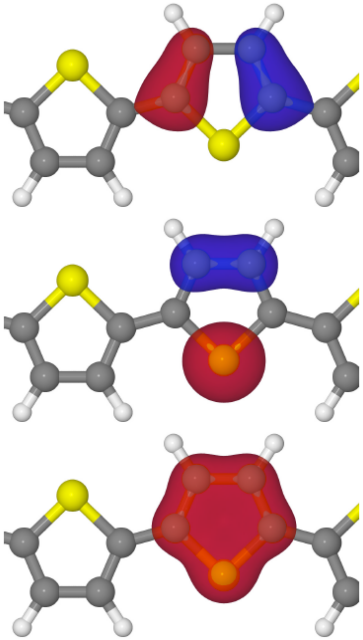
B is Debye–Waller factor (experimentally 20-50 Å^2), V – electronic coupling

Conjugated polymers

High electronic bandwidth along the polymer, but no technology to get long range translational order, so that the electronic conjugation length is limited to a few nm regardless of the molecular weight → can be considered as oligomers (molecular solids) for discussion of charge transport

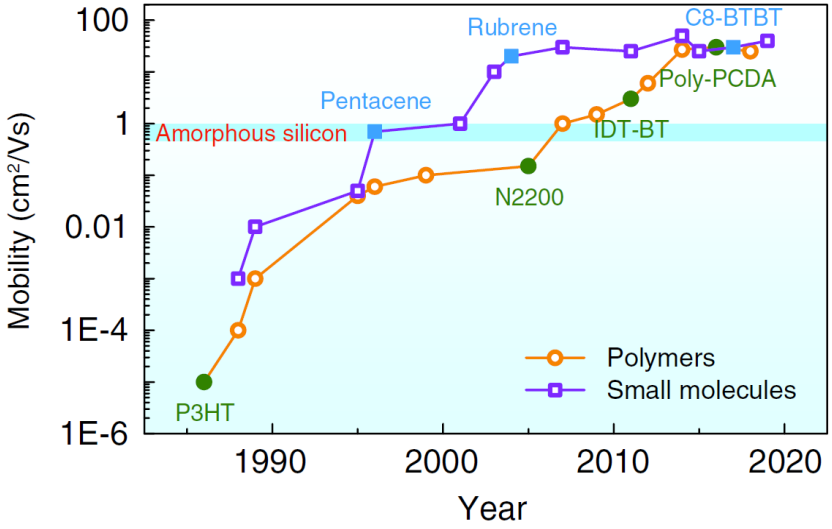




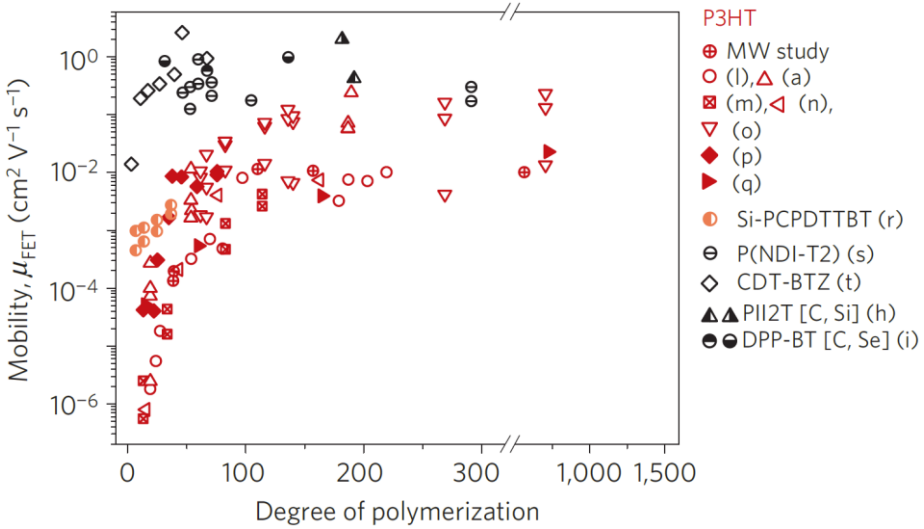


Molecular solids

Intramolecular connectivity is usually good → charge transport is determined by intermolecular connectivity and electronic traps



J Polym Sci 60, 311 (2021)

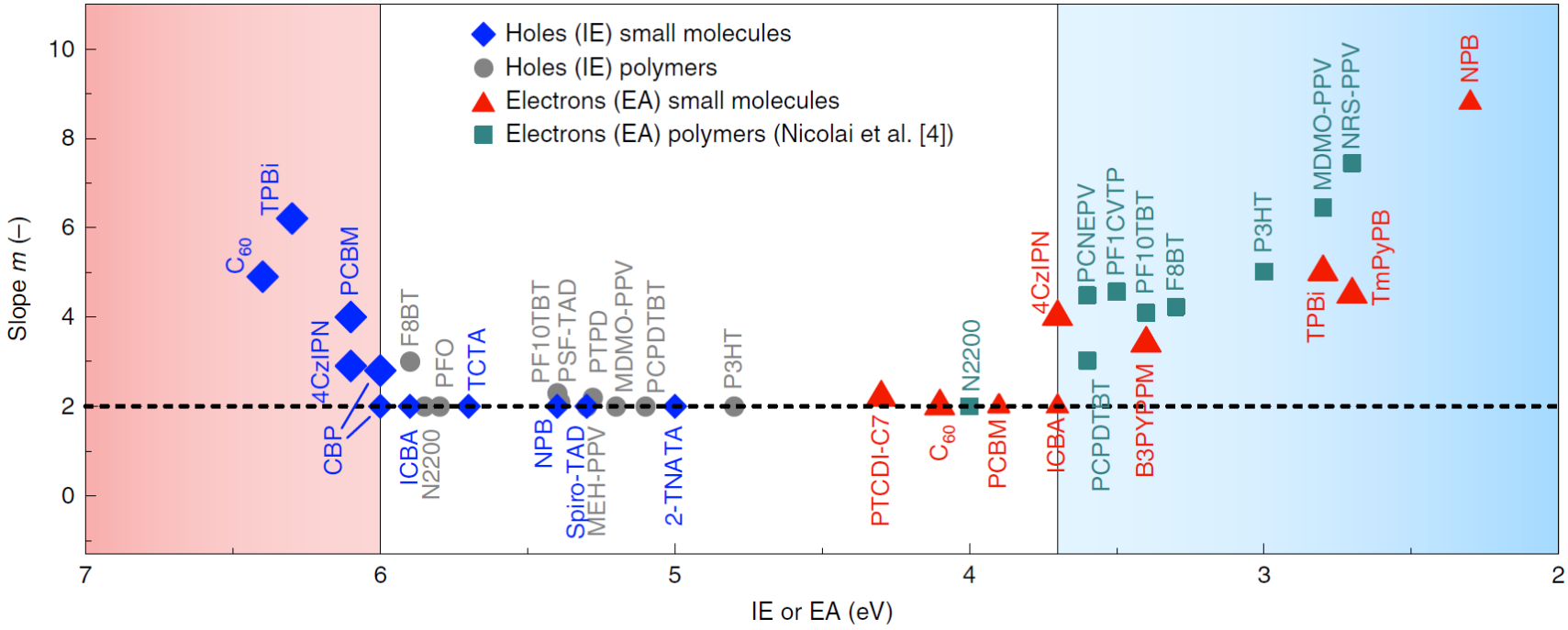


Nat Mater 12, 1038 (2013)

* Be careful: mobility is often overestimated by order of magnitude

Electronic traps

There is a window for trap-free charge transport



Nat Mater 18, 1182 (2019)

Known types of electronic connectivity

system	cc	η_1 (eV·Å)	η_2 (eV·Å)	η_3 (eV·Å)	bandspan (eV)	bandwidth (eV)	geometry	connectivity
1D systems								
R24	h	0.33	0.06	0.03	0.26	0.09	π-stack	1D
T1	h	1.23	0.01	0.00	0.54	0.19	slipped stack	1D
EH-IDTBR	e	1.32	0.22	0.03	0.55	0.17	slipped stack	1D
ITIC-Th	e	0.94	0.08	0.00	0.53	0.19	slipped stack	1D
ITIC-1Cl	e	0.74	0.07	0.00	0.46	0.17	broken mesh	1D
2D systems								
hexacene	h	0.75	0.65	0.04	1.08	0.28	herringbone	triangular
TIPS-pentacene	e	1.39	0.53	0.00	0.98	0.26	brickwork	oblique
3D systems								
F2-TCNQ	e	0.94	0.39	0.38	1.02	0.18	H-poor	3D
o-IDTBR (exp.geom.)	e	0.77	0.29	0.16	0.51	0.15	"wire mesh"	Fig. S4
o-IDTBR	e	1.04	0.35	0.19	0.65	0.19		
o-IDTBR model	e	0.99	0.39	0.33	0.60	0.17		
Y6 model	e	0.72	0.61	0.31	0.60	0.17		
Y6	e	0.99	0.92	0.39	0.88	0.26	"wire mesh"	
holes in o-IDTBR								
o-IDTBR	h	0.41	0.17	0.06	0.14	0.04		
o-IDTBR (exp.geom.)	h	0.32	0.14	0.03	0.13	0.05		

Chem Mater 33, 966 (2021)

Further reading

- *Wikipedia* OFET
- *Koehler* Section 3.3
- *Forrest* Chapter 8
- Z A Lamport *etal*, Tutorial: Organic field-effect transistors: Materials, structure and operation, J Appl Phys 124, 071101 (2018)
- H Sirringhaus, Organic Field-Effect Transistors: The Path Beyond Amorphous Silicon, Adv Mater 26, 1319 (2014)
- M Nikolka, H Sirringhaus, Conjugated Polymer-Based OFET Devices, in Conjugated Polymers: Properties, Processing, and Applications, ed J R Reynolds *etal* (CRC, 2019) p1
- X Wu *etal*, Roles of interfaces in the ideality of organic field-effect transistors, Nanoscale Horizons 5, 454 (2020)