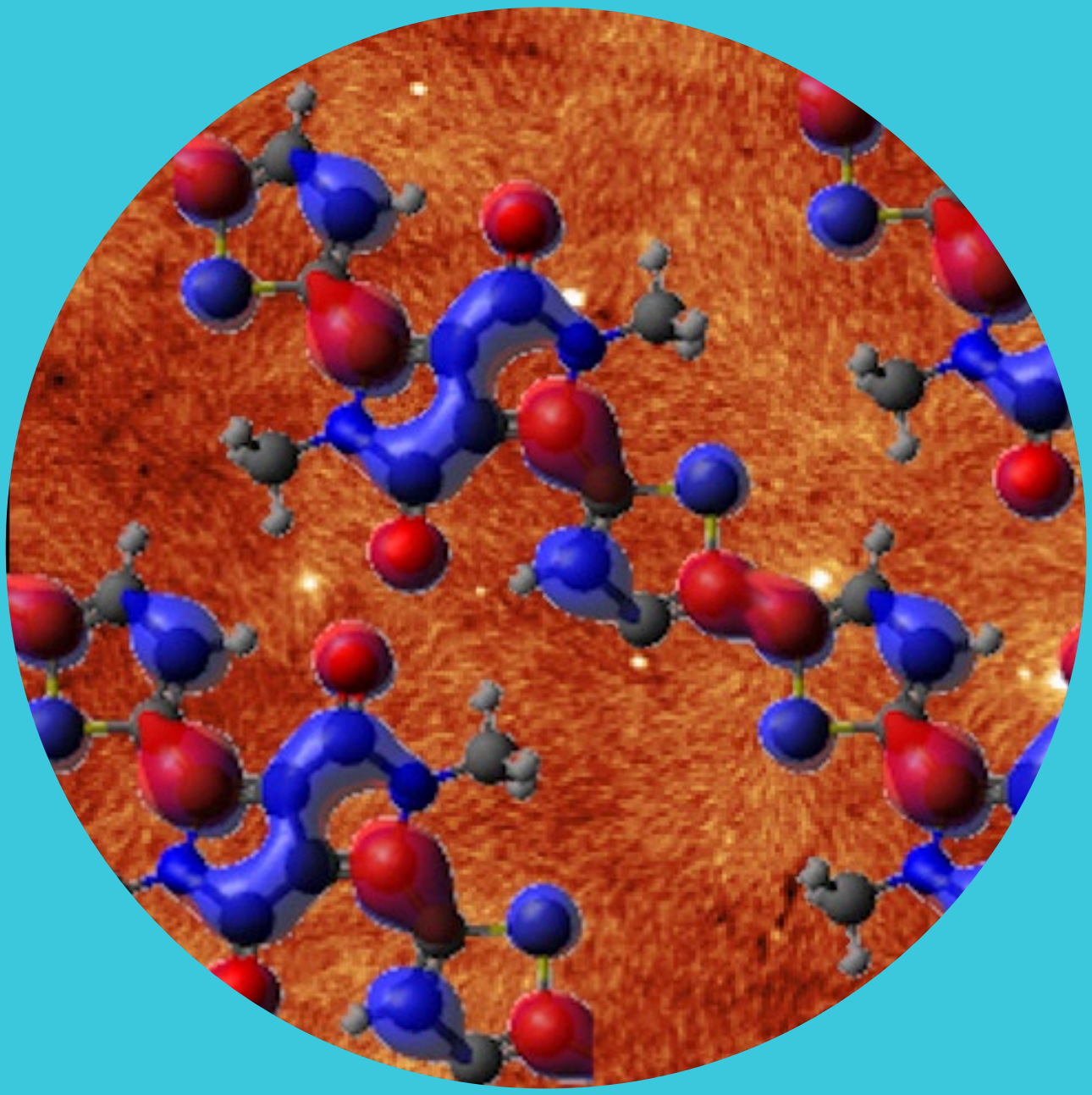
Researchers in Schools



Polymer Semiconductors

Molecular Lego

Pupil Name

Coursebook Designed by Dr. J. Moriarty

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Timetable and Assignment Submission

Timetable – Tutorials

Tutorial	Date	Time	Location
1	1/2/2022	14:55	F10
2	8/2/2022	14:55	F10
3	15/2/2022	14:55	F10
4	1/3/2022	14:55	F10
5	8/3/2022	14:55	F10
6 (Feedback)	22/3/2022	14:55	F10
7 (Feedback)	29/3/2022	14:55	F10

Timetable – Homework Assignments

Homework Assignment	Description	Due Date
Tutorial 1	Baseline Assignment	7/2/2022
Tutorial 2	Putting it all together	14/2/2022
Tutorial 3	DIY Data Analysis	28/2/2022
Tutorial 4	Dotting the i's	7/3/2022
Tutorial 5	Final Assignment	18/3/2022

Assignment Submission – Lateness and Plagiarism

Lateness	
Submission after midnight on 18th March	10 marks deducted
Plagiarism	
Some plagiarism	10 marks deducted
Moderate plagiarism	20 marks deducted
Extreme plagiarism	Automatic fail

Course Rationale

Plastics—or polymers if we're going to get technical[1]—are everywhere: from carrier bags to consumer goods, from artificial fabrics to aerospace, nearly all areas of modern life have put these versatile materials to use.

When most people think about polymers however, they don't often think of semiconductors: those materials like silicon that underpin the electronics that are responsible for so much of what makes the world today what it is. From as early as the 1960s however, chemists have been pushing the limits of what kinds of polymer it is possible to make, and in 1987 a team of Japanese scientists named Hiroshi Koezuka, Akira Tsumura, and Torahiko Ando succeeded in making the first transistor—the building block of all modern electronics—using a polymer semiconductor.

Compared to conventional semiconductors like silicon, polymers offer a number of advantages. Perhaps most important given the climate crisis is that they can be processed at much lower temperatures[2]. This carries with it several advantages, but in particular it means that creating devices can use much less energy than using conventional semiconductors, making their production both better for the environment and cheaper.

This lower temperature production, in combination with the solubility of these polymers in a variety of common solvents, opens up entirely new possibilities. By using such a polymer solution as an "ink", we might one day be able to print electronic devices like we currently print newspapers: running off mile after mile of, say, cheap solar panels.

In order to produce these materials, chemists and physicists have had to work together to figure out which molecules conduct electricity and which don't, and perhaps more importantly, why some are better than others. In fact, chemists have become so skilled at manipulating polymers that they can change individual atoms within a molecule. Physicists can then experiment to discover what effects that tiny change has and use those results to help the chemists pick new polymers that should perform even better. This cycle of production, experimentation and revision is called rational design and marks a new way of thinking about the world around us.

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1 We are.

2 Rarely more than 200 °C, and often at room temperature, compared to over 1,000 °C for silicon.

Uni Pathways Mark Scheme

Grade	Subject Knowledge	Critical Thinking	Written Communication
1st	The essay shows a breadth of knowledge and understanding of the key concepts and issues, through engaging with and interpreting a wide range of relevant sources. Knowledge is used to build and support highly effective arguments.	Analyses, key ideas, information, and arguments. Interprets meaning and makes connections. Identifies and critically evaluates key arguments and statements, deciding on their credibility, strength and relative significance, drawing convincing conclusions.	The essay has a clear and engaging structure, taking the reader from introduction to conclusion. The writing style is appropriate; key terms are used with fluency. There are no, or very few, errors in spelling or grammar. Referencing is used consistently and matches the style taught in the course.
2:1	The essay shows an understanding of key concepts and issues, drawing on a range of relevant sources Knowledge is used to build and support effective arguments.	Analyses key ideas, information and arguments. Identifies relevant data and evidence, deciding on their credibility and strength, drawing reasonable conclusions. Shows some understanding of the relative importance of data.	The essay has a clear structure and the main points are easy to follow. The introduction outlines the essay effectively and the conclusion summarises the main points. The writing style is appropriate; key terms are used correctly. There are few errors in spelling or grammar. Referencing is mostly consistent and matches the style taught in the course.
2:2	The essay shows an understanding of key concepts and issues, with no major misconceptions. Beginning to apply this knowledge to build and support arguments.	Begins to analyse ideas, information and arguments. Identifies some arguments and statements and attempts to evaluate their quality. Not yet showing understanding of the relative strengths and weaknesses of arguments.	The essay structure could be made clearer to better guide the reader through the arguments. The writing style is sometimes informal. Occasionally key terms are not used when it would be appropriate. There are some errors in spelling or grammar, but they do not get in the way of communicating the content. There is some consistency to the referencing.
3rd	Shows a developing understanding of key concepts and issues, with some misconceptions. Not yet applying this knowledge to build and support arguments.	Begins to analyse ideas and information. Describes statements and arguments while not yet evaluating them.	The grammar, spelling, style, and structure of the work need improving to communicate ideas to the reader. The essay has no or a limited introduction and conclusion. Key terms and references are not always used correctly.

Baseline Assignment: Pupil Feedback Report

Name of Pupil	
Name of School	
Name of RIS teacher	
Title of Assignment	

How your assignment is graded:

Grade	Marks	What this means
1st	70+	Performing to an excellent standard at A-level
2:1	60-69	Performing to a good standard at A-level
2:2	50-59	Performing to an excellent standard at GCSE
3rd	40-49	Performing to a good standard at GCSE
Working towards a pass	0-39	Performing below a good standard at GCSE
Did not submit	DNS	No assignment received by The Brilliant Club

Lateness	
Any lateness	10 marks deducted
Plagiarism	
Some plagiarism	10 marks deducted
Moderate plagiarism	20 marks deducted
Extreme plagiarism	Automatic fail

Marks

OVERALL MARK / 100		FINAL MARK / 100 (including any deductions)	
DEDUCTED MARKS		FINAL GRADE	
If marks have been deducted (e.g., late submission, plagiarism) the teacher should give an explanation in this section:			

Mark Breakdown and Feedback

Subject knowledge	
	mark
Critical thinking	
	mark
Written communication	
	mark

Final Assignment: Pupil Feedback Report

Name of Pupil	
Name of School	
Name of RIS teacher	
Title of Assignment	

How your assignment is graded:

Grade	Marks	What this means
1st	70+	Performing to an excellent standard at A-level
2:1	60-69	Performing to a good standard at A-level
2:2	50-59	Performing to an excellent standard at GCSE
3rd	40-49	Performing to a good standard at GCSE
Working towards a pass	0-39	Performing below a good standard at GCSE
Did not submit	DNS	No assignment received by The Brilliant Club

Lateness	
Any lateness	10 marks deducted
Plagiarism	
Some plagiarism	10 marks deducted
Moderate plagiarism	20 marks deducted
Extreme plagiarism	Automatic fail

Marks

OVERALL MARK / 100		FINAL MARK / 100 (including any deductions)	
DEDUCTED MARKS		FINAL GRADE	
If marks have been deducted (e.g. late submission, plagiarism) the teacher should give an explanation in this section:			

Mark Breakdown and Feedback

Subject knowledge	
	mark
Critical thinking	
	mark
Written communication	
	mark

Launch Event

The launch event is your opportunity to learn more about this course and Uni Pathways. You will watch some videos, listen to your teacher and have some discussion. Below is some room to make notes for some of the videos you will watch during the event.

Virtual Campus Tours

Notes…

The Scholars Programme Alumni

Notes…

Student Ambassadors

Notes…

Subject Vocabulary

Word	Definition	In a sentence
AFM	Atomic Force Microscopy: a technique for making high-resolution images using a probe to "feel out" a surface.	Atomic force microscopy can produce much higher resolution images than light microscopy.
Absorption Spectroscopy	A technique used to measure which frequencies of light a material absorbs.	Absorption spectroscopy can give us a lot of useful information about a material's electronic structure.
Conjugated Backbone	A long chain of atoms which all have π electrons.	The repeated double bonds between carbon atoms in polyacetylene give it a conjugated backbone.
Delocalised electrons	π electrons that, because they are weakly bound, can travel along a conjugated backbone.	Delocalised electrons can travel away from their atoms, creating an electrical current.
Energetic Disorder	How varied the energy levels of electrons within a material are.	Energetic disorder is a good predictor of mobility in polymer semiconductors.
Flexion	Bending something back on itself.	When you bend your elbow, your arm experiences flexion.
Intermolecular	Between/over different molecules.	Electrons have to hop between neighbouring molecules during intermolecular transport.
Intramolecular	Within one molecule.	Electrons are incredibly fast when travelling intramolecular distances.
Moiety	A named part of a molecule, larger than an atom, that can be observed in many other molecules.	Butyl acetate (a molecule that gives apples and honey their smell) contains an acetyl and a butyl group: both examples of moieties.
Mobility	How quickly electrical charge can flow through a material inside an electric field.	Graphene has a mobility of more than 200,000 $cm^2V^{-1}s^{-1}$, much higher than PBTTT: its mobility is 0.2 $cm^2V^{-1}s^{-1}$.

Molecule	A group of atoms that are bound together.	Water is an example of a simple molecule.
Monomer	The repeated pattern of atoms that makes up a polymer.	Polyethylene is made of ethene monomer units.
PDS	Photothermal deflection spectroscopy: a technique for measuring energetic disorder.	Photothermal deflection spectroscopy uses the physics of mirages to let us investigate the electronic structure of materials.
π (pi) electrons	Electrons that are involved in a chemical bond but only weakly bound between their atoms.	π electrons allow polymers to be semiconductors rather than insulators.
Polymer	A large molecule made up of a repeating pattern of atoms.	Plastics are examples of polymers.
Semiconductor	A material that can conduct electricity better than an insulator, but not as well as a conductor.	Semiconductors are the basis of all electronic technology.
Torsion	Twisting something along its length.	When you turn your hand palm-up or palm-down, your arm experiences torsion.

Tutorial 1 – Can Plastics Conduct Electricity?

Figure 1.1: A flexible phone made by Samsung using polymer semiconductors.

What is the Purpose of Tutorial 1?

By the end of this tutorial, you should be able to say:

- I can define key terms including polymer, semiconductor, conjugated backbone etc.
- I can structure a paragraph to clearly explain scientific concepts.
- I can explain how electricity travels through a polymer semiconductor over different length scales using a mixture of diagrams and text.

Preamble

Plastics are all around us! They contain our food, form the cases of our phones and computers, and are even used to make replacement knee joints. But can they conduct electricity?

Think, Pair, Share: What do you know about plastics and polymers? Are they conductors?

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Polymers

Plastics are part of a family of materials called polymers. Polymers are made up of many repeating parts with the same structure. The word polymer is from Ancient Greece and is made up of the words *polus* (which means "many") and *meros* (meaning "parts"): it literally means "many parts".

The individual parts of a polymer—the repeating groups of atoms—are called monomers. This is another Ancient Greek word made up of the words *mono* (meaning "one") and *meros*. Literally: "one part".

Exercise: Spot the Monomer

Here are some examples of polymers. Circle the monomer unit (the repeating set of atoms) in each one:

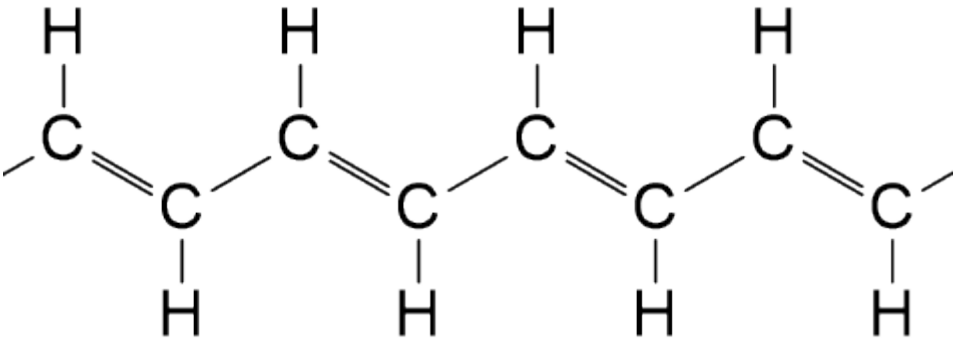

Figure 1.2: Polyacetylene

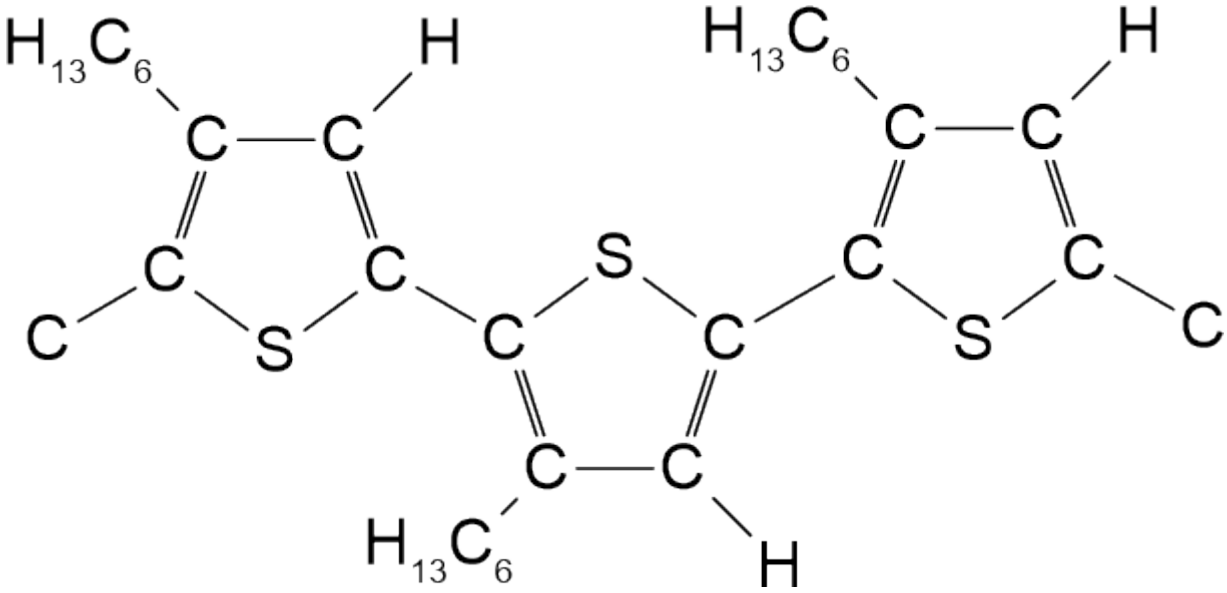

Figure 1.3: Polyhexylthiophene

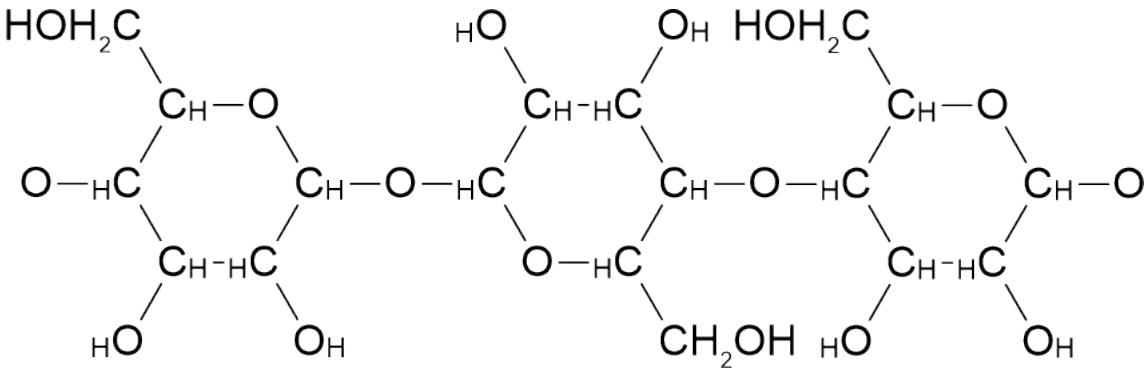

Figure 1.4: Cellulose

Semiconductors

You've already heard of electrical conductors—materials that can carry an electrical current—and electrical insulators—ones that can't[1]. Semiconductors are between the two: they conduct much better than an insulator[2], but not as well as a conductor.

Polymer Semiconductors

As it turns out, if you know a skilled enough chemist, you can make polymers that are semiconductors. It took a long time to figure this out—humans have used materials containing polymers like wool and linen since before recorded history, but we didn't know what they were until Hermann Staudinger produced the modern definition in 1920[3]—but in the 1960s researchers discovered that some polymers could be semiconductors. By 1987, the first transistor—a very important kind of electronic device—was made using a polymer called polythiophene by a trio of Japanese researchers: Hiroshi Koezuka, Akira Tsumura and Torahiko Ando.

Writing Scientifically

When we write about science it's important that we make sure that we do so clearly to avoid misunderstanding. The more complicated the science gets, the more this clarity is. A good way to do that is to plan what we're going to write ahead of time.

You should start with a clear idea of what your paragraph will be about, then make sure that everything you put in is on that subject. If you want to include more things, you can always make another paragraph: it's better to stay on topic! Don't worry about writing long sentences, but make sure they are all accurate and to the point. Make sure that if you need to use any scientific words you use them correctly.

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1 At least, not without hitting it with lightning and setting it on fire.

2 Again, before it's been lightning bolted and set on fire.

3 There was a lot of debate about this definition at the time, until another scientist called Herman Mark provided evidence to support Staudinger's theory eight years after he proposed it.

Exercise: The Good, The Bad and The Stylistically Ill-Advised

"We call the force produced by gravity on an object its weight. Like other forces it is measured in Newtons (N). Despite us often talking about how much something 'weighs', we are usually talking about mass (measured in kilograms, kg) in such cases. Mass remains the same wherever you are in the universe, while weight changes from place to place depending on the strength of the local gravitational field."

"Objects have weight that changes and mass that does not. On the moon things weigh less because it isn't as heavy as the Earth but on Jupiter they weigh more because it's heavier and on the Sun it would be even heavier because it's absolutely massive but it wouldn't matter anyway because most things would be burned up anyway by then."

Exercise: Let's write together

Now that we've learned about writing clear paragraphs, let's summarise what we've learned about polymer semiconductors.

…… …… …… …… …… …… …… …… …… …… …… …… …… …… ……	**Planning Space** **Polymers** **Semiconductors**

How Do You Make a Polymer into a Semiconductor?

We know that polymers can be semiconductors now, but how does that happen? What changes to turn them from insulators into semiconductors?

To answer that we have to look all the way down to their molecules. All polymer semiconductors we'll be looking at during this course share one important feature: a conjugated backbone.

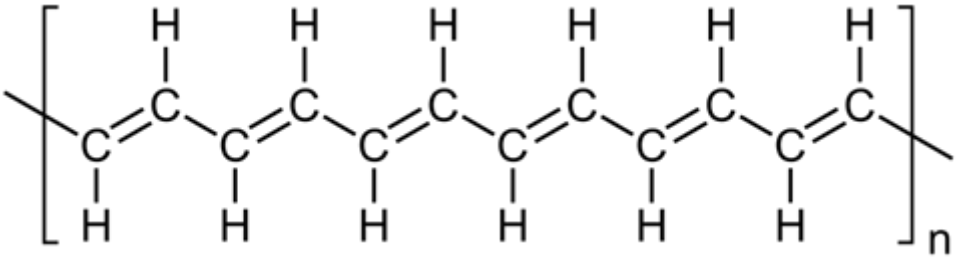

Figure 1.5: Chemical Structure of polyacetylene.

This is polyacetylene. Notice the way its monomer contains a carbon-carbon double bond. That double bond contains four electrons. When atoms bond together, their electrons are normally tightly bound between their nuclei. In these double bonds though, the second pair of electrons is only weakly bound to the nuclei. In fact, if you laid this page flat, these weakly bound electrons would stick out of the paper like this:

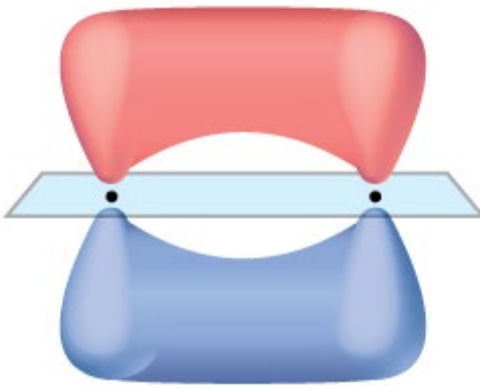

Figure 1.6: Distribution of delocalised electrons between two carbon atoms.

Where the blue rectangle is the page, and the black dots are the nuclei. Because the electrons can float around like this, they can actually jump from carbon atom to carbon atom. We call them delocalised electrons because they don't have to stay in one place: they can move along the polymer's "backbone" of carbon atoms. Since a movement of electrons like this is what we call an electrical current, we now have our explanation for what makes a polymer into a semiconductor: the pattern of alternating single and double carbon-carbon bonds called a conjugated backbone.

Exercise: More Writing!

Using the writing skills we practised together earlier, write a short paragraph explaining what a conjugated backbone is. Make sure to mention delocalised electrons in your answer.

....	**Planning Space**

Going Intermolecular

By itself though, travelling along a single polymer molecule doesn't get an electron very far. Even the longest polymers are only a few micrometres long[1]. To get any further, our electrons need to hop from one molecule to another.

Much like trying to jump across a river, this is easier when the molecules are closer together, because the electrons don't have to hop as far. At the electron level, the delocalised electron regions shown in *Fig 1.6* can overlap if two molecules are packed tightly enough against each other in a neat stack, so it's helpful if we can get the molecules to squeeze tightly together.

Even in an ideal world though, this intermolecular transport is still much slower than intramolecular transport along the conjugated backbone.

1 A micrometre is a millionth of a metre. Human hairs are about 100 micrometres wide.

Exercise: The backbone's connected to the… backbone?

Look at this diagram of a group of polymer semiconductor molecules. Don't worry about their chemical structure for now, just their general arrangement.

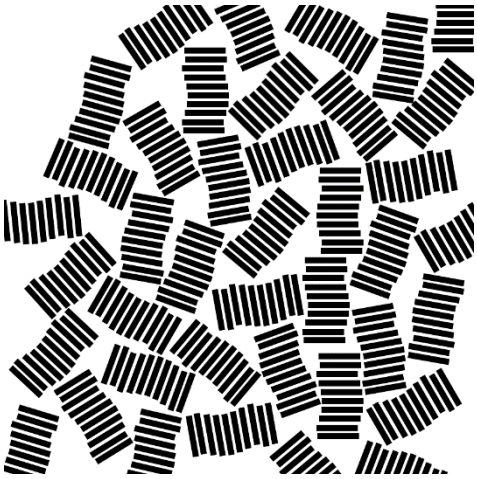

Figure 1.7: A group of nanorods comprised of many short molecules.

Let's think about how electrons flow through this mystery material and put our observations into a paragraph.

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Homework: Baseline Assignment

Explain how electricity flows through polymer semiconductors.

Details of the assignment:

Based on our first tutorial, write a short essay (400-500 words) explaining how polymers can conduct electricity, including diagrams to illustrate key points.

Success criteria – how to structure your assignment and what to include:

An introduction defining what polymers and semiconductors are and why polymer semiconductors are potentially useful.

An explanation of why some polymers are semiconductors while others are insulators. This should include details of: (a) different kinds of electron bonds; (b) delocalised electrons; and (c) the importance of a conjugated backbone. Use a diagram to illustrate these concepts.

How electrons travel through these materials at different length scales, paying attention to the differences between inter- and intramolecular transport, which is faster and why. Again, use a diagram to illustrate these concepts.

A short concluding paragraph on what you think is important in determining a polymer's mobility. Remember which kind of transport is faster and think about how you might be able to get more of it.

In this assignment, show me that you **understand**:	Show me that you **are able to**:
The terms 'polymer', 'semiconductor' and 'conjugated backbone'. What makes polymer semiconductors different from other polymers. How electricity travels through polymer semiconductors.	Write clearly and accurately about scientific topics. Structure your essay logically. Use diagrams appropriately to make your explanations clearer.

Tutorial 2 – Charge Carrier Mobility

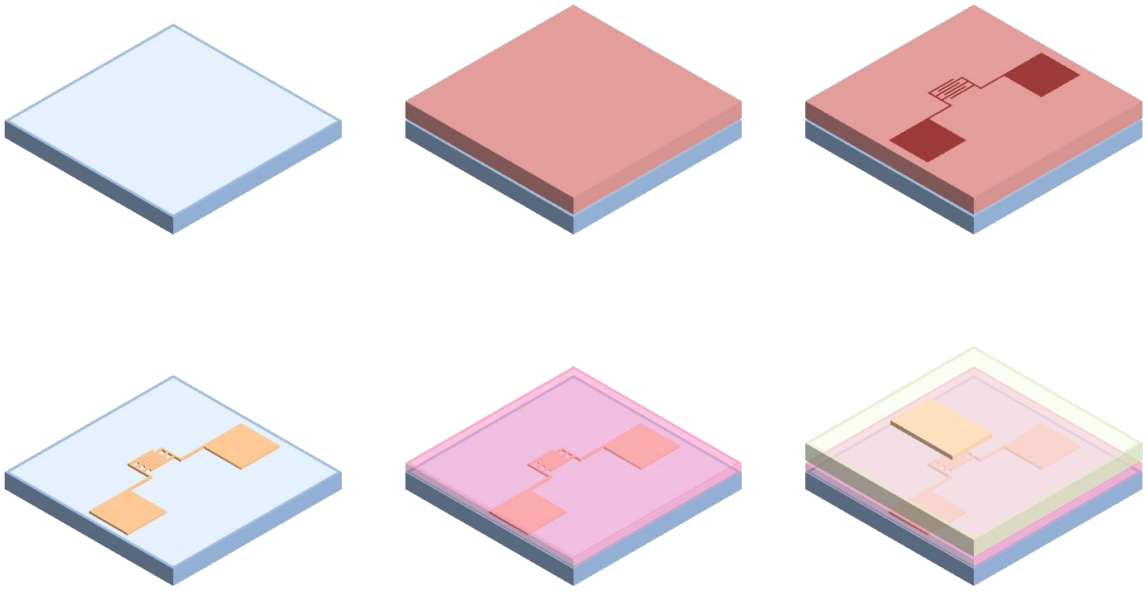

Figure 2.1 Step-by-step production of a polymer semiconductor transistor.

What is the Purpose of Tutorial 2?

By the end of this tutorial, you should be able to say:

- I can explain how charge transport is affected by a material's structure
- I can define mobility, including its units, and explain why it is important for semiconductor devices.
- I can calculate a material's mobility from transistor data.

Recap

Last time we learned what polymer semiconductors were and the basics of how they conduct electricity: delocalised electrons along their conjugated backbones can travel at both the intramolecular and intermolecular scales to produce a flow of charge: an electrical current.

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Kinks in the Backbone

While they are important in allowing a polymer to conduct electricity, a conjugated backbone isn't enough to make charge transport fast by itself. As we saw last time, very short molecules suffer because they rely much more on intermolecular transport. Likewise, various things can happen to disrupt these backbones.

Much like water travelling through a hose, if we bend a polymer molecule back on itself, the resulting 'kink' will effectively cut the conjugated backbone in half. At that point, delocalised electrons will have to hop between the two halves of the polymer chain. This bending is called flexion. Twisting the polymer—the technical term is torsion—has a similar effect: forcing the electrons into slow 'hopping' movement and reducing their mobility.

Exercise: Team Writing

Let's think of some good ways to describe how breaks in a conjugated backbone can make charge transport much more difficult.

....	**Planning Space**

Conductivity and Mobility

We've talked already about how conductive a material is, but what does that actually mean in terms of what the electrons inside it are doing? Going back to the analogy of a hose from earlier, we can think of an electrical current like a flow of water. How could we get more water to flow? What might make less flow?

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Conductivity is the physical quantity that tells us how well a material conducts electricity and is measured in units of siemens per metre (Sm^{-1}). A single siemens is equivalent to an inverse ohm[1] (Ω^{-1}). The formula for conductivity, the symbol for which is the Greek letter σ (sigma), is:

$$\boxed{\sigma = en\mu}$$

Where *e* is the charge on an electron (1.6×10^{-19} C), *n* is the number of electrons in the material per cubic metre (m^{-3}) and μ (another Greek letter, mu) is a quantity known as the mobility, which can be calculated with the formula.

$$\boxed{\mu = \frac{v}{E}}$$

Where *v* is velocity (units of metres per second; ms^{-1}) the electron moves when an electric field is applied to the material and *E* is the strength of that electric field (units of volts per metre; Vm^{-1}). While conductivity is about the material as a whole, the mobility is related to the electrons inside it: it tells us how fast they move in response to electric fields.

Exercise: Let's work out the units of mobility

[1] The Ohm is the unit of electrical resistance: how much a piece of material impedes electrical currents.

Measuring Mobility

Even more so than something like gravitational field strength, mobility is really tricky to measure because it's a feature of electrons. A simple approach is to build an electronic device called a transistor and use that to measure how fast the electrons move (how big the current is) when you apply a particular electric field.

$$\boxed{\mu = \frac{mL}{WV_DC}}$$

There's a lot going on here, so let's break it down in a table.

Property	**Symbol**	**Definition**	**Known?**
Mobility	μ	How fast electrons move in electric fields.	No
Gradient	m	Gradient from a current-voltage graph.	No
Channel length	L	Distance across the transistor's channel.	Yes
Channel width	W	Total width of the transistor's channel.	Yes
Drain-source voltage	V_D	Voltage between transistor's drain and source.	Yes
Capacitance	C	See below.	Yes

Capacitance is another one of those device properties that can be tricky to figure out, but don't worry! If you ever need it in this course I will have done the maths for you ahead of time and will give you the number. In simple terms, it's a measure of how much charge our transistor can store for a given area of channel.

Example: Calculating the mobility of P3HT

As an example, we're going to calculate the mobility of the electrons in a sample of P3HT.

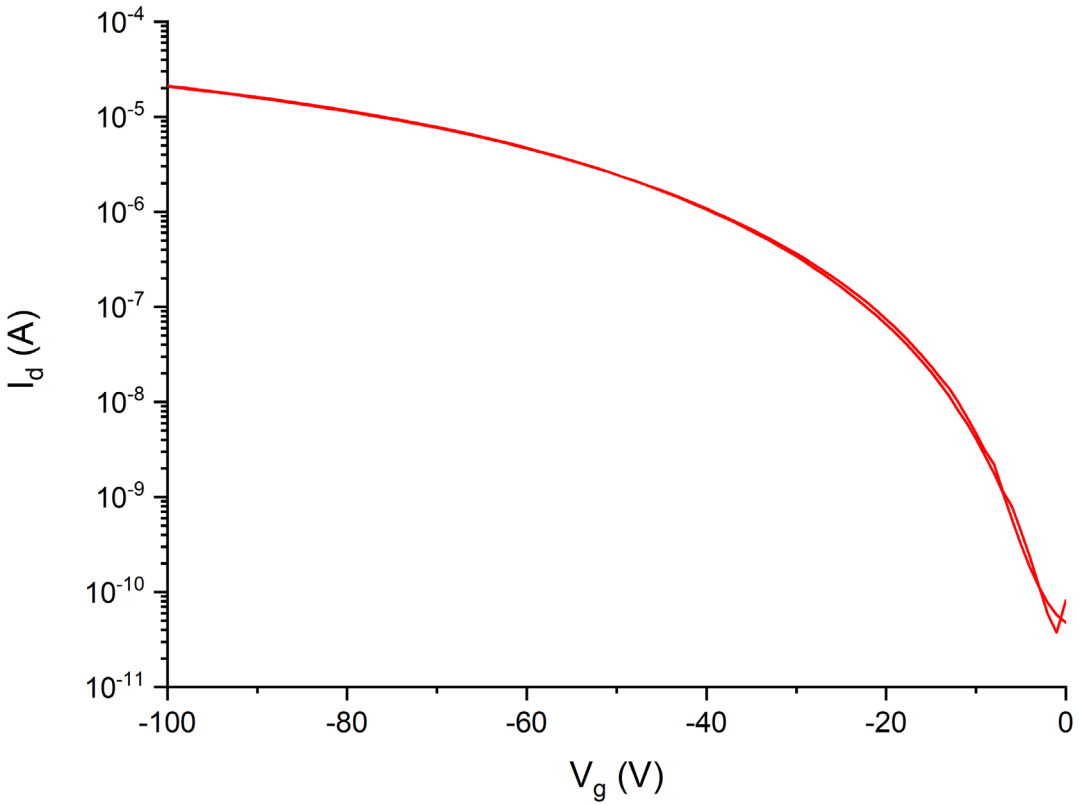


Figure 2.2: Current-voltage graph for a P3HT transistor.

I've done the complicated part of finding the gradient of the part of the graph we need already, so we just need to finish the calculation. We need to be careful though: the units are pretty awkward and we're going to have to use a lot of standard form before we're done! Even with a calculator, we need to make sure we input the division correctly.

$\mu = \frac{mL}{WV_DC}$	$m = 1.07\times10^{-6}$ A/V $L = 5$ μm $W = 1$ mm $V_D = 5$ V $C = 5.7\times10^{-9}$ F/cm^2

Homework: Putting it all together

Below are some graphs showing how transistors made using two different polymers performed in tests.

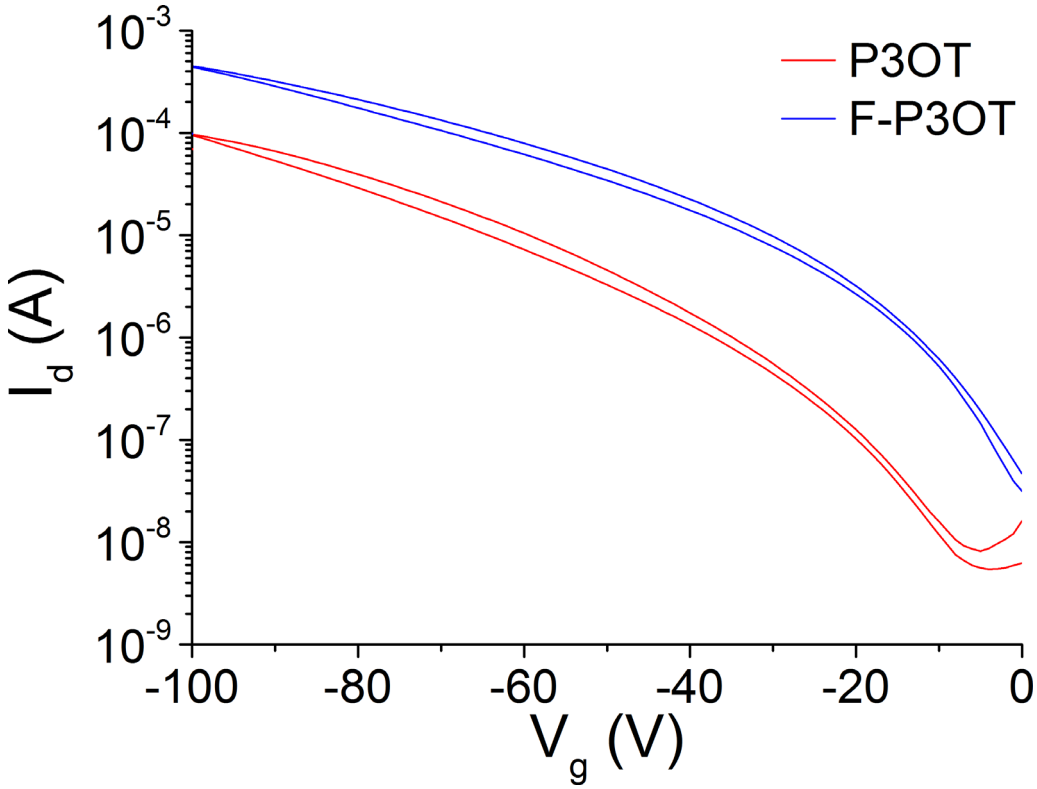


Figure 2.3: Current-voltage data from transistors made with different materials.

Calculate the mobility of each polymer using the method we've learnt today. Which performed better?

$\mu = \frac{mL}{WV_DC}$	m(blue) = 8.67×10^{-6} A/V m(red) = 1.86×10^{-6} A/V L = 5 µm W = 2 mm V_D = 5 V C = 6.2×10^{-9} F/cm^2

Tutorial 3: How do you look at an atom anyway?

Figure 3.1: Definitely not an atomic force microscope.

What is the Purpose of Tutorial 3?

By the end of this tutorial, you should be able to say:

- I can explain why different techniques are useful for examining a polymer's structure.
- I can analyse AFM, absorption spectroscopy and PDS data and write a summary of what it suggests about the material's structure and charge carrier mobility.
- I can explain the term 'energetic disorder' and why it impacts charge carrier mobility.

Atomic Force Microscopy

When we want to look at a polymer's molecules, a regular microscope isn't powerful enough to let us check if their conjugated backbone is distorted[1], but we can use some other methods to learn important things about their structure.

One simple approach is called atomic force microscopy (AFM). By dragging a tiny needle across a sample and measuring how much the needle moves up and down as it does, we can build up a picture of the surface by 'feel' at extremely high resolution.

[1] You'd need something called an electron microscope for that.

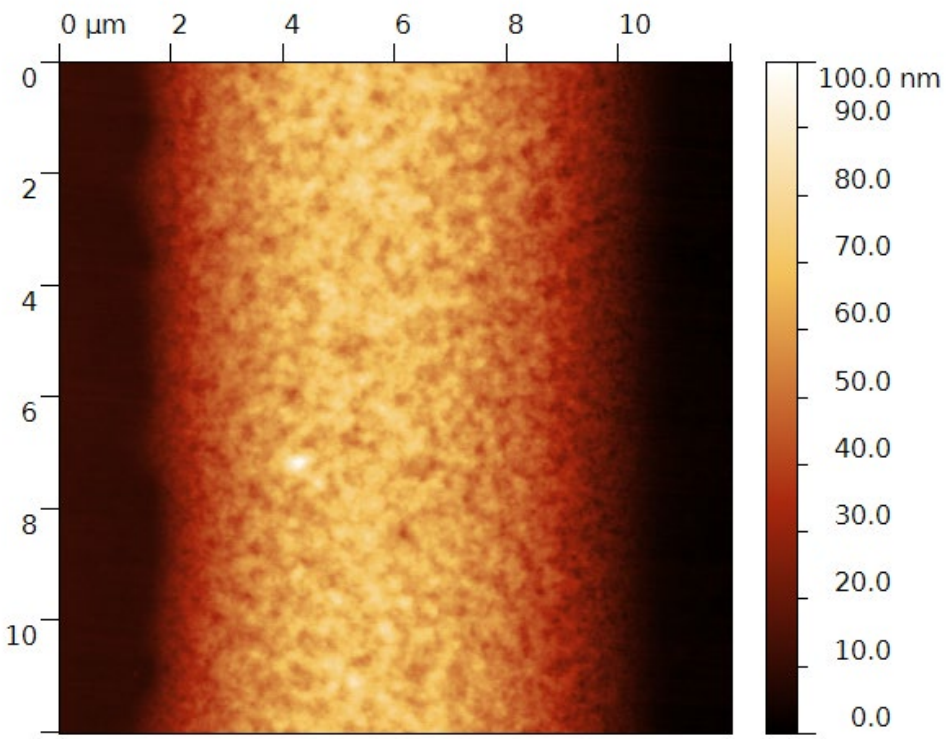
There are a few kinds of things we might want to look for in this microstructure. As we mentioned before, electrons find it easiest to travel within a single crystal of material; if we spot bigger crystals using AFM, we might expect that material to have a higher mobility.

On the other hand, if the polymer's microstructure contains a lot of small crystals, especially if they're arranged randomly, we might expect mobility to be lower.

Exercise: What is this a 'picture' of?

Below are three images produced from AFM data gathered from three different materials. This particular data has been presented so that the colour of a point on the image is related to the height of the surface at that point: brighter bits higher; darker bits lower.

Discuss in pairs what you think these surfaces are made up of. Are there a lot of large crystal structures? Is there any kind of pattern that you can see? How would you describe them to someone?



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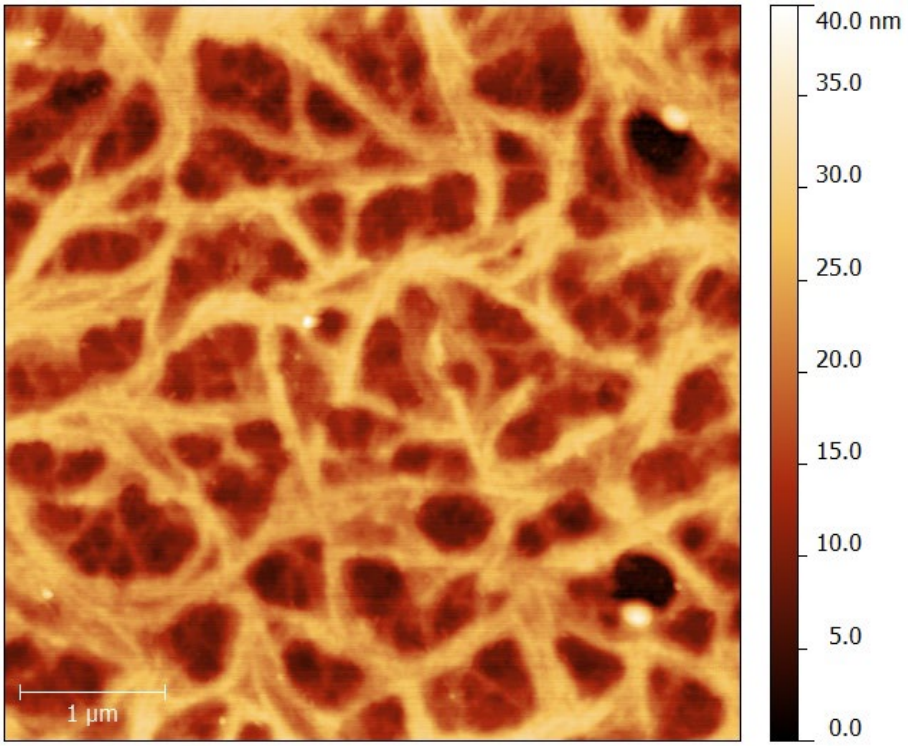
1 µm
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30.0
25.0
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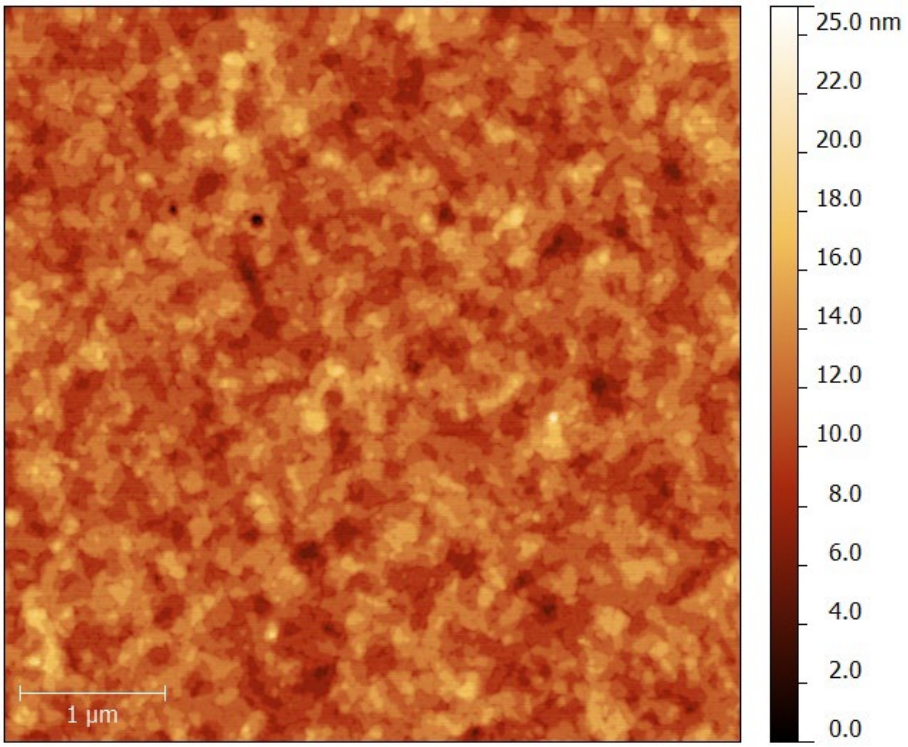
1 µm
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Because AFM is such a sensitive technique, its resolution is extremely high. Looking again at the AFM images above, can you work out what its resolution is?

Hint: Look at the scale bars. The area of the whole image is 512x512 pixels.

The vertical resolution of AFM is approximately ……..
The lateral resolution of AFM is approximately ……..

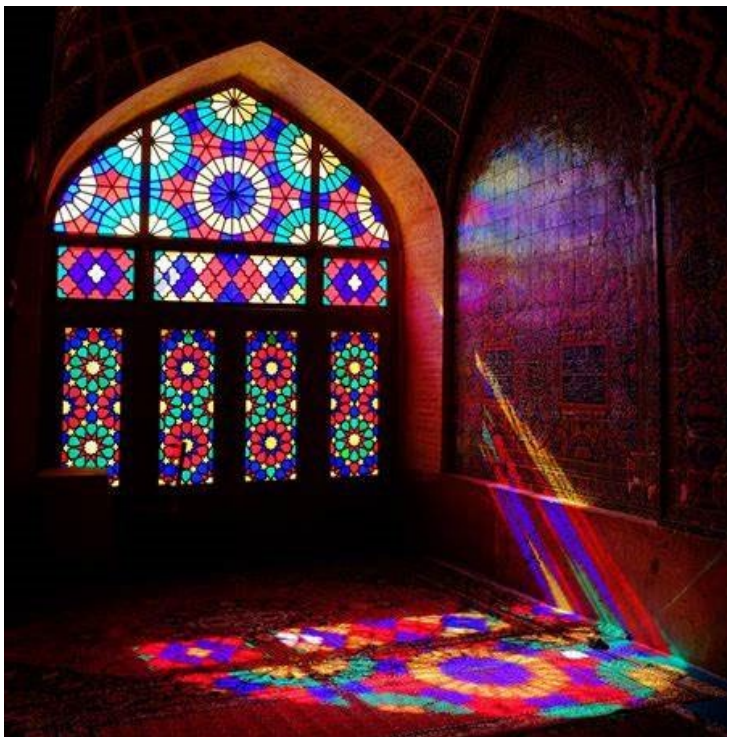
About a decade ago, we thought that finding these large crystal structures would guarantee high mobility, but in more recent years we've found materials that don't seem to have any such microstructure yet have some of the highest mobilities ever observed. This is because mobility depends on multiple different things, making it difficult to say that one thing in particular will increase it.

Other approaches to investigating a polymer's structure look at how the polymer interacts with light—specifically a laser. How a material reacts to light is determined by how the electrons inside it behave, so this kind of measurement can give us important details about what those electrons are doing: really useful when we're asking about their mobility!

This kind of science is called optoelectronics, a combination of the words optics and electronics which means how light and electricity interact within materials.

Absorption Spectroscopy

Perhaps the simplest way to look at how a material reacts to light is to shine light at it and see whether that light is absorbed or not. Consider a stained glass window.



The red sections absorb other frequencies (colours) of light, but let red light through, which continues on to our eyes, so we see red. The same process forms the coloured pattern on the floor, and all the other coloured sections.

In spectroscopy, we use a laser (which only produces a single colour of light at a time) to measure how much of that colour a material absorbs. By varying the colour over a range, we can build up a picture of which colours our material absorbs.

Exercise: Reading a Spectrum

Below are two spectra produced by shining different frequencies of light through a material. They are called absorption spectra. Below them is an image showing the visible light spectrum scaled to the frequencies on the x-axis.

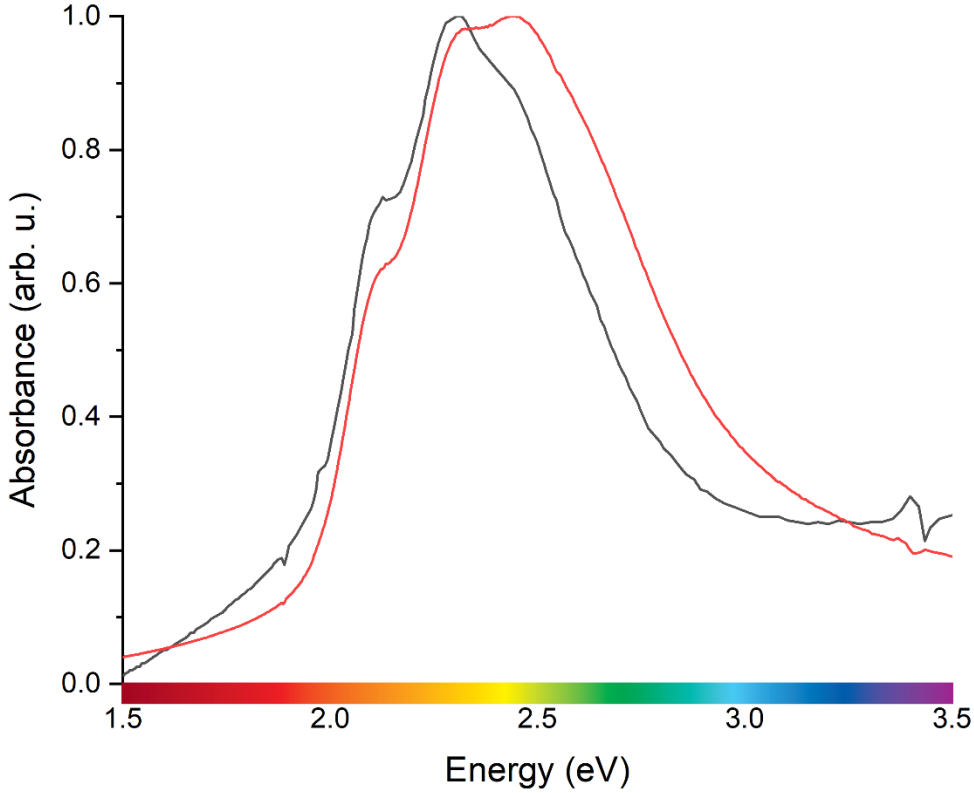


Figure 3.2: Absorption spectra of P3HT and fluorinated P3HT.

If you were viewing these materials with a white light shining through it, what colour would it be?

So It's Puce[1]. What does that tell us about electrons?

Once we have a spectrum, we need to remember that the colour of light determines how much energy it carries: blue light carries more energy than red. This is why electromagnetic radiation like x-rays and gamma rays can be dangerous: they carry a *lot* of energy.

Just like I added a visible light spectrum beneath the spectrum above, we can measure light by energy rather than colour. When light is absorbed by a material, that energy is transferred to its electrons. This causes the electrons to move to different energy levels[2]. We aren't going to worry about the exact details, but electrons that are more delocalised absorb lower energy light. This means that we can interpret the lowest energy peak in an absorption spectrum as an indicator of the conjugation length within the material.

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1 It's an actual colour. Look it up: it's from the French word for 'flea'!

2 Don't worry about the details. They're a more complicated way of modelling electrons than using shells.

Another important factor is the width of the features in a spectrum: broader features tell us that there's much more variation between different electrons in the material. This is a good indicator of higher disorder and lower mobility.

Exercise: Interpreting a Spectrum

Take another look at our last exercise. Based on what we now know about absorption spectra and charge carrier mobility, what can we say about the materials these spectra came from? Discuss in pairs and be prepared to feed back to the group.

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Photothermal Deflection Spectroscopy

While absorption spectroscopy can give us a lot of useful information about a material, it can be difficult to draw firm conclusions: some parts of a spectrum correlate with more ordered structures and improved mobility, but we aren't actually directly measuring either of these things.

However, there is a technique that lets us measure disorder: not just the structural disorder that we can get a feel for with AFM, but the disorder that the electrons themselves experience within the material. Just like mobility is the electron-scale version of conductivity, we can think of this energetic disorder as the electron-scale counterpart to the molecule-scale structural disorder.

The basic principle is the same as the one which causes mirages or heat haze: refraction. When you heat a material (we're using a laser again), the air above it warms up as a result of conduction and convection. This causes that air to refract less: not much, but enough for us to measure if we're careful!

By using a (different) laser to detect that change in refraction, we can then work backwards to see how our material responds to heating. Because this depends on the electrons in a material, we can directly measure their energetic disorder which, since they are the particles that transport charge, is directly correlated with mobility.

Example: Interpreting a PDS Spectrum

The figure below shows a pair of PDS spectra. We aren't going to worry about calculating exact values (the maths gets pretty heavy pretty quick), but it's easy enough to interpret data from a glance at a graph.

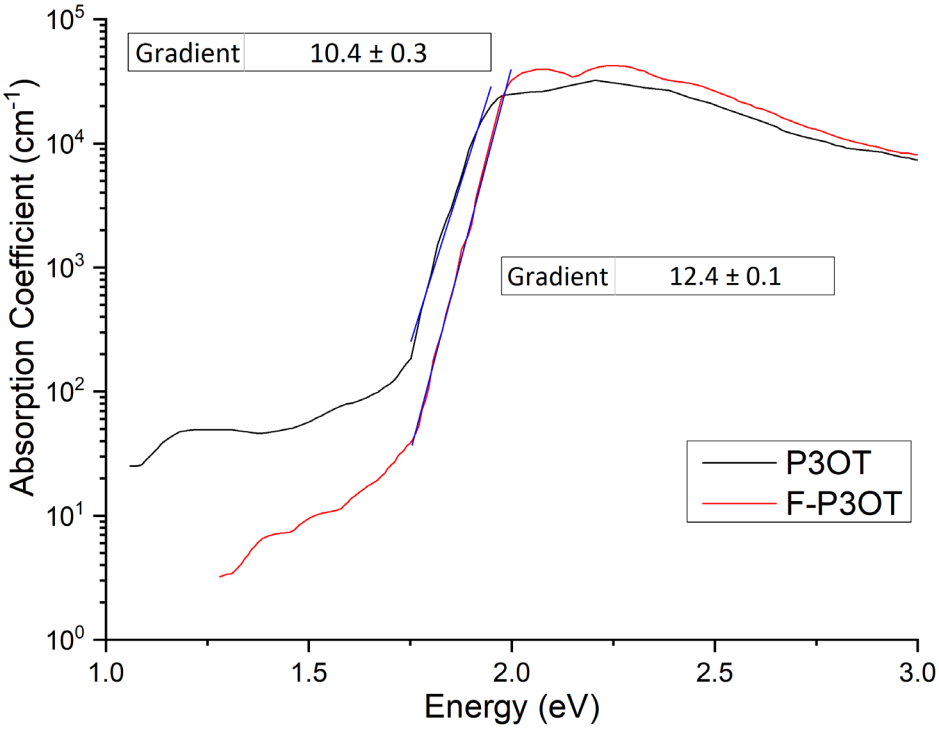

Figure 3.3: PDS spectra of P3OT and fluorinated P3OT.

The energetic disorder in a material is inversely proportional to the gradient of its PDS spectrum in the highlighted region of the graph. Based on this, what can we say about energetic disorder these two materials based on their PDS spectra? You should define 'inversely proportional' and use it in your answer.

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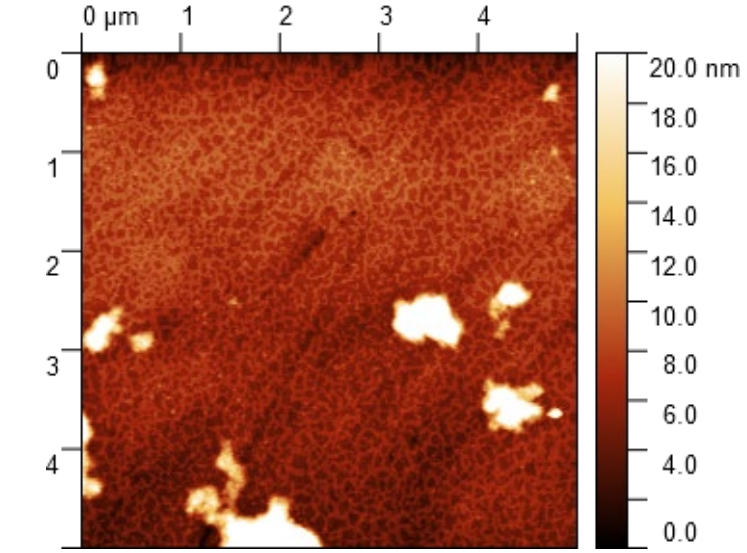
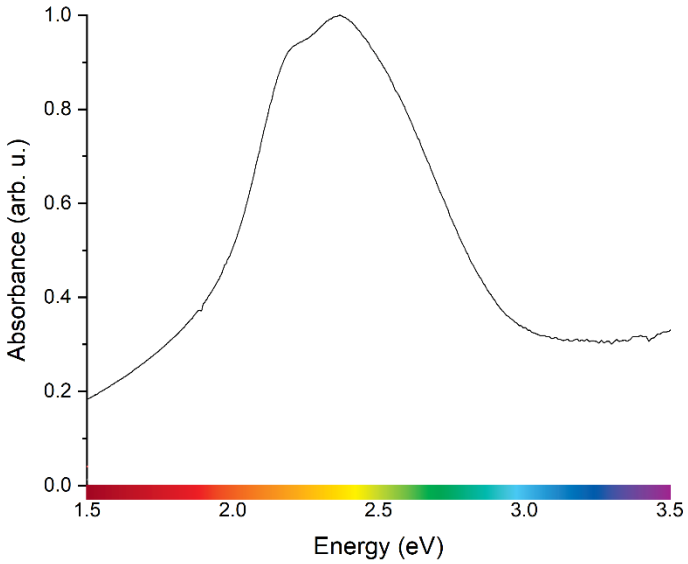
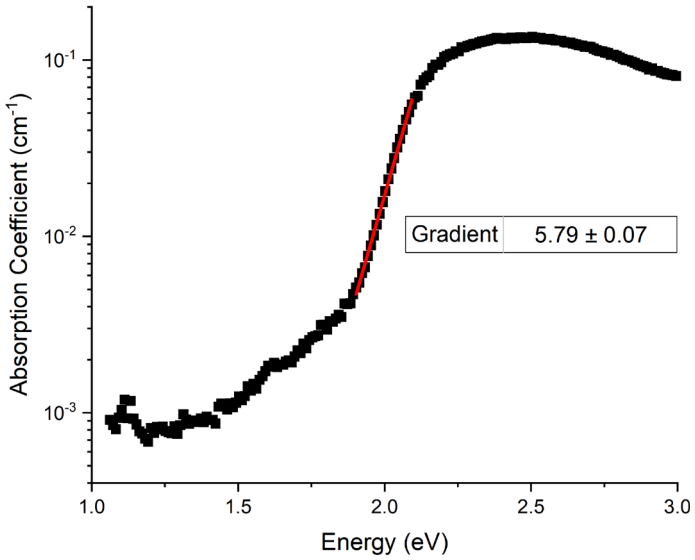
Homework: DIY Data Analysis

Below are atomic force microscopy, absorption spectroscopy and photothermal deflection spectroscopy data for a polymer. Drawing on what we have learned in this tutorial, write a short report describing these data and use them to predict whether you would expect this material to have high or low mobility compared to them.







Notes

Planning Space

Tutorial 4 – I Don't Like That Atom: Change It!

Figure 4.1: OK, it's a bit more complicated than this.[1]

What is the Purpose of Tutorial 4?

By the end of this tutorial, you should be able to say:

- I can define 'rational design' and propose approaches for improving a material's charge carrier mobility.
- I can list moieties that have been studied previously and explain why they were chosen.
- I can cite papers accurately.

Making New Semiconductors: Rational Design

As time went on and we discovered more and more about polymer semiconductors, we ended up with a few rules of thumb for what makes a material a good semiconductor—that is, a high-mobility semiconductor—in terms of that material's molecular structure. Combined with the constantly improving ability of chemists to make very subtle changes to molecules[2], this opened up a whole new world of possibilities for polymer

1 Lorch, M. (2015). *Molecules in Minecraft – Chemistry Blog*. Available at: http://www.chemistry-blog.com/2015/10/30/molecules-in-minecraft/ (Accessed 28 Nov 2021).

2 Seriously. "Swap that atom for a different one" is not off the table.

semiconductors. Instead of just using conventional semiconductors or using the polymers we already had available, scientists were in a position to actually pick and choose which groups of atoms to include in a polymer, and in which arrangement: we could use atoms like Lego bricks (or Minecraft blocks, if you prefer).

This led to a massive increase in the number of materials being studied as different groups tried all sorts of different things to see what approaches worked the best. This 'rational design' formed a feedback loop with the existing theoretical understanding of charge transport: existing theories were used to design new materials that were expected to perform well. When they did, they were refined; when they didn't, it was even better as we theories were adjusted to include new data. Then, a new set of materials were designed based on the new theories, and over and over again.

Exercise: Rationally Designing an Explanation of Rational Design

Discuss in pairs how you would explain the idea of rational design to someone who had never heard of it: both what the process involves and how it became possible. Be prepared to feedback to the group. We will use our ideas to come up with some descriptions of the concept before writing down our own versions.

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OK, Molecular Lego… Which are the chunky bricks?

Once we reached a point where we could start designing molecules, it quickly became obvious that there were some groups of atoms that were regularly producing high mobility materials. These groups of atoms are referred to as moieties (singular moiety), a word that we got from Old French which simply means 'a part of something' and is used to refer to groups of bonded atoms that pop up in lots of different molecules.

Exercise: Moiety Roll Call

Think about the chemistry you've learned in school so far. You probably know the names of quite a few moieties. Try and come up with a few in discussion with a partner. Be ready to feedback to the group.

Moiety	Chemical Formula	Chemical Structure

Useful Moieties

Some of the most useful moieties for making polymer semiconductors are the ones that provide us with particular properties that we want. For example, we know that if our molecule is flat, without any flexion or torsion in its conjugated backbone, mobility tends to be higher. This means that using flat moieties that by their very nature aren't going to bend or twist we can 'lock' our molecule into a flat (or planar to use the technical term) shape.

One such moiety is thiophene, a pentagonal ring of four carbon atoms and a sulphur atom. Due to its ring shape, it can't bend or twist, limiting the possible ways a molecule containing it can do so to the places it is bonded to it.

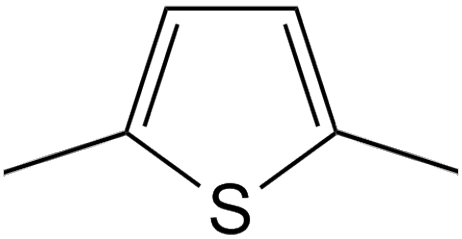

Figure 4.2: Chemical structure of thiophene.

Even better is another moiety based on the same kind of structure called thienothiophene, which is a pair of thiophene rings that share a pair of carbon atoms, effectively sticking them together along one of their edges. By doing so, the planar structure is locked in all along that unit. Not only that, but because a larger proportion of the conjugated backbone is part of this planar structure, the rest of the backbone is pushed into a planar structure as well.

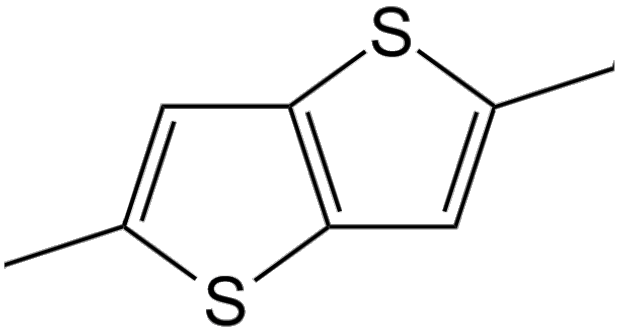

Figure 4.3: Chemical structure of thienothiophene.

This trend continues to this day: current materials of interest in polymer semiconductor research contain a very high proportion of these fused moieties with only a couple of places in the monomer unit consisting of a single bond that could in theory twist. However, rational design choices limit the ability of the molecules to twist even at these points, meaning that many of these new molecules are close to planar along their entire length.

Push-Pull Structures

Another aspect of a moiety, aside from how planar it is, relates to its effect on the electrons in the conjugated backbone. Some moieties are electron-rich, while others are electron-poor—relatively that is, we're not talking about anything as much as an ion. We can combine these together to make what are called 'push-pull' structures.

In a push-pull structure, electrons tend to be more delocalised because they are 'pulled' along by the electron-poor units and 'pushed' along by the electron-rich ones, resulting in better intramolecular transport.

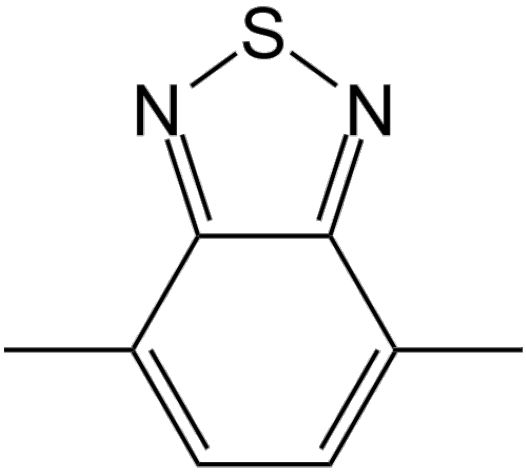

Figure 4.4: Chemical structure of benzothiadiazole (BT), a common 'push-pull' moiety.

How to Write About Research

An important aspect of research, especially in science, is that practically all work is built on work that came before it. This is a good thing, because without that collaborative effort we'd would be stuck trying to work out why wheels should be round for the billionth time.

When we're writing about science though, this means that we'll need to refer to other people's work, and in those situations it's vital that we clearly indicate what is someone else's work and what is our own. This process is called referencing and it's important that we get it right in order to avoid plagiarism: passing off someone else's work as if it's yours.

It might sound a bit complicated, but the actual process is very simple: if we want to reference another piece of work, we use a little number[1]. That little number matches a number in a list we put at the end of our work called a bibliography which contains the details of all the references we've used.

You should reference if you're:

- Discussing someone else's results.
- Quoting someone else's writing (and it needs to go in quotation marks).
- Paraphrasing someone else's writing.

The final point often trips people up: they think that changing a few words in a sentence is enough to make a piece of writing 'theirs' despite the writing being almost identical. It's fine to explain another piece of work in your own words, but make sure you aren't just changing a word here and there. Generally, it's better to summarise their point yourself unless their writing makes your point really well, in which case you should quote them directly. If you're using only a short quote you can drop it in your writing "*like this*", but for longer quotes (forty words is often used as a guideline) you need to separate them into their own quoted section:

> "*Something like this, but obviously it should be longer. The larger margins are useful to make it clear—in addition to the quotation marks—that the section of text is a quotation.*"

1 Like this, except it would contain the details of what we were referencing.

Referencing 101

We'll be using the University of Manchester's referencing style, known as the "Harvard Manchester" style. The full rules for this style of referencing can be found here:

https://subjects.library.manchester.ac.uk/referencing/referencing-harvard

The ones you will use the most are article and book references, which work like this:

Articles

- Author: surname with capital letter, followed by a comma and initials with a full stop after each.
- Year: publication year in parentheses followed by a full stop.
- Title of article: in single quotations followed by a comma.
- Full title of journal: in italics followed by a comma.
- Volume number: (Issue/Part number) followed by a comma.
- Page numbers: followed by a full stop.

For example, one of my papers would be (sections highlighted in different colours):

Fei, Z., Boufflet, P., Wood, S., Wade, J., Moriarty, J., Gann, E., Ratcliff, E. L., Mcneill, C. R., Sirringhaus, H., Kim, J. S. and Heeney, M., (2015). 'Influence of backbone fluorination in regioregular poly(3-alkyl-4-fluoro)thiophenes', *Journal of the American Chemical Society*, 137, 6866–6879.

Books

- Author: surname with capital letter, followed by a comma.
- Initials: in capitals with a full-stop after each.
- Year: publication year (not printing or impression) in parentheses followed by a full stop.
- Title: full title italicised. Only the first word and proper nouns should be capitalised. Follow with a full stop (unless there is a subtitle).
- Sub-title: follows a colon at the end of the full title. Only proper nouns should be capitalized. Followed by a full stop.
- Edition: only include if it is not a first edition. Use the relevant number followed by "edn." e.g. 4th edn.
- Place of publication: give town or city, and country if there is possible confusion with the UK. Follow with a colon.
- Publisher: publisher name followed by full stop.

For example, the book you're reading right now would be referenced:

Moriarty, J. (2022). *Polymer Semiconductors: Molecular LEGO*. Manchester, UK: Researchers in Schools.

Exercise: Citing Your Peers

We're going to make up our own books in a moment, including a title, year of publication and publisher if you want (you can just use Salford City Academy if you want). Then, we're going to practise referencing each other's work.

For example:

Moriarty (2022) emphasises the importance of accurately referencing the work of others[1].

…

1. Moriarty, J. (2022). Polymer Semiconductors: Molecular LEGO. Manchester, UK: Researchers in Schools.

My Book	

In the space below, write three sentences citing the work of your peers, followed by an accurate reference in the Harvard Manchester style (don't worry too much about writing in italics).

Sentence	
Reference	
Sentence	
Reference	
Sentence	
Reference	

Homework: Dotting the i's

Below are some significant papers in the polymer semiconductor field. Write a sentence for each summarising their key finding and reference the paper correctly.

1. The first polymer semiconductor transistor ever constructed using P3HT.

Sentence	
Reference	

Synthetic Metals

Volume 18, Issues 1–3, February 1987, Pages 699-704

Field-effect transistor with polythiophene thin film

H. Koezuka, A. Tsumura, T. Ando

2. Shirakawa et al.'s work on polyacetylene that won the Nobel Prize in Chemistry in 2000.

J. Chem. Soc., Chem. Commun., 1977, 578-580

Synthesis of electrically conducting organic polymers: halogen derivatives of polyacetylene, $(CH)_x$

Hideki Shirakawa, Edwin J. Louis, Alan G. MacDiarmid, Chwan K. Chiang and Alan J. Heeger

Sentence	
Reference	

3. Proof that the length of polymer molecules is proportional to their mobility.

Advanced Materials / Volume 15, Issue 18 / p. 1519-1522

Controlling the Field-Effect Mobility of Regioregular Polythiophene by Changing the Molecular Weight†

R.J. Kline, M.D. McGehee, E.N. Kadnikova, J. Liu, J.M.J. Fréchet

Sentence	
Reference	

Tutorial 5: Analysis of PBTTT

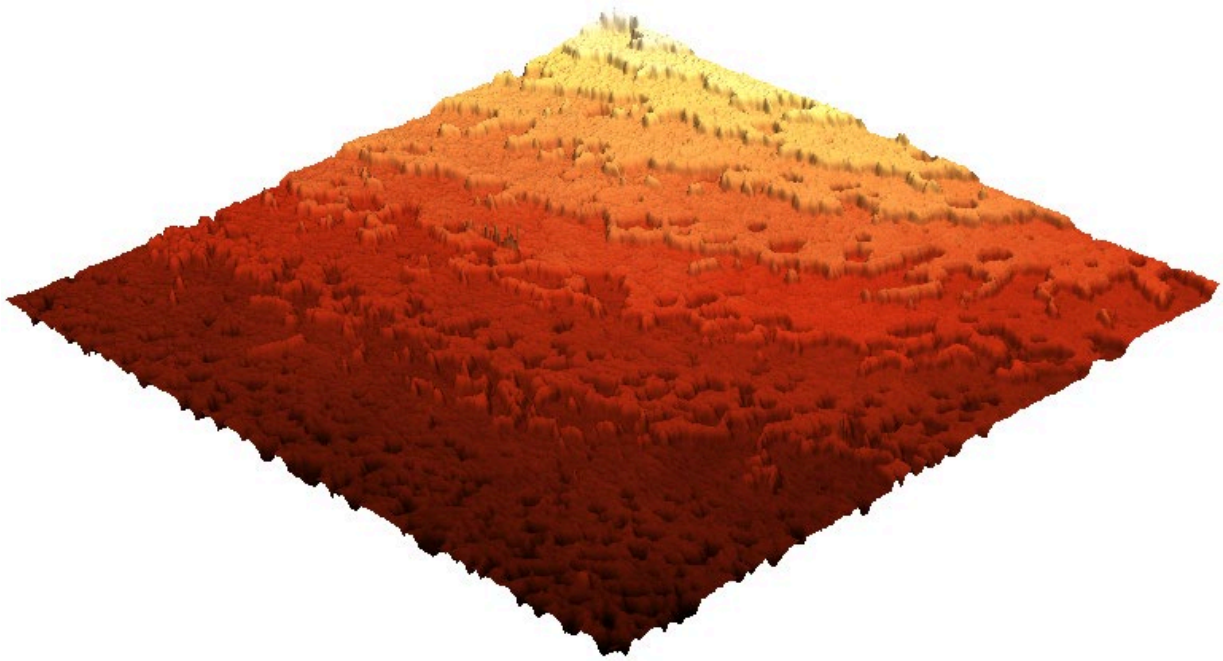

Figure 5.1: AFM Height Map of a terraced PBTTT film.

What is the Purpose of Tutorial 5?

By the end of this tutorial, you should be able to say:

- I can analyse the data for a polymer and report on my findings.
- I can reflect on the design strategies used and evaluate to what extent they were successful.
- I can compare PBTTT with other polymers, citing to other research as needed.

It stands for WHAT?

Now that we've discussed how polymers can conduct electricity, how we can measure their mobility, experiments that can investigate their structural and energetic disorder and the moieties used to influence these things, we're going to analyse a real material in the same way you'll be analysing your own materials for the final assignment.

Today, we're going to analyse poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene). Since that's way too long, we're going to call it PBTTT. To save time and paper, we often abbreviate the names of complicated polymers. To explain this in writing, we use their full name the first time we mention them, followed by the abbreviation we've chosen in brackets and after that we just use the abbreviation. For example:

We will examine poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene) (PBTTT).

Design Rationale

PBTTT was first written about in 2006 in the journal *Nature* by Iain McCulloch et al.[1][2]. The structure of its monomer unit is shown below. Based on what we've learned about moieties, why do you think it was designed this way?

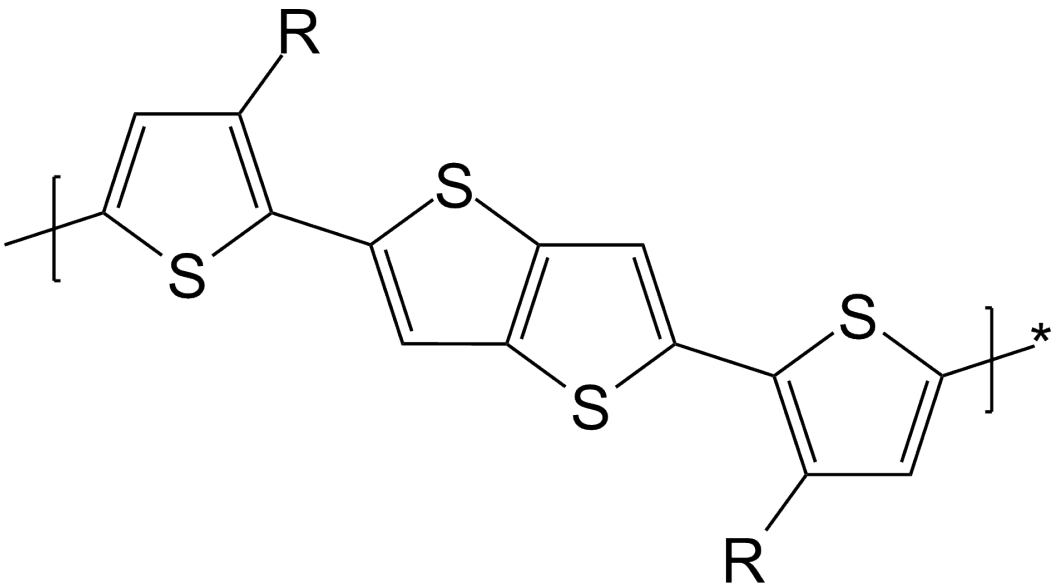

Fig 5.2: Molecular structure of PBTTT (carbon and hydrogen symbols omitted for clarity; R groups are tetradecyl ($C_{14}H_{29}$) chains).

Discuss in pairs for a minute, then we will discuss as a group. Would you have designed the material any differently?

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1 "et al." is a Latin phrase like "et cetera". It means "and others", indicating that an author had several co-authors.

2 McCulloch, I., Heeney, M., Bailey, C., Genevicius, K., MacDonald, I., Shkunov, M., Sparrowe, D., Tierney, S., Wagner, R., Zhang, W., Chabinyc, M.L., Kline, R.J., McGehee, M.D. and Toney, M.F. (2006). 'Liquid-crystalline semiconducting polymers with high charge-carrier mobility', Nature Materials, 5(4), 328–333.

Mobility Measurements

A current-voltage graph extracted from PBTTT transistors is shown below, with a line of best fit marked for the section of the graph we need to extract the gradient from. Using our formula for mobility from Tutorial 2, calculate the mobility of these PBTTT devices. Give your answer to 2 significant figures in the correct units.

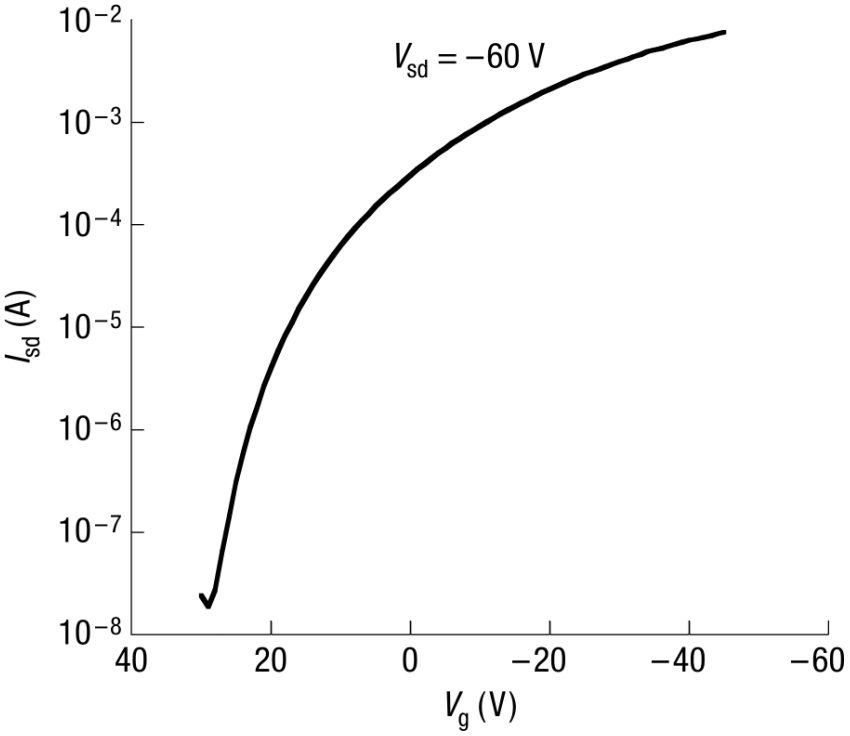

Figure 5.3: Current-voltage data from a PBTTT transistor[1].

$\mu = \frac{mL}{WV_DC}$	m = 2.15×10^{-5} A/V L = 5 μm W = 2 mm V_D = 5 V C = 1.5×10^{-8} F/cm^2

Prior to the development of PBTTT, P3HT transistors were producing mobility values of approximately 0.05 cm^{2}V^{-1}s^{-2}. How do your calculated mobility values compare to these?

……

……

[1] Adapted from McCulloch et al., *ibid*.

Atomic Force Microscopy

Shown below are AFM data from a film of PBTTT. Take a look at it in pairs. What are the main features you observe? How would you describe this structure to someone else? Remember to pay attention to the scales on the image when making your observations. Can you think of how its structure might influence its mobility?

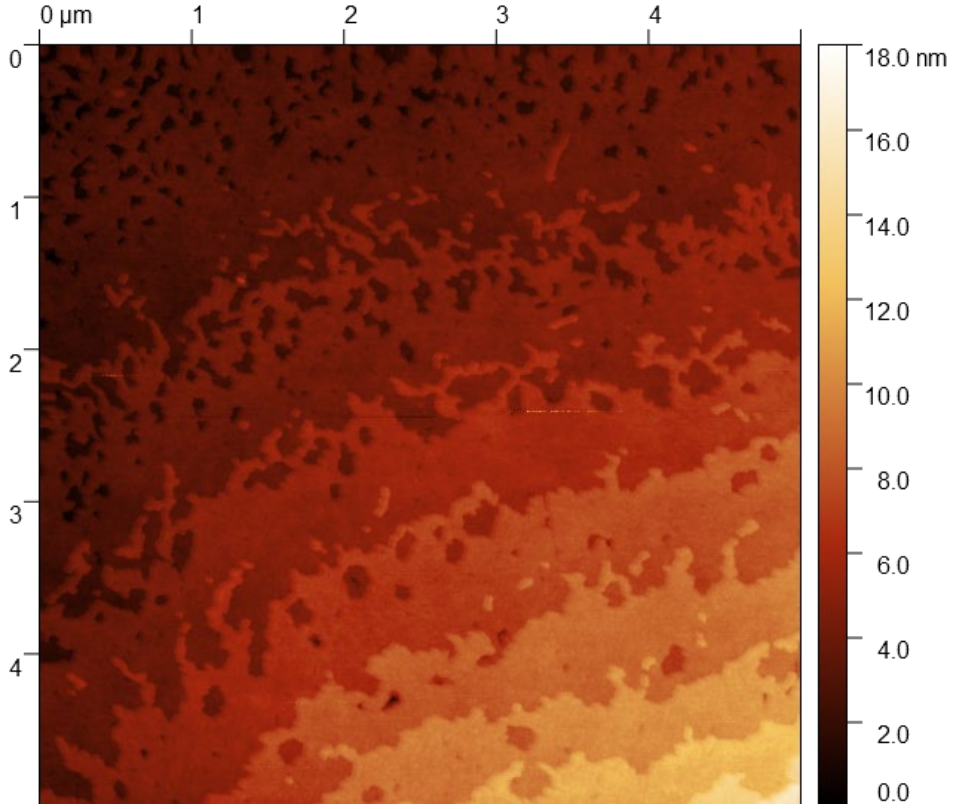

Figure 5.4: AFM height map of PBTTT film.

Be ready to feed back to the group. We'll write our interpretation of the data together.

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Absorption Spectroscopy

The next step in our analysis is to look at PBTTT's absorption spectrum, shown below. For comparison, a spectrum of P3HT is shown on the left. Look back to Tutorial 3 if you need to and make some notes on your observations. Think about of how the spectra compare in terms of both energy and breadth of features, as well as what that suggests about the electrons in these materials. Again, we'll discuss and write our interpretations as a group.

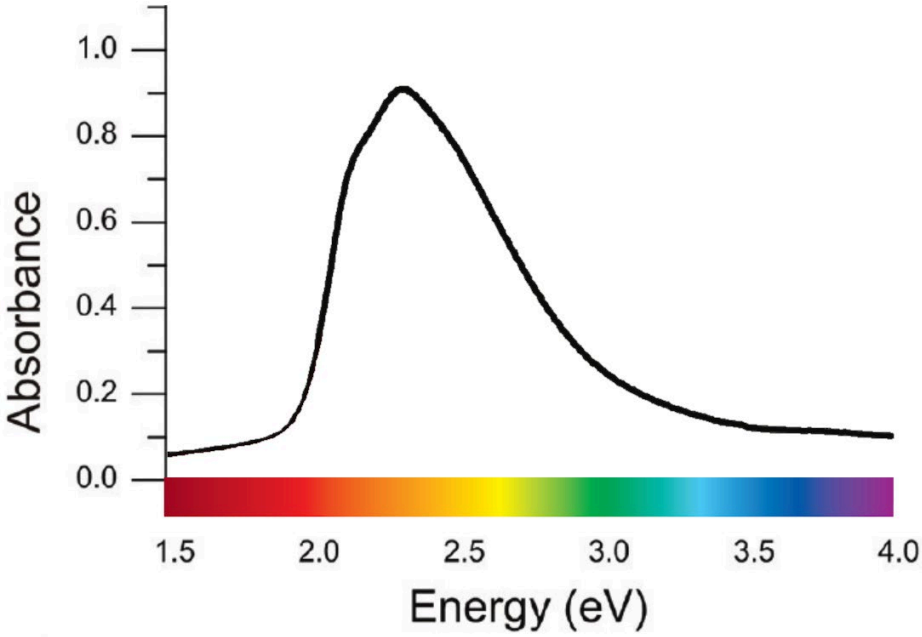

Figure 5.5: Absorption spectrum of PBTTT[1].

....	**Planning Space**

[1] Adapted from: Schuettfort, T., Watts, B., Thomsen, L., Lee, M., Sirringhaus, H. and McNeil, C., R. (2012). 'Microstructure of Polycrystalline PBTTT Films: Domain Mapping and Structure Formation', *ACS Nano*, 6 (2), 1849-1864.

Photothermal Deflection Spectroscopy

Now that we have a basic idea about what's going on at the electronic level in PBTTT, we can take a look at PDS data and see if that changes our interpretation or reinforces it. The spectrum for another polymer is provided for comparison.

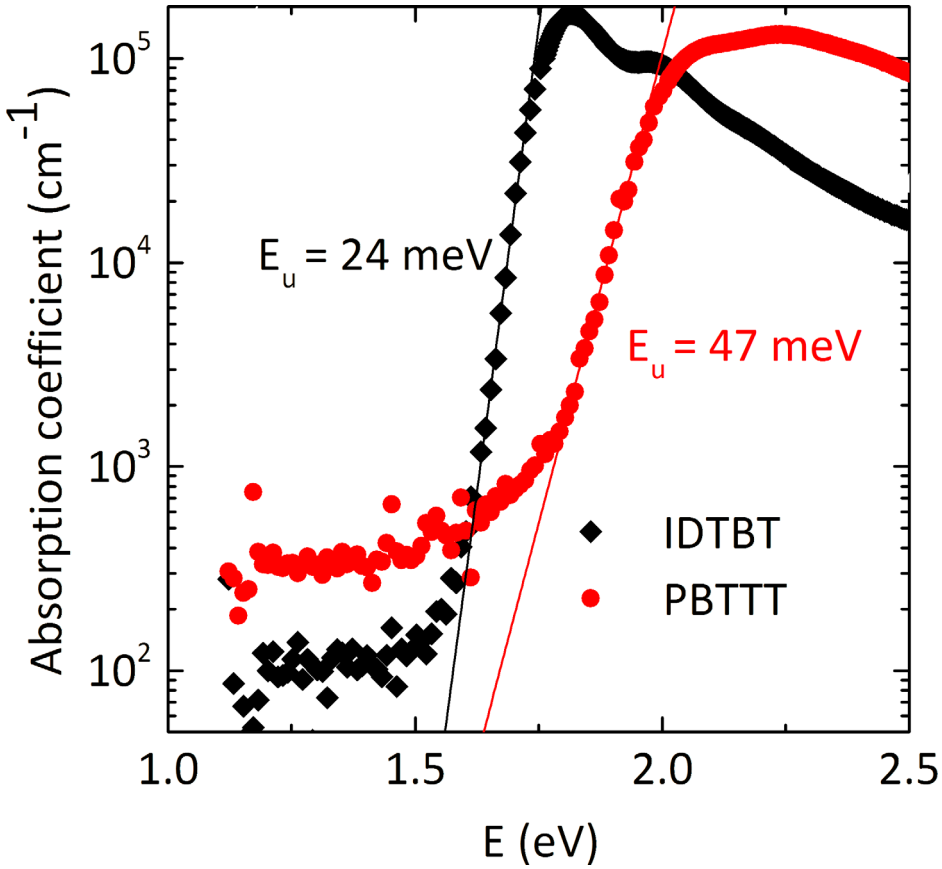

Figure 5.6 PDS spectrum of PBTTT and IDTBT, a more recently developed material.[1]

.....	**Planning Space**
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[1] Adapted from: Venkateshvaran, D., Nikolka, M., Sadhanala, A., Lemaur, V., Zelazny, M., Kepa, M., Hurhangee, M., Kronemeijer, A. J., Pecunia, V., Nasrallah, I., Romanov, I., Broch, K., McCulloch, I., Emin, D., Olivier, Y., Cornil, J., Beljonne, D. and Sirringhaus, H. (2014). 'Approaching disorder-free transport in high-mobility conjugated polymers.' *Nature* 515, 384–388.

Crossing the t's: Referencing

Now that we've spent some time writing about this research, we should make sure that we can accurately reference the work it drew on. The details for six relevant papers are shown below. Choose two and write down the reference for them using Harvard Manchester style.

Two-dimensional charge transport in self-organized, high-mobility conjugated polymers

H. Sirringhaus, P. J. Brown, R. H. Friend, M. M. Nielsen, K. Bechgaard, B. M. W. Langeveld-Voss, A. J. H. Spiering, R. A. J. Janssen, E. W. Meijer, P. Herwig & D. M. de Leeuw

Nature **401**, 685–688 (1999)

High-Performance Semiconducting Polythiophenes for Organic Thin-Film Transistors

Beng S. Ong, Yiliang Wu, Ping Liu, and Sandra Gardner

View Author Information

Cite this: *J. Am. Chem. Soc.* 2004, 126, 11, 3378−3379

Organic Field-Effect Transistors from Solution-Deposited Functionalized Acenes with Mobilities as High as 1 $cm^2/V{\cdot}s$

Marcia M. Payne, Sean R. Parkin, John E. Anthony, Chung-Chen Kuo, and Thomas N. Jackson

View Author Information

Cite this: *J. Am. Chem. Soc.* 2005, 127, 14, 4986−4987

Transport in polycrystalline polymer thin-film transistors

R. A. Street, J. E. Northrup, and A. Salleo
Phys. Rev. B **71**, 165202 – Published 5 April 2005

Integrated Optoelectronic Devices Based on Conjugated Polymers

HENNING SIRRINGHAUS, NIR TESSLER, AND , RICHARD H. FRIEND Authors Info & Affiliations

SCIENCE • 12 Jun 1998 • Vol 280, Issue 5370 • pp. 1741-1744

Soluble and processable regioregular poly(3-hexylthiophene) for thin film field-effect transistor applications with high mobility

Appl. Phys. Lett. **69**, 4108 (1996)

Zhenan Bao, Ananth Dodabalapur, *and* Andrew J. Lovinger

As a reminder, articles are referenced as follows:

- Author: surname with capital letter, followed by a comma.
- Initials: in capitals with a full-stop after each.
- Year: publication year in parentheses followed by a full stop.
- Title of article: in single quotations followed by a comma.
- Full title of journal: in italics followed by a comma.
- Volume number: (Issue/Part number) followed by a comma.
- Page numbers: followed by a full stop.

Citation 1: ……

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Citation 2: ……

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Homework: Final Assignment Draft

Analyse the data for your polymer and write a report comparing its mobility and structure with other materials we have analysed in the course.

Details of the assignment:

You have been given a set of data from a real polymer. Using the approaches we have practised in the tutorials, analyse this data and write a report on it. You should compare it to other materials we have covered, exploring any differences and similarities in mobility and structure.

Success criteria – how to structure your assignment and what to include:

An **introduction** showing the structure of your polymer, its full name, a suitable abbreviation that you will use to refer to it and a brief explanation of why it was designed in the way it was. Your introduction should also outline the structure of your assignment.

An **explanation** of charge transport in polymer semiconductors. You should draw on your baseline assignment for this section, refining it based on our other tutorials.

A **report** on its charge carrier mobility relative to other similar materials.

An **analysis and discussion** of your data explaining its mobility in terms of its physical and electronic structure. You should compare it with materials from our tutorials.

A **conclusion** summing up your main points and suggesting improvements that could be made using a rational design, justified by reference to evidence.

A **bibliography**, with references in the Harvard Manchester style.

In this assignment, show me that you **understand**:	Show me that you **are able to**:
The terms 'polymer', 'semiconductor' and 'conjugated backbone'. What makes polymer semiconductors different from other polymers. How electricity travels through polymer semiconductors.	Write clearly and accurately about scientific topics. Structure your essay logically. Use diagrams appropriately to make your explanations clearer.

Tutorial 6: Feedback tutorial

What is the Purpose of Tutorial 6?

- To receive feedback on your final assignment
- To respond to the feedback from your Uni Pathways teacher
- To write targets for improvement on your final assignment

Final assignment feedback from your Uni Pathways Teacher

Remember to look at the mark scheme to help you understand what you have done well so far, and how you can do even better in your final assignment.

Here are three things that my teacher thinks I did well in my draft assignment.
1. 2. 3.

Here are three things that my teacher thinks I could do to improve my final assignment.
1. 2. 3.

Tasks from my teacher to do during the feedback tutorial to help me improve.
My response:

Actions I will take to improve my final assignment after this tutorial…

Hand in date for my final assignment:	

Tutorial 7: Final Tutorial

What is the Purpose of Tutorial 7?

- To receive feedback and a grade on your final assignment.
- To reflect on the programme including what you enjoyed and what was challenging.
- To ask any questions you may have about university.

Final assignment feedback from my Uni Pathways Teacher

Final mark:	University style grade:
Here are three things that my teacher thinks I did well in my final assignment:	
1. 2. 3.	

Here are three things that my teacher thinks I should remember for when I am doing this kind of study in the future:
1. 2. 3.

University

What questions do you still have about university after taking part in Uni Pathways?

Reflecting on Uni Pathways

What did you most enjoy about Uni Pathways?	
What did you find challenging about the programme?	How did you overcome these challenges?

Notes

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