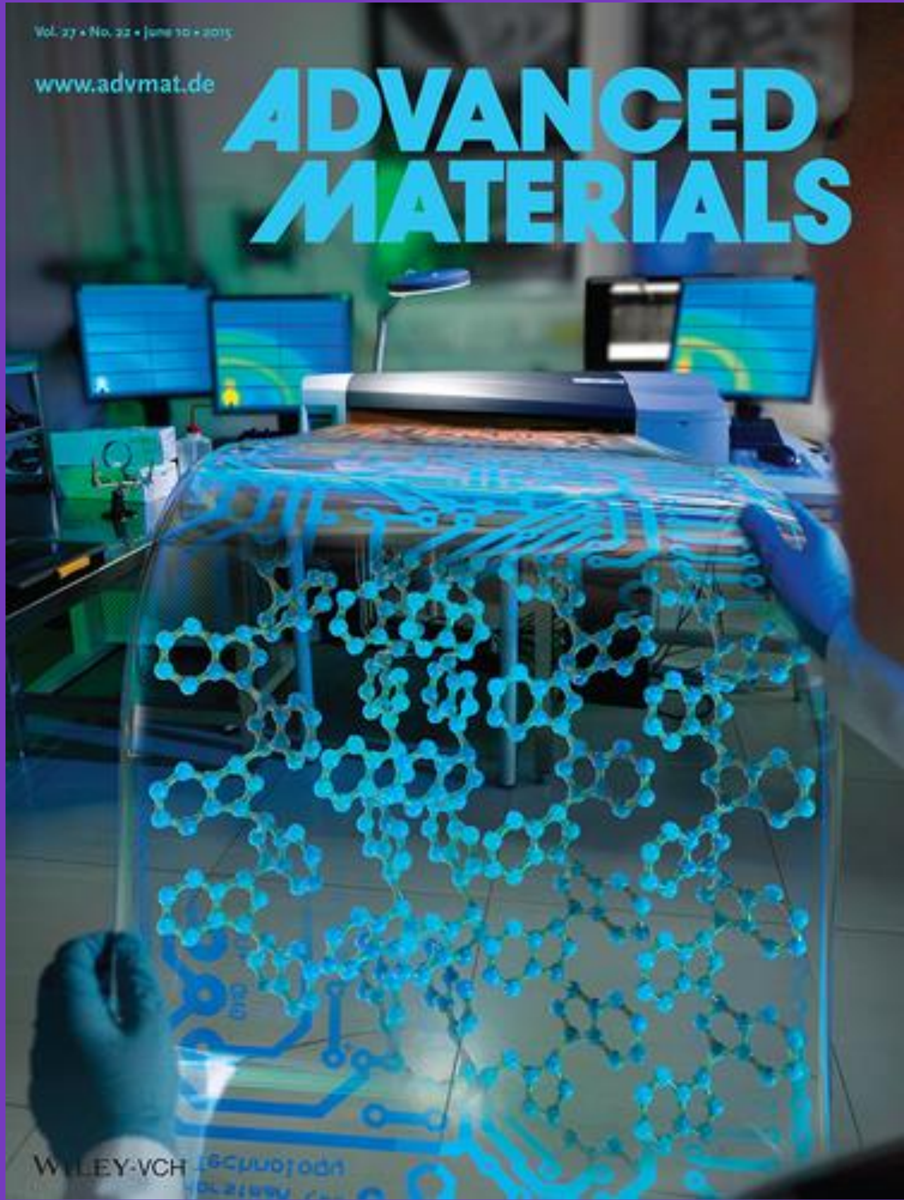
ELEC-E9210 Organic Electronics: Materials, Devices & Applications

Basics of Organic Materials

Aalto University
School of Electrical Engineering

https://organicelectronics.aalto.fi



What is Organic Electronics?

Have we ever **SEE / USE / OWN / HOLD / TOUCH / PLAY WITH** an organic device?

Lighting (LG)

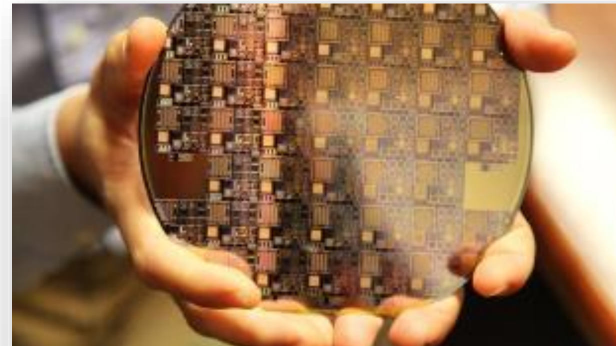
IBM ThinkPad X1 Fold (CES2020)

OLED TV (LG)

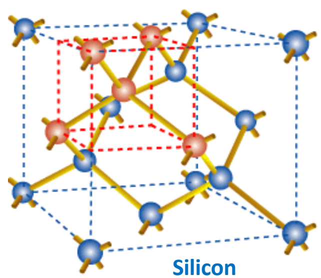
Smartphone (LG)

Organic Electronics

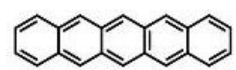
Conventional electronics



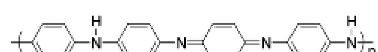
Inorganic Materials



Organic Materials



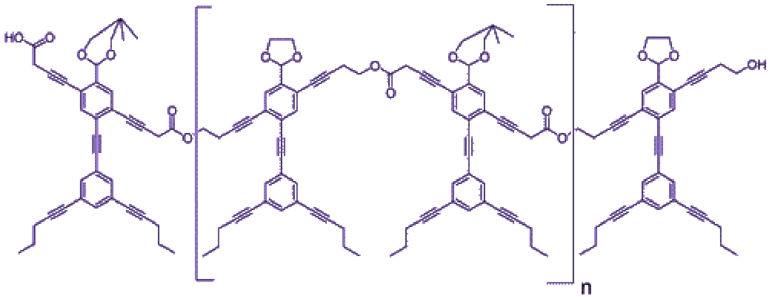
Pentacene



Polyaniline (PANI)

- flexible
- foldable
- light-weight
- low-cost
- high throughput

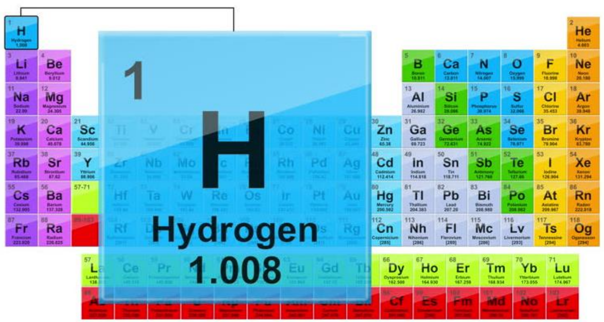
Organic Materials

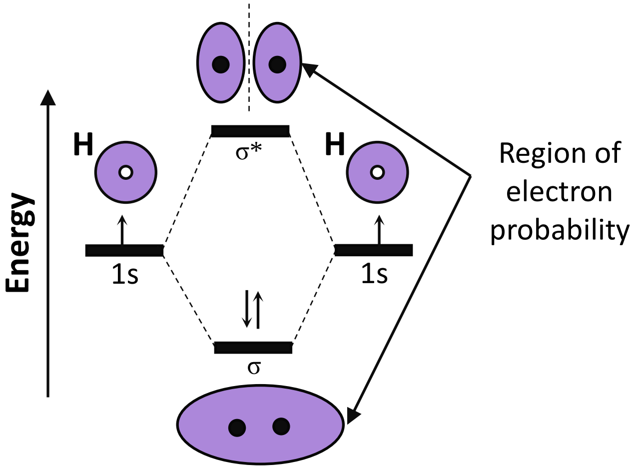


- Organic materials (organic semiconductors, OSC) are composed primarily (90%) of **carbon**, **hydrogen** and **oxygen** and contain a great quantity of ***alternating single*** and ***double bonds*** (*i.e.* π-conjugated materials).
- Atoms are held together by ***van der Waals forces*** (covalent bonds).
- Organic materials can be either ***small molecules*** or ***polymers***, and can preferentially transport holes (*p*-type) or electrons (*n*-type), sometimes both charges.

Atomic Orbitals (H_2-atom)

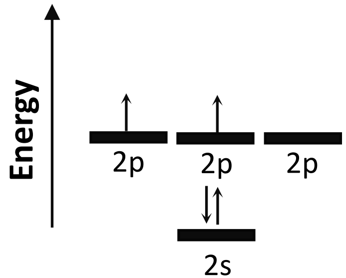
Atomic orbitals allow for the visualization of *the probability of finding an electron near a nucleus* (for a given series of quantum number)

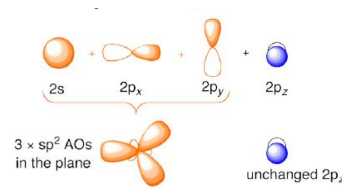




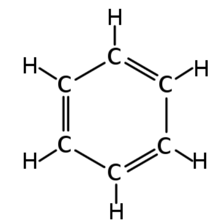
Electrons fill the atomic orbitals from the lowest towards higher energy

C-C Bond Atomic Orbitals





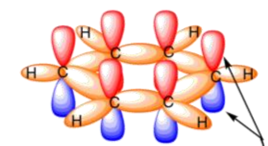
benzene



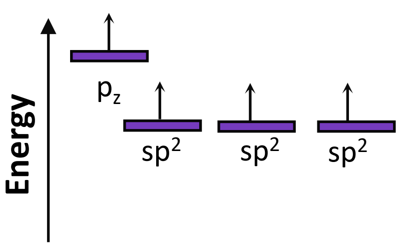
Orbitals can go from pure *s*, *p*, *d* and *f*-type to hybridized.
Hybridization leads to unique optoelectronic properties

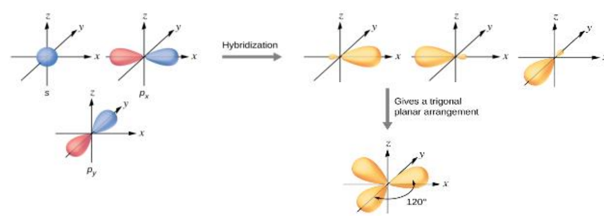
Hybridization
sp²

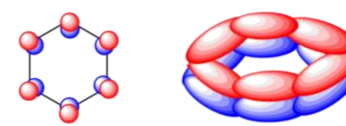
increases unpaired e⁻



a single p orbital
different phases shown
in red and black





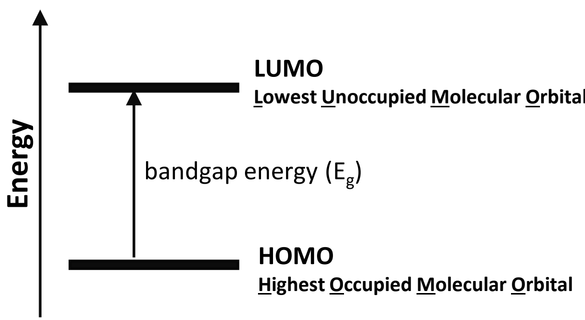


the lowest energy MO for benzene has
all the p orbitals combining in-phase

Atomic to Molecular Orbitals

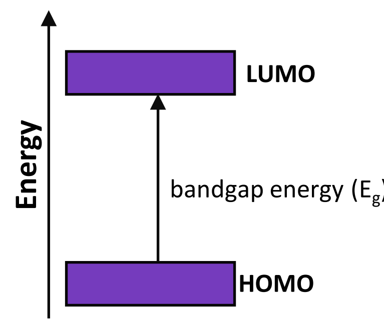
Atomic orbitals can be extended to ***molecular orbitals*** in case of compounds

Single (isolated) molecule



discrete energy levels

molecules



molecules proximity leads to *solid state bands* (analogue of band structure in inorganic SC)

Fermi-Dirac distribution

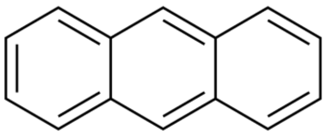
f(E) is the probability that a state at energy E is populated

$$f(E) = \frac{1}{e^{\frac{E-E_F}{kT}} + 1}$$

kT@RT (24meV)

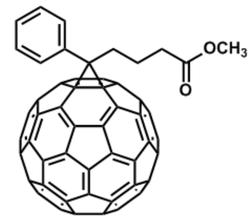
Polymers & Small Molecules

Small-molecules

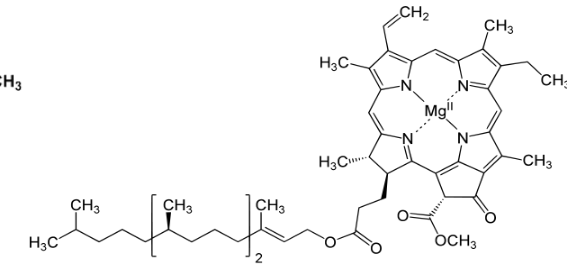


ANTHRACENE

C_{60}



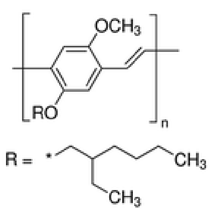
[60]PCBM



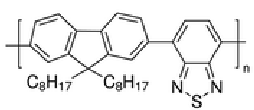
CHLOROPHYLL A

Polymers

repeating unit (details later)

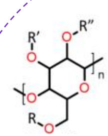


MEH-PPV

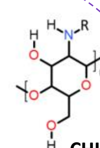


F8BT

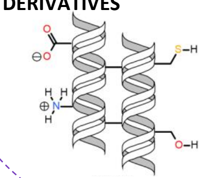
natural



STARCH/CELLULOSE DERIVATIVES

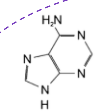


CHITIN/ CHITOSAN

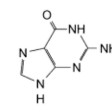


KERATIN

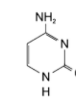
nucleotide



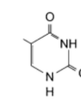
ADENINE



GUANINE

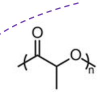


CYTOSINE

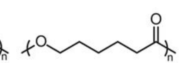


THYMINE

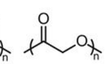
synthetic (*i.e.* plastic)



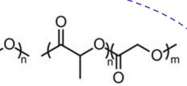
PLA



PCL



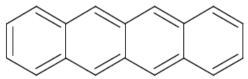
PGA



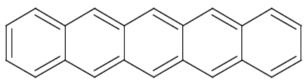
PLGA

Electron vs. *Hole*-transporting OSC

p-type OSC



tetracene



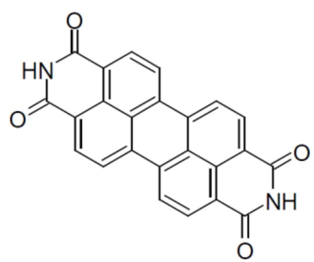
pentacene

conjugated C-backbone ringed primarily by H (H is less electronegative than the C-core and donates an electron to it) leads to an ***e*-rich backbone** and favors ***loss of an electron***

n-type OSC

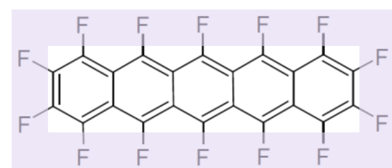
conjugated backbone needs to be electron deficient so that LUMO falls lower and gain an additional e^-

C60 is naturally *e*-transporting

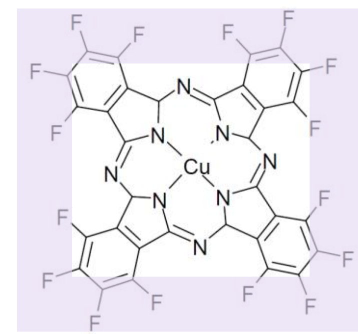


perylene 3,4,9,10 tetracarboxydiimide and perylene derivatives

Fluorination is an efficient process for *e*-rich materials



per-fluorinated pentacene



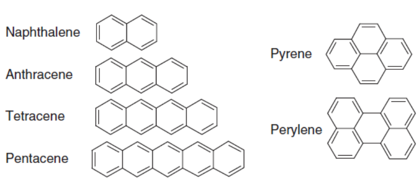
hexadecafluoro copper pthalocyanine

Organic Semiconductors (OSC)

Organic Semiconductors

molecular ***crystals***

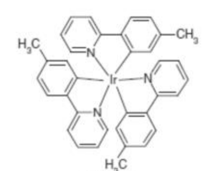
ordered arrangement, with molecules held together by van-der-Waals forces. Higher charge mobility (compared to amorphous films), relevant for electronics applications (*i.e.* transistor)



amorphous molecular films

classified based on either fabrication method (evaporation, coating) or electronic function (application), often suitable for large scale applications

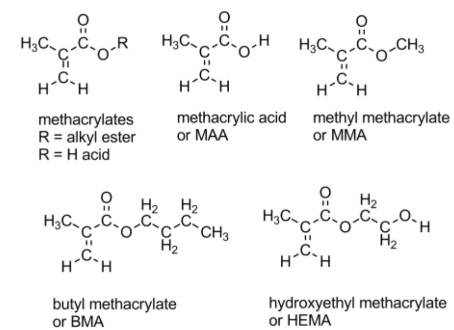
$Ir(ppy)_3$ for evaporation



$Ir(ppy)_3$ for solution processing

polymer

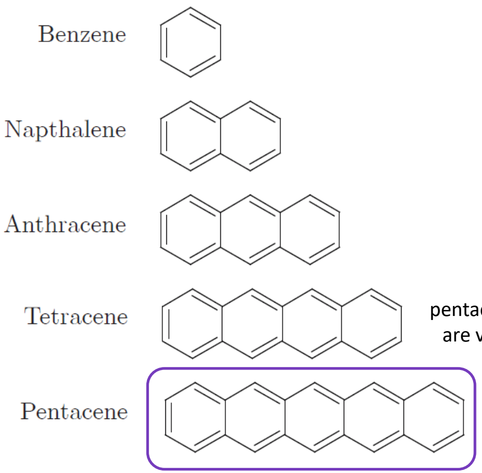
chain of covalently coupled molecules (monomers), often can be processed by solution methods and easy to blend for enhanced functionalities



About Small Molecules

- ***fused ring structures*** are common building blocks for OSCs
- many fused ring assemblies are ***planar*** and ***rigid,*** leading to different stacking/packing properties
- materials can form ***polycrystalline films*** when deposited @RT (or near). Higher order degree (better π-π overlap between neighboring molecules) improves charge transport
- large crystals/polycrystalline layers are possible under appropriate growth conditions

Acenes



pentacene & tetracene are very broadly used

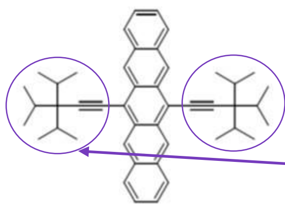
- not easily soluble→ *limited fabrication methods* (*i.e.* vacuum deposition)
- easy oxidation → *limit crystallization* properties and *charge transport*
- crystallize in two phases, with no lattice match (limit performances)

Modifying Small Molecules

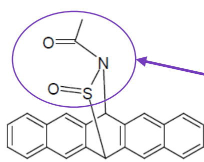
attaching a bulky groups to the molecule
(6,13 position easily oxidizes)

- higher degree of crystallization
- higher solubility

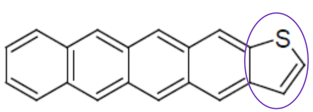
acenes



pentacene TIPS
(can be purified and
vacuum deposited)

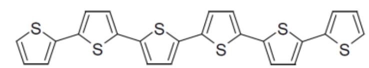


soluble pentacene
precursor which, upon
heating, lead to insoluble
thin film

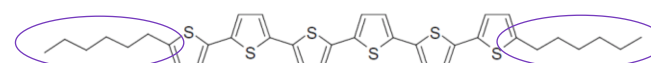


incorporating a *thiophene ring*
increases the solubility (reduced
HOMO-LUMO conjugation length)

oligothiophenes

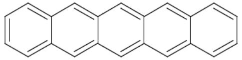


α-hexithiophene

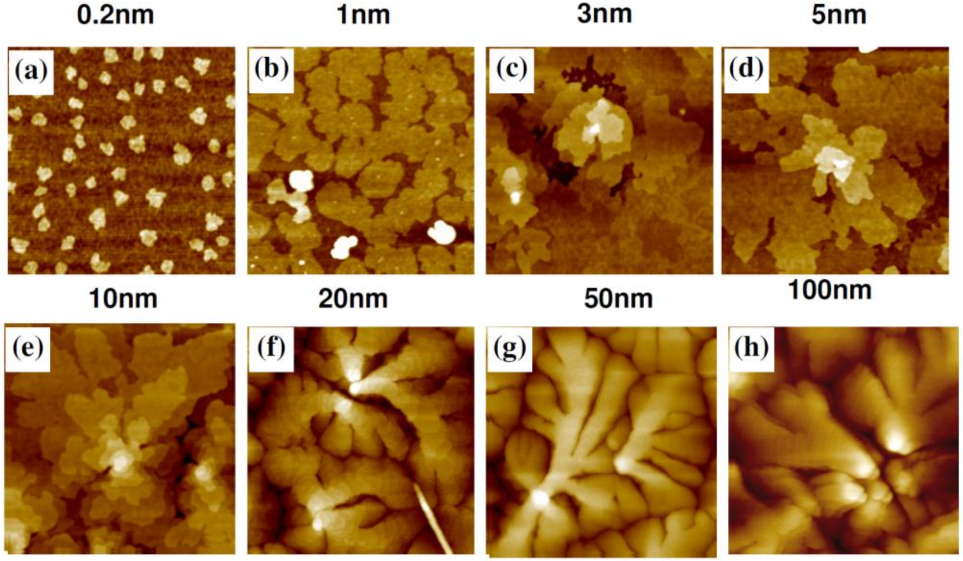


improved crystallinity by addition
of 2 *alkane groups*

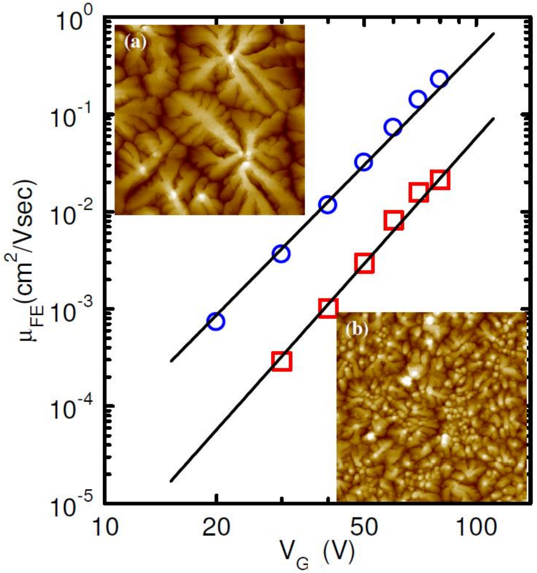
Small Molecules & Morphology



pentacene



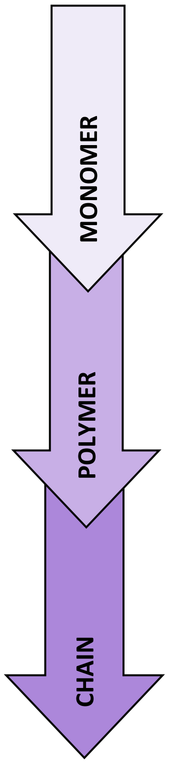
AFM images of pentacene on SiO_2, with variable thickness from 0.2 to 100nm (T_{sub}=40ºC, R_{dep}=0.2Å/s, scan size 2µmx2µm)



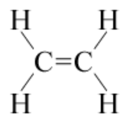
Room-temperature mobility for pentacene OFET grown at different deposition rate of 0.2Å/s (○) and 2Å/s (□) with (a) and (b) corresponding AFM images

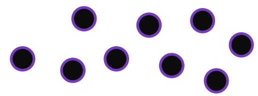
https://shodhganga.inflibnet.ac.in/bitstream/10603/120058/8/08_chapter%203.pdf

About Polymers



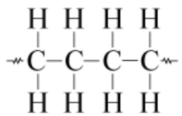
ethylene

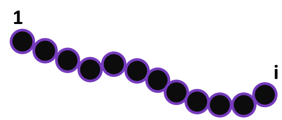




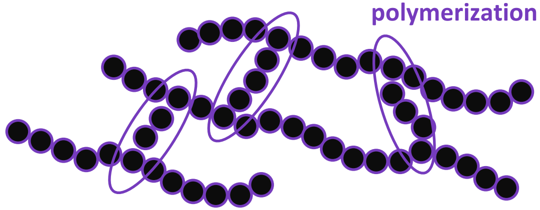
monomer molar mass, M_0

polyethylene





$polymer\ mass,\ M_i = i\ M_0$



$$x_i = \frac{n_i}{\sum_i n_i}$$ *i*-mer molar mass

$$M_n = M_0 \frac{\sum_i i n_i}{\sum_i n_i}$$ number-average molecular weight

$$w_i = \frac{i n_i}{\sum_i n_i}$$ *i*-mer weight fraction

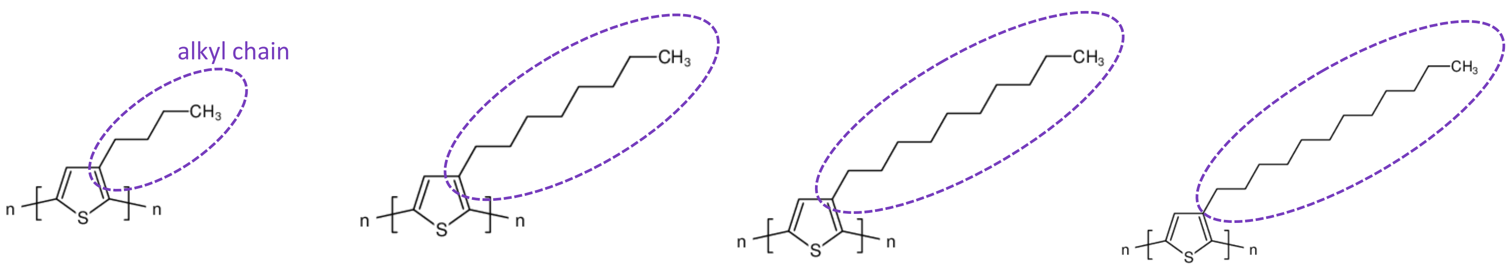
$$M_w = \sum_i w_i M_i = M_0 \frac{\sum_i i^2 n_i}{\sum_i i n_i}$$ weight-average molecular weight

$$D = \frac{M_w}{M_n}$$ dispersity of a polymer

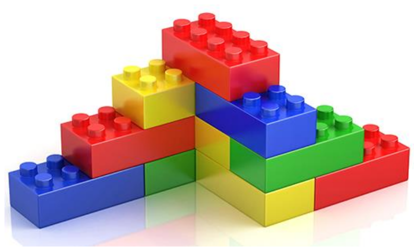
Tuning & Designing Polymers

through synthesis

Poly(3-alkylthiophene-2,5-diyl)

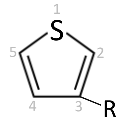


Poly(3-butylthiophene-2,5-diyl) **Poly(3-octylthiophene-2,5-diyl)** **Poly(3-decylthiophene-2,5-diyl)** **Poly(3-dodecylthiophene-2,5-diyl)**



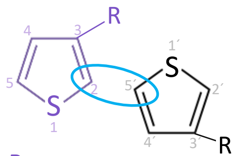
- differences in molecular packing and volume occupied can lead to different properties (optical, mechanical, …)
- higher crystallinity increases the polymer charge transport capability in solid state

Polymers & Regio-regularity

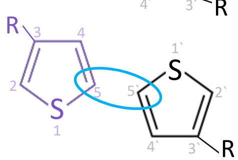


Thiophene (monomer)

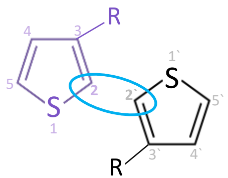
thiophene rings may be connected either
head-to tail, ***tail-to-tail*** or **head-to-head**



head-to-tail



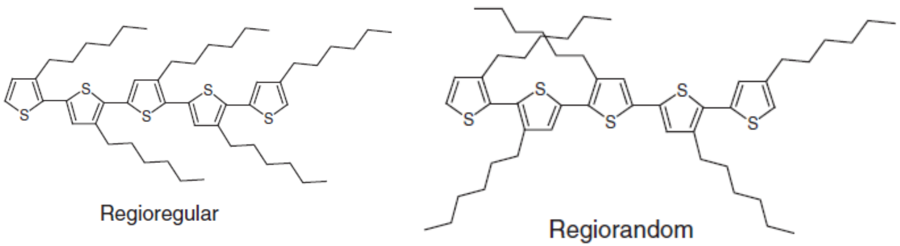
tail-to-tail



head-to-head

(Degree of) **region-regularity** is measured through the **number of *head-to-tail*** linkages in the polymer (100% regioregular: all *head-to-tail*)

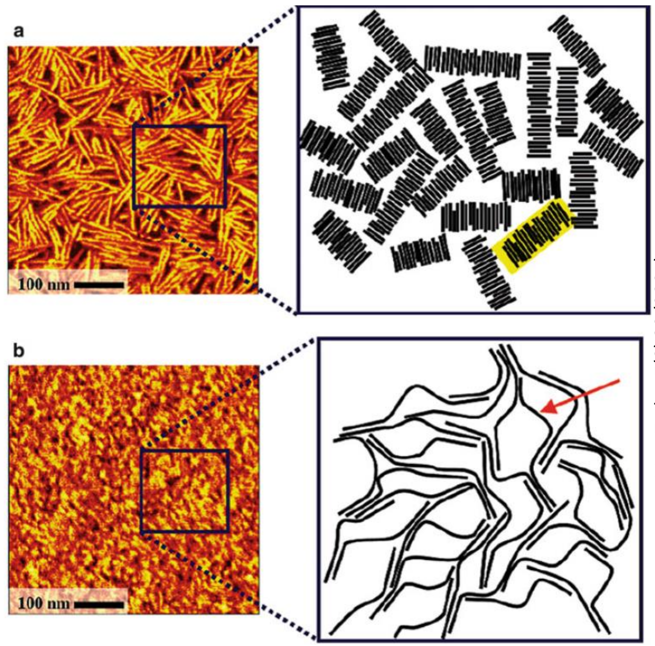
P3HT (poly-thiophene)



Head-to-tail links lead to *more crystalline materials*

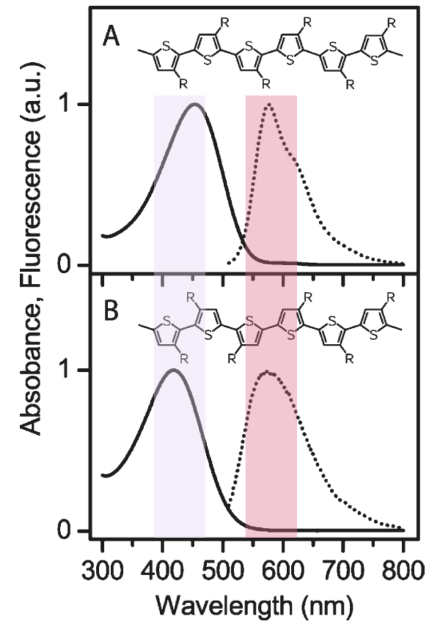
Side chains regular arrangement allows *for more regular packing*

Polymer Regio-regularity: Morphology & Properties



Mat. Today **7**(9) 20 (2004)

Atomic force microscopy images of region-regular P3HT films with M_w of (a) 31.1kD and (b) 3.2 kD. The large molecular weight polymer forms a more ordered crystalline film.



J. Phys. Chem. Lett. **2**, 1400 (2011)

Normalized absorption (solid) and fluorescence (dotted line) of (A) region-regular (97% HT-HT) and (B) region-random (64% HT-HT) P3HT in chloroform.

Summary

- Organic materials are composed primarily (90%) of ***carbon***, ***hydrogen*** and ***oxygen*** held together by ***van der Waals forces***
- ***Small molecules*** or ***polymers***, and can transport either h^+ or e^-, often both
    - *polymer*: repeated chain of single monomer in more complex structures
- ***Different morphologies*** can be found for same organic materials, depending on molecular packing, fabrication process and condition, with an overall ***effect on functional properties***

Next

- ***Characterization*** of ***Organic Materials***
- ***Optical*** and ***electronic properties*** of OSC