

Organic Chemistry and Your Cellphone: Organic Light-Emitting Diodes

by

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Introduction

Derek and Alex were shopping for TVs in Best Buy, when they came across a new Samsung 55" OLED TV. Alex was excited, as he'd heard excellent things about OLED displays, until he saw the price—\$9000! When Alex displayed amazement, Derek was skeptical.

"You don't want that—it's far too expensive, and they always break."

"Isn't my cellphone made of an OLED display? Why can't it be applied to TVs?"

Derek, having a broader knowledge of chemistry than Alex, tried to explain why OLEDs are expensive and fragile. "Normal light-emitting diodes are much more robust—you spill anything on an OLED display and it's ruined."

Alex, on the other hand, was mesmerized by the pretty colors and decided he wanted to learn more about OLEDs, and started reading. He found a *Nature* paper on conducting polymers by Burroughes, *et al.*, and started from there.



Organic light-emitting diodes have revolutionized society over the past 20 years. Flat-panel TV sets and cellphones/tablets all use OLED technology to provide high definition screens without the need for bulky cathode ray tubes. This has allowed the creation of a number of devices that are smaller, cheaper and more flexible than CRT monitors. The key to these screens is the discovery of conducting organic polymers. Previously, organic molecules were only known as insulators and were not considered useful for electronic applications. While more recent OLED devices are quite complex, the initial design is extremely simple and can be analyzed using basic knowledge of organic chemistry.

In this case, you will determine how to synthesize a conducting polymer from basic organic chemicals, how to vary its structure to alter the color of emitted light (essential for the creation of color displays), and determine how and why it functions.

Instructions

Before Class

1. Read and familiarize yourself with the following articles.
 - Read the first page of "Light-emitting diodes based on conjugated polymers," J.H. Burroughes, *et al.*, *Nature* (1990), 347, p. 539. You are only required to read page 539; the end of the article focuses on the physics and electronics of the material, and we will focus on the chemistry and synthesis. This article is freely available (as of September 2013) at the following addresses:
 - <http://www.nature.com/nature/journal/v347/n6293/pdf/347539a0.pdf> (PDF of original article)
 - <http://www.nature.com/physics/looking-back/burroughes/index.html> (text-based version; read only the first four paragraphs and Figure 1.)
 - Excerpt from "OLED," an article from *Wikipedia*, the free encyclopedia (included below).

- Excerpts from “Recent advances in conjugated polymers for light emitting devices,” AlSalhi, *et al.*, *Int. J. Mol. Sci.*, 2011, p.2036.
 - Read chapters 14, 15 and 16 (“Conjugated Compounds and Ultraviolet Spectroscopy”; “Benzene and Aromaticity”; “Chemistry of Benzene”) in your assigned organic chemistry textbook (McMurry, *Organic Chemistry*, 8th ed.).
2. Answer the pre-case study questions (below) and be prepared to submit your responses to your discussion group when you arrive to class.
 3. Read and familiarize yourself with the case study questions (below); these will be discussed and answered in groups during class.

In Class

1. You will be divided into collaborative groups to discuss the pre-case study questions. Identify the major issues of the case and determine what types of questions need to be answered.
2. Work in your collaborative groups and arrive at answers to the case study questions.

After Class

Complete the post-case study individual report (below). The due date for this final report will be announced in class.

Pre-Class Questions

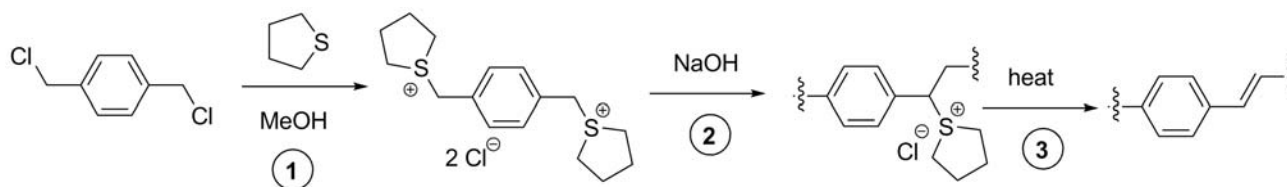
1. Provide brief definitions for the following terms.
 - a. conjugation
 - b. polymer
 - c. HOMO and LUMO
2. Answer the following questions.
 - a. Why do conjugated compounds absorb light in the ultraviolet region?
 - b. Why do more conjugated compounds absorb at higher wavelengths/lower energies?
 - c. What is required for organic compounds to absorb in the visible light region?

In-Class Questions

1. Polymer Synthesis

The synthetic scheme for the synthesis of poly(phenylene vinylene) (PPV) from Burroughes, *et al.*, is shown below.

Figure 1.



- a. Draw the mechanism for step ①.
- b. Draw the mechanism for the polymerization step ②. Why do these reaction conditions cause polymer formation?
- c. Why can elimination step ③ occur on simple heating? Why is this a good procedure to form materials for commercial use?

2. Electroluminescence

The definition of electroluminescence is the release of light from a material upon application of an electric field.

- Draw the molecular orbital diagrams of 1,3-butadiene and 1,3,5-hexatriene (see McMurry, chapter 14). Label the HOMO and LUMO in each case. Which molecule has the smallest energy gap between HOMO and LUMO? What does that tell you about the frequency of light absorbed by the two molecules?
- The HOMO/LUMO gap of a species tells you the frequency of light absorbed. Draw the molecular orbital diagrams of 1,3-butadiene *before* and *after* one electron is added to the LUMO by application of an external electric field. Upon removal of this electron, the extra energy is released as light. What frequency will that light have?
- For useful materials, the emitted light should be in the *visible* region of the electromagnetic spectrum. Why must long conjugated *polymers* be used as these materials rather than small molecules?

3. Color Variance

A desirable feature of OLEDs is the ability to closely tune the emission frequency to release light of different colors. This can be achieved by varying the substituents on the PPV polymer.

- Two common PPV variants are called BuEH-PPV and BEH-PPV, and their structures are shown in Figure 2. If PPV itself (and BuEH-PPV) emits light in the green/yellow-green region, whereas BEH-PPV emits red light, what does that tell you about their respective HOMO-LUMO gaps?
- Based on that information, what type of substituents would you add to the PPV aromatic rings to favor the emission of *blue* light?
- You can synthesize the PPV precursor below in one step from p-xylene. How? (see McMurry, chapter 16).

Figure 2.

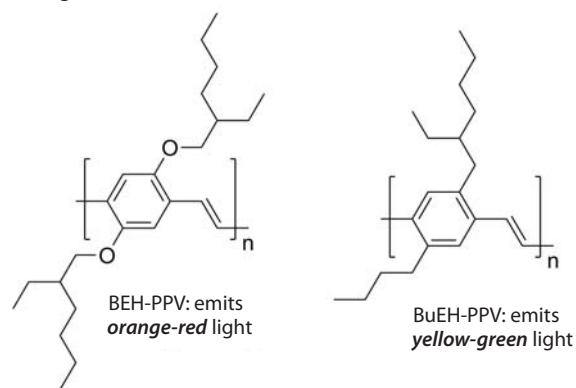
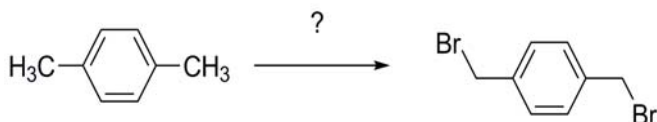
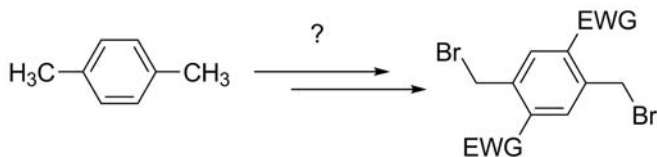


Figure 3.



- If you wanted to create a PPV precursor with *two electron-withdrawing groups* in *two* steps from p-xylene, how would you do it? Which electron-withdrawing groups would you choose, and why?

Figure 4.



4. Drawbacks

While OLEDs are extremely useful, there are challenges in converting them into everyday devices.

- Inorganic LEDs are robust and can stand up to physical impact and chemical exposure. Would you expect OLEDs to be more or less robust than inorganic LEDs? Why?
- A “defect” is defined in this case as an interruption of the conjugation in the polymer. How might this damage or change the light-emitting properties of the material?

- c. For example, imagine that you spilled lemon juice (aqueous citric acid) on your phone. Draw the repeating unit of PPV, and draw the mechanism of reaction of this species with aqueous acid. Would this cause a “defect”? How likely is this reaction? Can you think of any other common species in everyday life that can react with systems such as these?

Post-Case Study Report

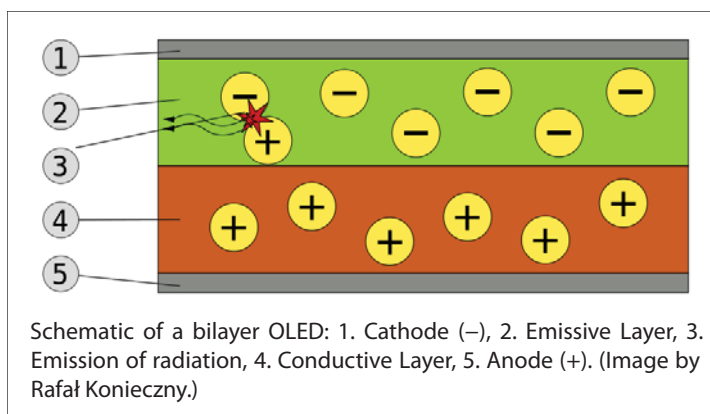
In a 1–2 page report, use your answers from the case study questions and information from further reading of the related articles to describe how PPV is made and how it acts as a light emitting diode. Also describe how its structure can be altered to change the color of light emitted by the LED. Summarize the benefits and drawbacks of OLEDs over inorganic semiconductors.

Excerpt from “OLED”

Source: *Wikipedia*, the free encyclopedia, entry on “OLED,” <http://en.wikipedia.org/wiki/OLED>. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/3.0/>).

Working Principle

A typical OLED is composed of a layer of organic materials situated between two electrodes, the anode and cathode, all deposited on a substrate. The organic molecules are electrically conductive as a result of delocalization of pi electrons caused by conjugation over all or part of the molecule. These materials have conductivity levels ranging from insulators to conductors, and therefore are considered organic semiconductors. The highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) of organic semiconductors are analogous to the valence and conduction bands of inorganic semiconductors.



Originally, the most basic polymer OLEDs consisted of a single organic layer. One example was the first light-emitting device synthesised by J. H. Burroughes et al., which involved a single layer of poly(p-phenylene vinylene). However multilayer OLEDs can be fabricated with two or more layers in order to improve device efficiency. As well as conductive properties, different materials may be chosen to aid charge injection at electrodes by providing a more gradual electronic profile, or block a charge from reaching the opposite electrode and being wasted. Many modern OLEDs incorporate a simple bilayer structure, consisting of a conductive layer and an emissive layer. More recent developments in OLED architecture improves quantum efficiency (up to 19%) by using a graded heterojunction. In the graded heterojunction architecture, the composition of hole and electron-transport materials varies continuously within the emissive layer with a dopant emitter. The graded heterojunction architecture combines the benefits of both conventional architectures by improving charge injection while simultaneously balancing charge transport within the emissive region.

During operation, a voltage is applied across the OLED such that the anode is positive with respect to the cathode. Anodes are picked based upon the fact of how good their optical transparency, electrical conductivity, and chemical stability are. A current of electrons flows through the device from cathode to anode, as electrons are injected into the LUMO of the organic layer at the cathode and withdrawn from the HOMO at the anode. This latter process may also be described as the injection of electron holes into the HOMO. Electrostatic forces bring the electrons and the holes towards each other and they recombine forming an exciton, a bound state of the electron and hole. This happens closer to the emissive layer, because in organic semiconductors holes are generally more mobile than electrons. The decay of this excited state results in a relaxation of the energy levels of the electron, accompanied by emission of radiation whose frequency is in the visible region. The frequency of this radiation depends on the band gap of the material, in this case the difference in energy between the HOMO and LUMO.

Excerpts from “Recent advances in conjugated polymers for light emitting devices”

Source: AlSalhi, M.; Alam, J.; Dass, L.; Raja, M. Recent advances in conjugated polymers for light emitting devices. *Int. J. Mol. Sci.* 2011, 12(3), 2036-2054; doi:10.3390/ijms12032036. <http://www.mdpi.com/1422-0067/12/3/2036>. © 2013 by the authors. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/3.0/>).

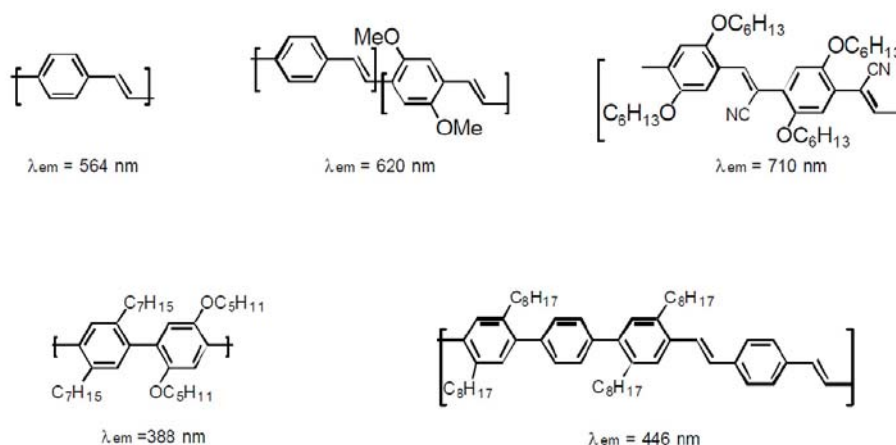
1. Introduction

In 1977, Alan J. Heeger, Alan MacDiarmid and Hideki Shirakawa found out that a thin film of polyacetylene could be oxidized with iodine vapors, turning the material into a conductor. This sensational finding earned them the 2000 Nobel Prize in Chemistry. Thanks to their pioneering discoveries, this versatile plastic conductor, which is a type of polymer with extended conjugated backbone, is now researched in a large international field with significant academic and industrial activities. In the 1980s, the future for conjugated polymers in commercial development further attracted tremendous scientific and industrial interest due to their potential in achieving the goal of light emitting device technology that is economically viable for solid-state lighting and displays, which offer significant gains in power efficiency, color quality, and life time at lower cost and less environmental impact than traditional incandescent and fluorescent lighting [1–9]. The features of conjugated polymers that made them particularly promising to light emitting devices are the large nonlinear optical figure of merit, electronic structure, energy band gap, high optical damage thresholds, ultrafast optical responses and architectural flexibility along with processing advantages and mechanical properties of polymers [10–14]. Basically, conjugated polymers are organic macromolecules which consist of at least one chain of alternating double- and single-bonds. They derive their semiconducting properties from having the extensive delocalization of π -electron bonding along the polymer chain and this delocalized π electron system makes them capable of absorbing sunlight, creating photogenerated charge carriers and transporting these charge carriers. Moreover, these significant properties can be altered by the inclusion of functional side groups as well as substitution of the intractable conducting polymers backbone with alkyl and alkoxy substituents [15–21]. ...

2. Recent Literature Survey

... [I]n the late 1980s, a group headed by Prof. Richard Friend of Cambridge University, UK, discovered a new application for these polymers, namely as an electroluminescent device. His work showed that the semiconductive conjugated polymer poly (p-phenylenevinylene) (PPV) showed electroluminescent characteristics if an appropriate choice of contact layers was made. Since then, tremendous progress in this field has been made in many aspects such as fundamental science in order to realize commercial applications, opportunities for processing, device structures and performances in addition to new conjugated polymers and their derivatives as electroluminescent materials [38–51] where some of promising electroluminescent conjugated polymers and their derivatives are shown in Figure 2. ...

Figure 2. Conjugated polymeric light emitting materials.



Poly (*p*-phenylene vinylene) (PPV, or polyphenylene vinylene) is a bright yellow, fluorescent conjugated polymer. Its emission maxima at 551 nm (2.25 eV) and 520 nm (2.4 eV) are in the yellow-green region of the visible spectrum. PPV is the only polymer of this type that has so far been successfully processed into a highly ordered crystalline thin film. PPV and its derivatives are conducting polymers of the rigid-rod polymer family. They are the only conjugated polymers that have been successfully processed in film with high levels of crystallinity. PPV is easily synthesized in good purity and high molecular weight. Although insoluble in water, its precursors can be manipulated in aqueous solution. The small optical band gap and its bright yellow fluorescence make PPV a candidate in many electronic applications such as light-emitting diodes (LED) and photovoltaic devices. Moreover, PPV can be easily doped to form electrically conductive materials. Its physical and electronic properties can be altered by the inclusion of functional side groups. Although PPV is a very promising light emitting conjugated polymer, some processing problems exist. The unsubstituted form of PPV is insoluble in organic solvents, with proper chemical modifications of the polymer backbone it can be dissolved in organic solvents and their physical and electronic properties can also be altered by the inclusion of functional side groups [58–63]....

3. Overview on Organic Solid State Lighting Technology

A modern approach of conjugated polymers as peculiar light emitting materials is their suitability for achieving efficient solid state lighting (SSL) [133–143]. In contrast to conventional point source LEDs, conjugated polymer based LEDs distribute light throughout the surface area and are not restricted by their size. This brings about the possibility of having high luminance flux without glare.

3.1. OLED Lighting

Conjugated polymer based devices such as organic light-emitting diodes (OLED) are a new light emitting medium [144,145], in which the emitting layer material of the LED is an organic compound, known as an organic light emitting diode (OLED) [146–150]. OLEDs produce light in much the same way that ordinary LEDs do, except that the positive and negative charges originate in organic compounds rather than in crystalline semiconductors. They emit light across the visible, ultraviolet and infra red wavelengths, with very high brightness and have the potential for energy efficient solutions [151–156]. From the commercial market point of view, OLEDs are promising devices for thinner, lighter, and higher-resolution displays for next generation televisions, computers, electronic books, and billboards. A lot of exciting OLED gadgets have been introduced, including the Google Nexus-One and Nexus-S, Samsung's Jet, Wave and Galaxy-S, Nokia's N8, E7 and C7, three WP7 phones, and several HTC phones [157].

OLEDs have the potential to outperform all other light sources. OLED is not a lamp, nor just a light source—it is a new light emitting medium without sacrificing the aesthetic appeal and essential lighting properties: lumen maintenance, sustainability, low cost and efficiency [158]. Reported record efficiencies of 110 lm/W for green light and performance targets of ongoing research and development activities focused on white emission indicate the potential of OLEDs to emerge as a solid state lighting source for a wide variety of potential applications, including ambient and technical lighting as well as signage applications, such as exit signs or logos. As an example, Osram Opto Semiconductors has introduced Orbeos, its first OLED light source, which is aimed at premium-quality functional lighting applications such as architecture, hotels and catering, offices, private homes and shops. The Orbeos OLED panel has a round lamp surface of 80 mm diameter, is 2.1 mm thick and weighs 24 g. Osram believes that these limited dimensions will ensure plenty of different usage options. The panel's efficiency is quoted as 25 lm/W, which Osram states is better than conventional halogen lamps. It has a warm-white color temperature of 2,800 K, with a Color Rendering Index CRI of up to 80, making it suited to lighting that is “atmospheric and functional at the same time.”

According to Osram, OLEDs “rate highly with their pleasant, non-glare light” and open up totally new design possibilities for architects, lighting planners and designers, making it possible to create illuminated areas such as lit ceilings or partitions. Orbeos can be switched on and off without delay, and is continuously dimmable. Unlike LEDs, heat management is simple. The panel contains no mercury and emits no UV or infrared radiation. Its brightness level

is usually $1,000 \text{ cd/m}^2$ with power input of less than a watt. In ideal operating conditions it has a lifespan of around 5,000 hours.

3.2. OLEDs' Lighting Benefits

Energy policies encourage technologies that can offer maximum energy savings; OLED technology falls into this category. OLEDs offer many advantages over both LCDs and LEDs. Adoption of OLED lighting has the following advantages:

- OLEDs have a significantly lower price than LCDs or plasma displays due to the fact that they can be printed onto any suitable substrate using an inkjet printer or even screen printing technologies.
- The ability of OLEDs to be printed onto flexible substrates has opened the gate to several new applications, like roll-up displays and displays embedded in fabrics.
- OLED pixels directly emit light, thus provides a greater range of colors, brightness, and viewing angle than LCDs.
- One remarkable advantage of OLEDs is the ability of color tuning.
- Energy saving potential.
- Mercury-free.
- New freedom in design.
- OLED substrates can be plastic rather than the glass used for LEDs and LCDs.
- High luminous efficacy.

