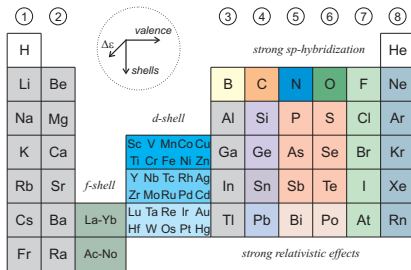


Intro 1/4: What is organic semiconductor

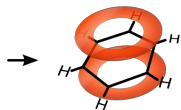
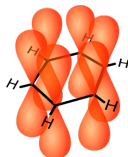
1. **Organic** – built from C with terminal H, possibly with isovalent substitutions (N for CH, O/S for CH₂, F/Cl for H)
2. **π -conjugated** – only π -electrons on frontier orbitals



The periodic table is color-coded to show regions relevant to organic semiconductors:

- Region 1 (H):** Hydrogen (H)
- Region 2 (Li, Be):** Alkali and alkaline earth metals
- Region 3 (B, C, N, O, F):** Strong sp -hybridization (highlighted in blue, orange, and green)
- Region 4 (Al, Si, P, S, Cl):** d -shell elements (highlighted in purple, orange, and green)
- Region 5 (Ga, Ge, As, Se, Br):** f -shell elements (highlighted in orange, orange, and green)
- Region 6 (In, Sn, Sb, Te, I):** f -shell elements (highlighted in orange, orange, and green)
- Region 7 (Tl, Pb, Bi, Po, At):** f -shell elements (highlighted in orange, orange, and green)
- Region 8 (He, Ne, Ar, Kr, Xe, Rn):** Noble gases

Labels on the table include: ΔE , valence, shells, d -shell, f -shell, and strong relativistic effects.



$$t_{sp^2} = 3.26 \frac{\hbar^2}{md^2} \gg t_{pp\pi} = 0.63 \frac{\hbar^2}{md^2}$$

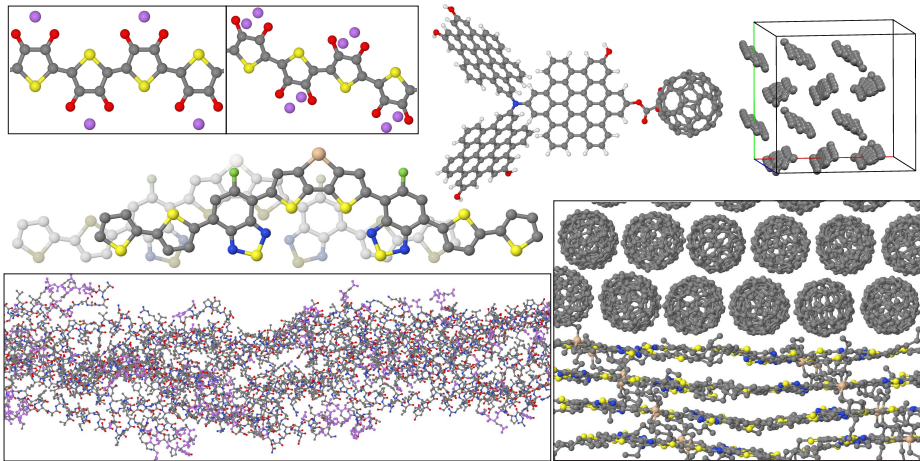
(Harrison's parameterization)

- Also **metal-organic** – include d -elements via $pd\pi$
- Also **hybrid** – include any electronic system in resonance

Number of organic semiconductors is comparable to number of inorganic ones
Display is an example of a competitive application

Intro 2/4: Structural diversity

From 0D to 3D, from rigid to soft, often heterogeneous with multiscale structuring



Intro 3/4: Some applications of organic semiconductors

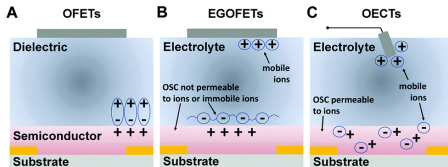
Any electronic device can be made all-organic

Light emitters (most successful)



Adv Mater 33, 2005630 (2021)

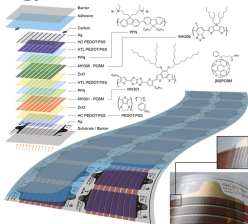
Transistors (most ubiquitous)



J Mater Chem C 6, 11778 (2018)

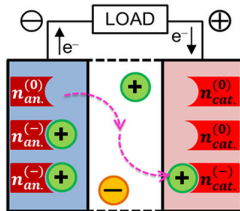
Solar cells (approaching 20% PCE)

Adv Energy Mater 11, 2002653 (2021)



Energy Environ Sci 7, 2925 (2014)

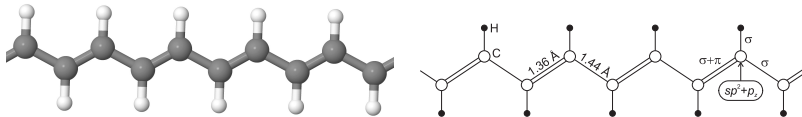
Batteries (early research)



Chem Rev 120, 6490 (2020)

Intro 4/4: Challenges in modeling organic semiconductors

- Electron-electron correlations in low dimensional systems
 - ▶ Trans-polyacetylene (tPA) – 5 electrons in repeating unit – smallest real-world material for which majority of mainstream approaches fail



- Strong mode-specific electron-phonon coupling + soft structure
 - ▶ tPA – Peierls transition (C–C bond stretching mode) and solitons
 - ▶ Bond Length Alternation (BLA)
 - ▶ polaron formation
 - ▶ vibronic progression in spectra
- Scale gap problem – what is modeled is not what is measured

