Announcements

Homework 3/10:
- Is due now.
  - Please email it to me if you have not already done so.
  - I will return it one week from today later (October 26th).

Homework 4/10:
- Is online now.
- Due Tuesday October 26th at the start of the lecture (2:00pm).
- I will return it one week later (November 2nd).
- Homework 4 will consist of content covered in Lectures 7 and 8.
Additional Information

- The course textbook (Brotherton) – Chapter 10 covers the basics of this subject.
- This is another very active area of research, so there are plenty of reviews on the subject.
  - https://pubs.rsc.org/en/content/articlelanding/2010/cs/b909902f#!divAbstract

Lecture 8

- Organic Chemistry Background.
- Electronic Structure of Organic Semiconductors.
- Organic Thin-Film Transistors.
- OTFT Performance.
Organic Chemistry
Background

Organic Compounds
• When we hear organic, we normally think:
  
  100% ORGANIC

• When we (scientists) say organic compounds, we generally mean compounds containing at least one carbon atom.
• They are normally drawn like this:
Organic Compounds

- However, the definition is not really that strict.
- $C_{60}$ (fullerene) is generally referred to as an organic semiconductor:
- Carbon nanotubes and graphene are not generally referred to as organic semiconductors:

Hybrid Semiconductors

- Some compounds are described as being hybrid inorganic-organic compounds.
- More on these in the next lecture.
Why Organic Electronics?

- So why would we be interested in organic electronics?
- Plastics are organic compounds.

\[
\text{Polypropylene} \quad \text{Polyvinylidene Chloride} \\
\begin{array}{c}
\text{Polyethylene} \\
\text{Polystyrene}
\end{array}
\]

- And plastics have interesting mechanical properties...

Why Organic Electronics?

- Rather than just having a plastic substrate, what if the whole device could be organic (plastic)?

- We could then in theory produce much more versatile electronics.
- Leading to electronics with a wide range of physical form factors.
Why Organic Electronics?

• The cost has the potential to be incredibly low.
• If we could produce plastic electronics at a comparable cost to consumer plastics, it could change everything.

• We are a long way off this at the moment.

Solar Power

• Being able to easily-deploy very cheap solar cells is also very attractive.
Organic Molecules

- Before we look at the properties of organic molecules, let’s have a very quick refresh on the notation used in organic chemistry.
- Carbon is a group 14 element (like silicon), and therefore has 4 valence electrons:
  \[
  C = [\text{He}] 2s^2 2p^2
  \]

Alkanes

- The organic molecules we are concerned with are all covalent.
- I.e. carbon atoms will be sharing electrons.
- The most simple set of organic compounds are the **alkanes**.
- Starting with methane (CH\(_4\)):
Alkanes

• We would normally draw methane (CH\textsubscript{4}): as follows:

• Other alkenes would be drawn as:

- Ethane (C\textsubscript{2}H\textsubscript{6})
- Propane (C\textsubscript{3}H\textsubscript{8})
- Butane (C\textsubscript{4}H\textsubscript{10})

Caffeine

• Using this notation, things can get very complicated very quickly.

• Take caffeine (C\textsubscript{8}H\textsubscript{10}N\textsubscript{4}O\textsubscript{2}) for example:

• Sometimes called “skeletal formula”, “line-angle formula” or “shorthand formula”.

• In organic chemistry, we use the following notation:
Shorthand Notation

• There are a few rules for shorthand notation. For us, we will just be interested in two:

1). Hydrogens are Implicit.
   • They bond to carbons via single bonds in any available positions.
   • I.e. they are where they should be.

2). Carbons exist in unlabeled positions
   • Any unlabeled vertex is now a carbon atom.
   • Lines to nowhere are bonds to carbons.
Electronic Structure of Organic Semiconductors

Traditional Polymers

- Consider a traditional, insulating, plastic such as polyethylene (PE).
  - Every carbon bonds to 4 other atoms.
  - Two carbons and 2 hydrogens (expect at ends).
  - All electrons are involved in single covalent bonds, so there are no free (delocalized) electrons.
  - **PE is a good insulator.**
Trans-Polyacetylene

- Now consider the following polymer (longhand):

\[
\begin{array}{c}
\text{C} \equiv \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{C} \\
\text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\
\end{array}
\]

- Each carbon bonds to 3 other atoms.
- What happens to the other valence electron?
- We will now quickly discuss how such a polymer could exist.

\[s^2 \text{ Hybridization}\]

- The ground state of carbon is:

\[
\text{C} = [\text{He}] 2s^2 2p^2 \quad \text{Or} \quad \text{C} = 1s^2 2s^2 2p^2
\]

- If one electron is excited from the 2s to the 2p state the configuration becomes:

\[
\text{C}^* = [\text{He}] 2s^1 2p^3 \quad \text{Or} \quad \text{C}^* = 1s^2 2s^1 2p^3
\]

- This could be provided through extra energy during synthesis for example.
- In this case we now have one 2s electron and three 2s electrons to participate in bonding.
\( sp^2 \) Hybridization

- As we have discussed before, these states can \textit{hybridize} into a linear combination of orbitals.
- For a material such as trans-polyacetylene, \textbf{two of the three} 2p orbitals, and the \textbf{one} 2s orbital, hybridize into \textbf{three} \( sp^2 \) orbitals:

\[
\text{Or, in Dirac Notation, each electron is described as:} \\
|sp^2\rangle = \frac{1}{3}|2s\rangle + \frac{2}{3}|2p\rangle
\]

- These three orbitals are highly directional.
- It is energetically favorable for the three \( sp^2 \) orbitals to form a planar structure with 120° between each lobe.
- This explains the three valence electrons, but recall we have 4 valence electrons in carbon: 
  \( C^* = 1s^22s^12p^3 \)
- We have \textbf{one extra} 2p orbital.
**$sp^2$ Hybridization**

- It turns out the remaining $p$ orbital will orientate with lobes above and below the plane of the $sp^2$ orbitals.
- The $sp^2$ orbitals from each carbon atom strongly overlap with the two adjacent carbon atoms and one adjacent hydrogen atom.

$$\text{C} = \text{C} \cdots \text{C}$$

**$sp^2$ Hybridization**

- This strong, in-phase, orbital overlap results in strong covalent bonds, called $\sigma$-bonds.
- The remaining $p$ orbital forms another weak bond with one of the adjacent carbon atoms.
- These weak bonds are called $\pi$-bonds.
Conjugation

• Because this second, weak, bond is only made with one of each carbon’s neighbors, we describe the polymer as having alternating single and double bonds along the backbone:

\[
\begin{array}{cccccccc}
C & C & C & C & C & C & C & C \\
H & H & H & H & H & H & H \\
& & & & & & & \\
\end{array}
\]

• An organic molecule consisting of alternating single and double bonds is called conjugated.

• Trans-polyacetylene is a conjugated polymer.

Conjugation

• In reality, electrons don’t really behave like this.

• The electrons delocalize across the backbone:

• Because these delocalized states are only half filled (one bond per every two carbon atoms), the electrons behave as if they are in a half-filled band.

• I.e. there is space for the electrons to move along the polymer backbone.

• I.e. the plastic conducts electricity!
Doped Polyacetylene

- In 1977 Alan MacDiarmid, Alan Heeger, and Hideki Shirakawa published a paper on doped trans-polyacetylene.

> VOLUME 39, NUMBER 17 PHYSICAL REVIEW LETTERS 24 October 1977

Electrical Conductivity in Doped Polyacetylene

C. K. Chiang, C. R. Pincher, Jr., Y. W. Park, and A. J. Heeger
Department of Physics and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104

and

H. Shirakawa, E. J. Louie, S. C. Gau, and Alan G. MacDiarmid
Department of Chemistry and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104

Received 22 June 1977

- You need to induce charges into the polymer to get them to move. They did this via doping with AsF$_5$.

Doped Polyacetylene

- The conductivity was observed to be very high (~100 $\Omega$cm$^{-1}$)

- It won them the 2000 Nobel Prize.

The Nobel Prize in Chemistry 2000
Benzene

- Before we can talk about devices, let us discuss one more example system.
- Benzene \((C_6H_2)\) is a conjugated molecule:
  
  **Longhand**
  
  \[
  \begin{align*}
  &\text{C} = \text{C} \\
  &\text{H} = \text{H} \\
  &\text{C} = \text{C} \\
  &\text{H} = \text{H}
  \end{align*}
  \]

  **Shorthand**
  
  \[
  \left\{ \begin{array}{c}
  \text{C} = \text{C} \\
  \text{H} = \text{H} \\ 
  \text{C} = \text{C} \\
  \text{H} = \text{H}
  \end{array} \right\}
  \]

- It is a bit like “curled-up” polyacetylene.

Benzene

- As with polyacetylene, three \(sp^2\) hybridized electrons participate in strong \(\sigma\)-bonding with adjacent carbons and hydrogens. Leaving the lobes of \(p\)-orbitals above and below the ring.

- And as before, these orbitals delocalize to form an electron cloud.
Benzene Orbitals

- At this point it is worth reminding ourselves **what orbitals are**.
- They are surfaces, in real space, of equal wavefunction amplitude.
- They are possible states that exist (as defined by quantum mechanics).
- They can be occupied with electrons.
- But they can also be empty, and ready to accept electrons, which then have the described wavefunction.

For each molecule, a range of different orbitals exist.
- Each with a different energy.
- The Pauli-Exclusion principle states that only 2 electrons can occupy each state.
- The states are filled according Hund’s Rules. From low energy to high.

Benzene Orbitals

• Under normal conditions, the 6 lowest energy states are occupied with the 6 delocalized $p$-electrons.

• The energy of the highest occupied molecular orbital is called the HOMO.

• The energy of the lowest unoccupied molecular orbital is called the LUMO.

• There is an energy gap between these states.

The LUMO

• The LUMO is the lowest energy state which is able to accommodate extra electrons.

• So we could add an electron to this state, and it would be transported.

• I.e. it behaves like the conduction band of a traditional semiconductor.
The HOMO

- Similarly, the HOMO is the highest energy state that is completely full of electrons.
- So we could add a hole (remove an electron) to this state, and it would be transported.
- I.e. it behaves like the \textit{valence band} of a traditional semiconductor.

Organic Semiconductors

- So for a conjugated molecule we can picture the system as having the following density of states:
Organic Semiconductors

• Most organic semiconductors have much more complicated density of states:

![Density of States](image1)


Organic Semiconductors

• And the delocalized molecular orbitals can be much more complicated than we have discussed so far:

![Molecular Orbitals](image2)

Organic Thin-Film Transistors

- Sometimes you will hear organic transistors being referred to as organic thin-film transistors (OTFTs).
- Alternatively they are referred to organic field effect transistors (OFETS).
- These terms mean the same thing.
- There a range of OTFT architectures, depending on location of electrodes, and dielectric.
Organic Thin-Film Transistors

- We will not talk in detail about all the steps involved in forming OTFTs today.
- We will cover some basics in Lecture 10.
- Many processes for OTFTs are still experimental.
- We will cover dielectrics in more detail in Lecture 11.
- We will cover electrodes in more detail in Lecture 12.

OTFT Performance
Transport

- As we talked about earlier, transport in organic occurs through hybridized $p$-orbitals.

- So the overlap of these directional orbitals is very important, and the molecular packing is therefore very important.

- Unlike oxides, where disorder is less important.

Morphology

- So as you can expect, the micro-morphology of organic semiconductors is extremely important.

- Traditionally it has always been believed that crystallinity is good.

- There is a lot of evidence for this in vacuum-deposited films, like pentacene:
Morphology

- This was always also assumed to be the case in solution-processable materials (such as polymers) as well.
- Poly(3-hexylthiophene) (often just called P3HT) is a good example material.
- The side-chains are not conjugated, and therefore do not contribute to transport.
  - They are present to improve solubility.

Morphology

- So transport occurs through the conjugated thiophene faces
- Sometimes called $\pi - \pi$ stacking.
  - Because there is overlap due to $\pi$ bonding
- Therefore how molecules pack on substrate matters:
  - “Edge-on”
  - “Face-on”
Morphology

- There is evidence to support this:

- This has been the long-held assumption about organic transistor design.

Morphology

- The morphology of organic semiconductors is normally extremely complex:

- Especially when multiple semiconductors are blended.
Backbone Transport

- There have been some recent reports of charges being transported down the backbone of certain polymers.

- Potentially less dependence on morphology / order.

Electrons vs Holes

- We have previously seen (Lecture 2) that the ability of charges to be injected and transported depends on the energetic alignment of the electrodes with the bands of the semiconductor:
P-Type OTFTs

- So good hole-transporting (p-type) materials have good alignment of the HOMO with the work function of injecting electrodes.

N-Type OTFTs

- So good electron-transporting (n-type) materials have good alignment of the LUMO with the work function of injecting electrodes.
N-Type Materials

- It has been shown\[^1\] that the standard redox potentials of water and oxygen with many organic semiconductors lies around 4 eV.
- This means that any organic semiconductors with a LUMO $\lesssim 4$ eV are likely to be unstable in the presence of water and oxygen (air).
- For this reason there are much fewer stable n-type organic semiconductors than p-type.


Charge Transport

- Many organic semiconductors show a gate-field dependent mobility.
- For this reason, and the fact that, theoretically, all transport must occur via hoping between overlapping orbitals, variable range hoping (VRH) is normally used to model transport in OTFTs.
OTFT Mobility

- OTFTs have now been studied for > 30 years, so the field is quite mature.

\[ \mu_{\text{sat}} = \frac{2L}{WC_{\text{ox}}} \left( \frac{d\sqrt{I_D}}{dV_G} \right)^2 \]

- Unfortunately, some of the most recent values > 10 cm²/Vs are not reliable.

- The gradual channel model is being applied when it is not valid to do so.

\[ \mu_{\text{lin}} = \frac{L}{WC_{\text{ox}}V_D} \frac{dI_D}{dV_G} \]
OTFT Mobility

- When plotting mobility vs gate voltage for OTFTs, normally some sort of dependence is observed.

- Unfortunately, some groups will take the peak value, even when it is not appropriate to do so.

- So what is the real mobility of OTFTs?

- Current values are only lab based, as these devices have not yet been commercialized.

- But the very best, reliable, values are roughly:
  - \( \mu_h \approx 15 \text{ cm}^2/\text{Vs} \).
  - \( \mu_e \approx 5 \text{ cm}^2/\text{Vs} \).

- For the few prototype commercial devices we have seen, we can probably say:
  - \( \mu_h \approx 0.5 – 1.0 \text{ cm}^2/\text{Vs} \).

- But progress continues to be made!
Next Time...

- Carbon-based systems:

- Other material systems.