CONDUCTIVE POLYMERS

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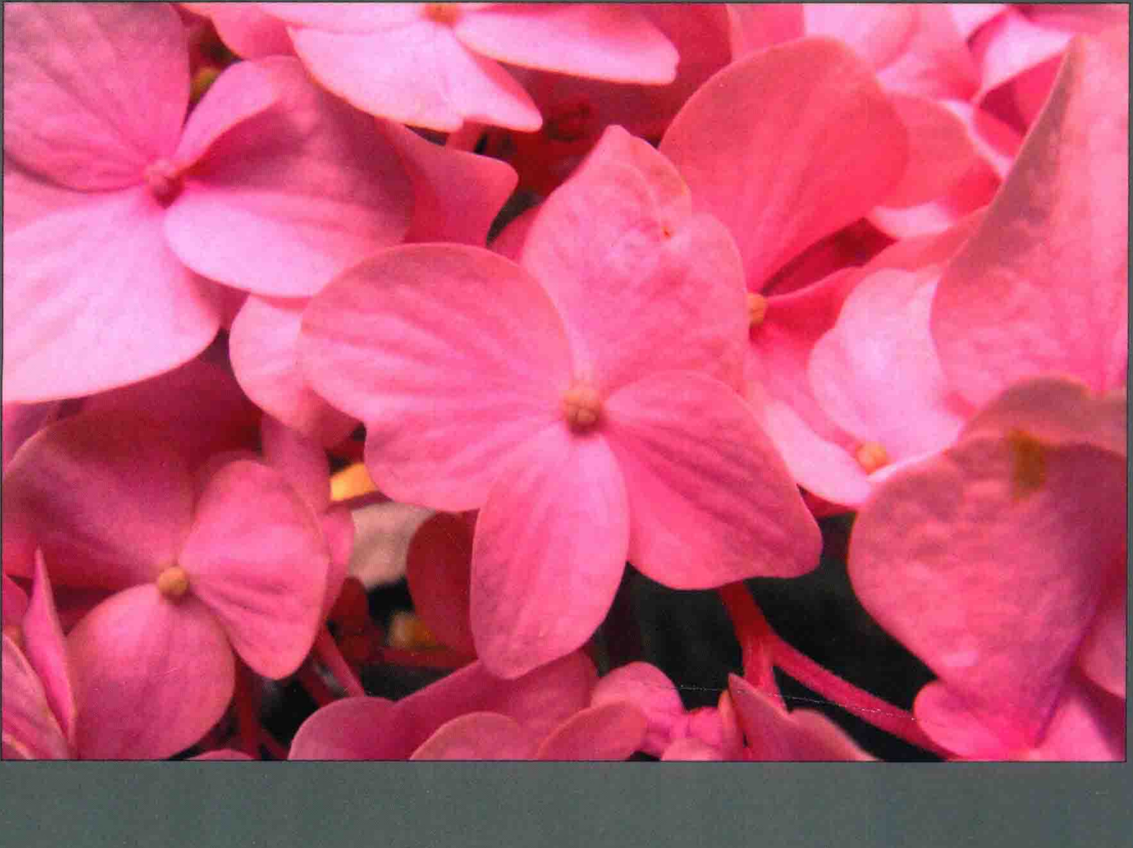

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Introduction

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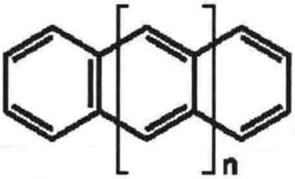
A large and diverse editor base collaboratively wrote the book, not a single author. After a long process of discussion and debate, the chapters gradually took on a neutral point of view reached through consensus. Additional editors expanded and contributed to chapters striving to achieve balance and comprehensive coverage. This reduced the regional or cultural bias found in many other books and provided access and breadth on subject matter otherwise little documented.

Acene



The general structural formula for acenes

Acenes or **polyacenes** is a class of organic compounds and polycyclic aromatic hydrocarbons made up of linearly fused benzene rings. The larger representatives have potential interest in optoelectronic applications and are actively researched in chemistry and electrical engineering. Pentacene has been incorporated into organic field-effect transistors, reaching charge carrier mobilities as high as 5 cm/Vs.

The first 6 unsubstituted members are listed in table 1.

The last members, hexacene and heptacene, are very reactive and have only been isolated in a matrix. However, bis(trialkylsilylethynylated) versions of hexacene and heptacene have been isolated as crystalline solids.

Larger acenes

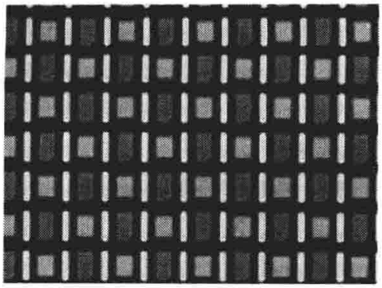
Due to their increased conjugation length the larger acenes are also studied . They are also building blocks for nanotubes and graphene. Unsubstituted **octacene** (n=8) and **nonacene** (n=9) have been detected in matrix isolation. A stable nonacene derivative has also been reported . Due to the electronic effects of the thioaryl substituents the compound is not a diradical but a closed-shell compound with the lowest HOMO-LUMO gap reported for any acene.

Related compounds

A related group of compounds with 1,2-fused rings and with helical not linear structures are the helicenes. Polyquinanes and quinenes are fused cyclopentane rings.

Source (edited): "http://en.wikipedia.org/wiki/Acene"

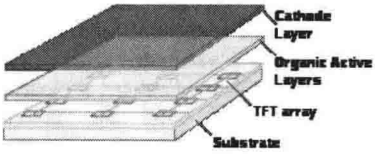
Active-matrix OLED



Magnified image of the AMOLED screen on the Google Nexus One smartphone using the RGBG system of the PenTile Matrix Family.

Active-matrix OLED (Active-matrix organic light-emitting diode or **AMOLED)** is a display technology for use in mobile devices and televisions. OLED describes a specific type of thin film display technology in which organic compounds form the electroluminescent material, and active matrix refers to the technology behind the addressing of pixels. As of 2011, AMOLED technology is used in mobile phones, media players and digital cameras and continues to make progress toward low-power, low-cost and large-size (for example 40 inch) applications.

Technical



Schematic of an active matrix OLED display

An active matrix OLED display consists of a matrix of OLED pixels that generate light upon electrical activation that have been deposited or integrated onto a thin film transistor (TFT) array, which functions as a series of switches to control the current flowing to each individual pixel.

Typically, this continuous current flow is controlled by at least two TFTs at each pixel, one to start and stop the charging of a storage capacitor and the second to provide a voltage source at the level needed to create a constant current to the pixel and eliminating need for the very high currents required for passive matrix OLED operation.

TFT backplane technology is crucial in the fabrication of AMOLED displays. Two primary TFT backplane technologies, namely polycrystalline silicon (poly-Si) and amorphous silicon (a-Si), are used today in AMOLEDs. These technologies offer the potential for fabricating the active matrix backplanes at low temperatures (below 150°C) directly onto flexible plastic substrates for producing flexible AMOLED displays.

Manufacturers have developed in-cell touch panels, integrating the production of capacitive sensor arrays in the AMOLED module fabrication process. In-cell sensor AMOLED fabricators include AU Optronics and Samsung. Samsung has marketed their version of this technology as Super AMOLED. Clear Black Display or CBD is an AMOLED display with a polarized filter on top.

Advantages

Active-matrix OLED displays provide higher refresh rates than their passive-matrix OLED counterparts, and they consume significantly less power. This advantage makes active-matrix OLEDs well suited for portable electronics, where power consumption is critical to battery life.

The amount of power the display consumes varies significantly depending on the color and brightness shown. As an example, one commercial QVGA OLED display consumes 3 watts while showing black text on a white background, but only 0.7 watts showing white text on a black background.

Disadvantages

AMOLED displays (10,000 cd/me2) may be difficult to view in direct sunlight compared to LCDs. Samsung's Super AMOLED technology addresses this issue by reducing the size of gaps between layers of the screen.

The organic materials used in AMOLED displays are prone to degradation over a period of time. However, technology has been developed to compensate for material degradation.

Current demand for AMOLED screens is high and due to supply shortages of the Samsung-produced displays, certain models of HTC smartphones have been changed to use Sony's SLCD displays in the future. Construction of new production facilities in 2011 will increase the production of AMOLED screens to cope with demand.

Commercial devices

Phones:

- Dell Venue Pro
- Google Nexus One
- Google Nexus S (Super AMOLED)
- HTC Desire
- HTC Droid Incredible
- HTC Legend
- LG Franklin Phone
- Nokia C7-00
- Nokia C6-01 (CBD)
- Nokia E7-00 (CBD)
- Nokia N8
- Nokia N85
- Nokia N86 8MP
- Nokia N9
- Orange San Francisco (Initial models)
- Samsung AMOLED Beam SPH-W9600
- Samsung Epic 4G
- Samsung i7500 Galaxy
- Samsung Haptic Beam SPH-W7900
- Samsung SPH-m900 Moment
- Samsung i8910
- Samsung Jet
- Samsung Omnia 2
- Samsung Impression
- Samsung Rogue
- Samsung Transform
- Samsung Galaxy S series (Super AMOLED)
- Samsung Galaxy S II (Super AMOLED Plus)
- Samsung Wave S8500 (Super AMOLED)

- Samsung Focus (Super AMOLED)
- Samsung Omnia 7 (Super AMOLED)
- Samsung Infuse 4G (SGH-i997) (Super AMOLED Plus)
- ZTE Blade (Initial Models)

Music Players:

- Cowon S9
- Cowon J3
- Iriver Clix
- Iriver Spinn
- Zune HD

Video game Consoles:

- GP2X Wiz
- PlayStation Vita

Music Creation Hardware:

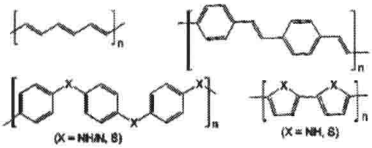
- Dave Smith Instruments "Tempest"

Digital Cameras:

- Samsung EX1
- Samsung NX10
- Samsung WB2000

Source (edited): "http://en.wikipedia.org/wiki/Active-matrix_OLED"

Conductive polymer



Chemical structures of some conductive polymers. From top left clockwise: polyacetylene; polyphenylene vinylene; polypyrrole (X = NH) and polythiophene (X = S); and polyaniline (X = NH/N) and polyphenylene sulfide (X = S).

Conductive polymers or, more precisely, **intrinsically conducting polymers** (ICPs) are organic polymers that conduct electricity. Such compounds may have metallic conductivity or can be semiconductors. The biggest advantage of conductive polymers is their processability, mainly by dispersion. Conductive polymers are generally not plastics, i.e., they are not thermoformable. But, like insulating polymers, they are organic materials. They can offer high electrical conductivity but do not show mechanical properties as other commercially used polymers do. The electrical properties can be fine-tuned using the methods of organic synthesis and by advanced dispersion techniques.

Types

The linear-backbone "polymer blacks" (polyacetylene, polypyrrole, and polyaniline) and their copolymers are the main class of conductive polymers. Historically, these are known as melanins. Poly(p-phenylene vinylene) (PPV) and its soluble derivatives have emerged as the prototypical electroluminescent semiconducting polymers. Today, poly(3-alkylthiophenes) are the archetypical materials for solar cells and transistors.

The following table presents some organic conductive polymers according to their composition. **The well-studied classes are written in bold** and *the less well studied ones are in italic.*

Synthesis

There are many methods for the synthesis of conductive polymers. Most conductive polymers are prepared by oxidative coupling of monocyclic precursors. Such reactions entail dehydrogenation:

$n\ H–[X]–H \rightarrow H–[X]–H + 2(n-1)\ H + 2(n-1)\ e$

The low solubility of most polymers presents challenges. Some researchers have addressed this through the formation of nanostructures and surfactant-stabilized conducting polymer dispersions in water. These include polyaniline nanofibers and PEDOT:PSS. These materials have lower molecular weights than that of some materials previously explored in the literature. However, in some cases, the molecular weight need not be high to achieve the desired properties.

Molecular basis of electrical conductivity

The conductivity of such polymers is the result of several processes. E.g., in traditional polymers such as polyethylenes, the valence electrons are bound in sp hybridized covalent bonds. Such "sigma-bonding electrons" have low mobility and do not contribute to the electrical conductivity of the material. However, in conjugated materials, the situation is completely different. Conducting polymers have backbones of contiguous sp hybridized carbon centers. One valence electron on each center resides in a p orbital, which is orthogonal to the other three sigma-bonds. The electrons in these delocalized orbitals have high mobility when the material is "doped" by oxidation, which removes some of these delocalized electrons. Thus, the conjugated p-orbitals form a one-dimensional electronic band, and the electrons within this band become mobile when it is partially emptied. The band structures of conductive polymers can easily be calculated with a tight binding model. In principle, these same materials can be doped by reduction, which adds electrons to an otherwise unfilled band. In practice, most organic conductors are doped oxidatively to give p-type materials. The redox doping of organic conductors is analogous to the doping of silicon semiconductors, whereby a small fraction silicon atoms are replaced by electron-rich (e.g., phosphorus) or electron-poor (e.g. boron) atoms to create n-type and p-type semiconductors, respectively.

Although typically "doping" conductive polymers involves oxidizing or reducing the material, conductive organic polymers associated with a protic solvent may also be "self-doped."

The most notable difference between conductive polymers and inorganic semiconductors is the electron mobility, which until very recently was dramatically lower in conductive polymers than their inorganic counterparts. This difference is diminishing with the invention of new polymers and the development of new processing techniques. Low charge carrier mobility is related to structural disorder. In fact, as with inorganic amorphous semiconductors, conduction in such relatively disordered materials is mostly a function of "mobility gaps" with phonon-assisted hopping, polaron-assisted tunneling, etc., between localized states. Recently, it has been reported that Quantum Decoherence on localized electron states might be the fundamental mechanism behind electron transport in conductive polymers.

The conjugated polymers in their undoped, pristine state are semiconductors or insulators. As such, the energy gap can be > 2 eV, which is too great for thermally activated conduction. Therefore, undoped conjugated polymers, such as polythiophenes, polyacetylenes only have a low electrical conductivity of around 10 to 10 S/cm. Even at a very low level of doping (< 1%), electrical conductivity increases several orders of magnitude up to values of around 0.1 S/cm. Subsequent doping of the conducting polymers will result in a saturation of the conductivity at values around 0.1–10 kS/cm for different polymers. Highest values reported up to now are for the conductivity of stretch oriented polyacetylene with confirmed values of about 80 kS/cm. Although the pi-electrons in polyactetylene are delocalized along the chain, pristine polyacetylene is not a metal. Polyacetylene has alternating single and double bonds which have lengths of 1.44 and 1.36 Å, respectively. Upon doping, the bond alteration is diminished in conductivity increases. Non-doping increases in conductivity can also be accomplished in a field effect transistor (organic FET or OFET) and by irradiation. Some materials also exhibit negative differential resistance and voltage-controlled "switching" analogous to that seen in inorganic amorphous semiconductors.

Despite intensive research, the relationship between morphology, chain structure and conductivity is poorly understood yet. Generally it is assumed, that conductivity should be higher for the higher degree of crystallinity and better alignment of the chains; however, this could not be confirmed for PEDOT and polyaniline which are largely amorphous.

Properties and applications

Conductive polymers enjoy few large-scale applications due to their poor processability. They have been known to have promise in antistatic materials and they have been incorporated into commercial displays and batteries, but there have had limitations due to the manufacturing costs, material inconsistencies, toxicity, poor solubility in solvents, and inability to directly melt process. Literature suggests they are also promising in organic solar cells, printing electronic circuits, organic light-emitting diodes, actuators, electrochromism, supercapacitors, biosensors, flexible transparent displays, electromagnetic shielding and possibly replacement for the popular transparent conductor indium tin oxide. Conducting polymers are rapidly gaining attraction in new applications with increasingly processable materials with better electrical and physical properties and lower costs. The new nanostructured forms of conducting polymers particularly, provide fresh air to this field with their higher surface area and better dispersability.

With the availability of stable and reproducible dispersions, PEDOT and polyaniline have gained some large scale applications. While PEDOT (poly(3,4-ethylenedioxythiophene)) is mainly used in antistatic applications and as a transparent conductive layer in form of PEDOT:PSS dispersions (PSS=polystyrene sulfonic acid), polyaniline is widely used for printed circuit board manufacturing – in the final finish, for protecting copper from corrosion and preventing its solderability.

Electroluminescence

Electroluminescence is light emission stimulated by electrical current. In organic compounds, electroluminescence has been known since the early 1950s, when Bernanose and coworkers first produced electroluminescence in crystalline thin films of acridine orange and quinacrine. In 1960, researchers at Dow Chemical developed AC-driven electroluminescent cells using doping. In some cases, similar light emission is observed when a voltage is applied to a thin layer of a conductive organic polymer film. While electroluminescence was originally mostly of academic interest, the increased conductivity of modern conductive polymers means enough power can be put through the device at low voltages to generate practical amounts of light. This property has led to the development of flat panel displays using organic LEDs, solar panels, and optical amplifiers.

Barriers to applications

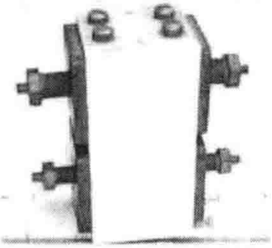
Since most conductive polymers require oxidative doping, the properties of the resulting state are crucial. Such materials are salt-like (polymer salt), which diminishes their solubility in organic solvents and water and hence their processability. Furthermore, the charged organic backbone is often unstable towards atmospheric moisture. Compared to metals, organic conductors can be expensive requiring multi-step synthesis. The poor processability for many polymers requires the introduction of solubilizing or substituents, which can further complicate the synthesis.

Experimental and theoretical thermodynamical evidence suggests that conductive polymers may even be completely and principally insoluble so that they can processed only by dispersion.

Trends

Most recent emphasis is on organic light emitting diodes and organic polymer solar cells. The Organic Electronics Association is an international platform to promote applications of organic semiconductors. Conductive polymer products with embedded and improved electromagnetic interference (EMI) and electrostatic discharge (ESD) protection have led to both prototypes and products. For example, Polymer Electronics Research Center at University of Auckland is developing a range of novel DNA sensor technologies based on conducting polymers, photoluminescent polymers and inorganic nanocrystals (quantum dots) for simple, rapid and sensitive gene detection. Typical conductive polymers must be "doped" to produce high conductivity. To date, there remains to be discovered an organic polymer that is *intrinsically* electrically conducting.

History



voltage-controlled switch, an organic polymer electronic device from 1974. Now in the Smithsonian Chips collection.

There are multiple reviews of the history of the field. The first report on polyaniline goes back to the discovery of aniline. In the mid-19th century, Letheby reported the electrochemical and chemical oxidation products of aniline in acidic media, noting that reduced form was colourless but the oxidized forms were deep blue. In the early 20th century, German chemists named several compounds "aniline black" and "pyrrole black" and used them industrially. Classically, such polymer "blacks", their parent compound polyacetylene, and their co-polymers were called "Melanins".

The first highly-conductive organic compounds were the charge transfer complexes. In the 1950s, researchers reported that polycyclic aromatic compounds formed semi-conducting charge-transfer complex salts with halogens. In 1954, researchers at Bell Labs and elsewhere reported organic charge transfer complexes with resistivities as low as 8 ohms-cm. In the early 1970s, salts of tetrathiafulvalene were shown to exhibit almost metallic conductivity, while superconductivity was demonstrated in 1980. Broad research on charge transfer salts continues today. While these compounds were technically not polymers, this indicated that organic compounds can carry current. While organic conductors were previously intermittently discussed, the field was particularly energized by the prediction of superconductivity following the discovery of BCS theory.

In 1963 Australians Bolto, DE Weiss, and coworkers reported iodine-doped oxidized polypyrrole blacks with resistivities as low as 1 ohm/cm. This Australian group eventually claimed to reach resistivities as low as 0.03 ohm·cm with other conductive organic polymers. This resistivity is roughly equivalent to present-day efforts. The 1964 monograph *Organic Semiconductors* cites multiple reports of similar high-conductivity oxidized polyacetylenes. With the notable exception of Charge transfer complexes (some of which are even superconductors), organic molecules were previously considered insulators or at best weakly conducting semiconductors. Subsequently, DeSurville and coworkers reported high conductivity in a polyaniline. Likewise, in 1980, Diaz and Logan reported films of polyaniline that can serve as electrodes.

Similarly, much early work on the physics and chemistry of conductive polymers was done under the melanin rubrick. This was because of the medical relevance of this material. For example, in the 1960s Blois *et al.* showed semiconduction in melanins, as well as further defining their physical structures and properties Nicolaus *et al.* further defined the conductive polymer structures. Classically, all polyacetylenes, polypyrroles and polyanilines are melanins, "The most simple melanin can be considered the acetylene-black from which it is possible to derive all the others.. Substitution does not qualitatively influence the physical properties like conductivity, colour, EPR, which remain unaltered."

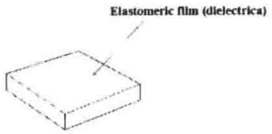
However, while mostly operating in the quantum realm of less than 100 nanometers, "molecular" electronic processes can collectively manifest on a macro scale. Examples include quantum tunneling, negative resistance, phonon-assisted hopping, polarons, and the like. Thus, macro-scale active organic electronic devices were described decades before molecular-scale ones. E.g., in 1974, John McGinness and his coworkers described the putative "first experimental demonstration of an operating molecular electronic device". This was an "active" organic-polymer electronic device, a voltage-controlled bistable switch. As its active element, this device used DOPA-melanin, a well-characterized self-doping copolymer of polyaniline, polypyrrole, and polyacetylene. The "ON" state of this device exhibited almost metallic conductivity, and exhibited low conductivity with switching, with as much as five orders of magnitude shifts in current. Their material also exhibited classic negative differential resistance.

In 1977, Alan J. Heeger, Alan MacDiarmid and Hideki Shirakawa reported similar high conductivity in oxidized iodine-doped polyacetylene. This research earned them the 2000 Nobel prize in Chemistry *"For the discovery and development of conductive polymers."* The Nobel citation made no reference to Weiss *et al.'s* similar earlier work (see Nobel Prize controversies). Because of the numerous earlier reports of similar compounds, reviewers question the Nobel citation's *discovery* assignment. Thus, Inzelt notes that, while the Nobelists deserve credit for publicising and popularizing the field, conductive polymers were " *..produced, studied and even applied* " well before their work.

Source (edited): "http://en.wikipedia.org/wiki/Conductive_polymer"

Dielectric elastomers

Dielectric elastomers (DEs) are smart material systems which produce large strains (up to 300%) and belong to the group of electroactive polymers (EAP). Based on their simple working principle dielectric elastomer actuators (DEA) transform electric energy directly into mechanical work. DE are lightweight, have a high elastic energy density and are investigated since the late 90's. Many potential applications exist as prototypes. Every year in spring a SPIE conference takes place in San Diego where the newest research results concerning DEA are exchanged.



Working principle of dielectric elastomer actuators. An elastomeric film is coated on both sides with electrodes. The electrodes are connected to a circuit. By applying a voltage U the electrostatic pressure p acts. Due to the mechanical compression the elastomer film contracts in the thickness direction and expands in the film plane directions. The elastomer film moves back to its original position when it is short-circuited.

Working principle

A DEA is a compliant capacitor (see image), where a passive elastomer film is sandwiched between two compliant electrodes. When a voltage U is applied, the electrostatic pressure p arising from the Coulomb forces acting between the electrodes. Therefore the electrodes squeeze the elastomer film. The equivalent electromechanical pressure p is twice the electrostatic pressure p and is given by the following equation:

$$p_{eq} = \varepsilon_0 \varepsilon_r \frac{U^2}{z^2}$$

where ε_0 is the vacuum permittivity, ε_r is the dielectric constant of the polymer and z is the thickness of the elastomer film. Usually, strains of DEA are in the order of 10–35%, maximum values are up to 300%.

Materials

For the elastomer often silicones and acrylic elastomers are used. In particular, the acrylic elastomer VHB 4910, commercially available from the company 3M has shown the largest activation strain (300%), a high elastic energy density and a high electrical breakdown strength. Basically, the requirements for an elastomer material for DEA are

- The material should have a low stiffness (especially when large strains are required);
- The dielectric constant should be high;
- The electrical breakdown strength should be high.

A possibility to enhance the electrical breakdown strength is to prestretch the elastomer film mechanically. Further reasons for prestretching the elastomer are the following:

- The thickness of the film decreases. A lower voltage has to be applied to obtain the same electrostatic pressure;
- The prestrain avoids compressive stresses in the film plane directions which might be responsible for failure.

The elastomers show a visco-hyperelastic behavior. Models which describe large strains and viscoelasticity are required for the calculation of such actuators.

Several different types of electrodes are used in the research (e.g. graphite powder, silicone oil / graphite mixtures, gold electrodes, etc.). The electrode should be conductive and compliant. The compliance of the electrode is important in order that the elastomer is not constrained mechanically in its elongation by the electrode.

Configurations

Several configurations exist for dielectric elastomer actuators:

- Framed/In-Plane actuators: A framed or in-plane actuator is an elastomeric film coated/printed with two electrodes. Typically a frame or support structure will be mounted around the film. Examples are expanding circles, planars (single and multiple phase)
- Cylindrical/Roll actuators: Coated elastomer films are rolled around an axis. By activation, a force and an elongation appear in axial direction. The roll actuators can be rolled around a compression spring or rolled without a core. The application of such cylindrical actuators are artificial muscles (prosthetics), mini- and microrobots, and valves.
- Diaphragm actuators: A diaphragm actuator is made as a planar construction which is then biased in the z-axis to produce out of plane motion. Artificial Muscle, Inc. offers a Universal Muscle Actuator (UMA) that is a double diaphragm.
- Shell-like actuators: Planar elastomer films are coated at specific locations in form of different electrode segments. With a well-directed activation of the cells with the voltage, the foils assume complex three-dimensional shapes. Such shell-like actuators may be utilized for the propulsion of vehicles through air or water, e.g. for blimps.
- Stack actuators: By stacking up several planar actuators the force and the deformation can be enlarged. Especially an actuator which shortens by activation can be realized.
- Thickness Mode Actuators: The force and stroke of DEA's can be taken in the z-direction. Thickness mode are a typically a flat film that

may have a stack of multiple layers to increase displacement.

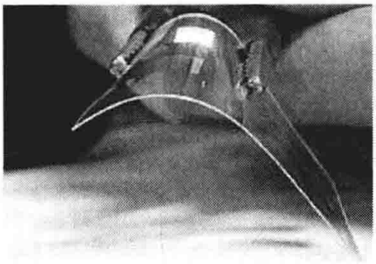
Applications

Dielectric elastomers offer a wide variety of potential applications as a novel actuator technology that can replace many electromagnetic actuators, pneumatics, and piezo actuators. And dielectric elastomers can enable actuators to be integrated into applications that were previously infeasible. A list of some applications for dielectric elastomers are:

- Haptic Feedback
- Pumps
- Valves
- Robotics
- Prosthetics
- Power Generation
- Optical Positioners such for autofocus, zoom, image stabilization
- Sensing of force and pressure
- Active Braille Displays
- Speakers
- Deformable surfaces for optics and aerospace

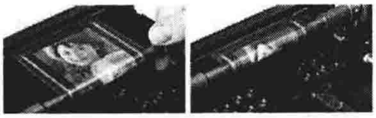
Source (edited): "http://en.wikipedia.org/wiki/Dielectric_elastomers"

Flexible organic light-emitting diode



Demonstration of a flexible OLED device

Demonstration of a battery driven flexible OLED lamp from Merck KGaA



Demonstration of a 4.1" prototype flexible display from Sony

A **flexible organic light emitting diode (FOLED)** is a type of organic light-emitting diode (OLED) incorporating a flexible plastic substrate on which the electroluminescent organic semiconductor is deposited. This enables the device to be bent or rolled while still operating. Currently the focus of research in industrial and academic groups, flexible OLEDs form one method of fabricating a rollable display.

Technical Details and Applications

An OLED emits light due to the electroluminescence of thin films of organic semiconductors approximately 100 nm thick. Regular OLEDs are usually fabricated on a glass substrate, but by replacing glass with a flexible plastic such as polyethylene terephthalate (PET) among others, OLEDs can be made both bendable and lightweight.

Such materials may not be suitable for comparable devices based on inorganic semiconductors due to the need for lattice matching and the high temperature fabrication procedure involved.

In contrast, flexible OLED devices can be fabricated by deposition of the organic layer onto the substrate using a method derived from inkjet printing, allowing the inexpensive and roll-to-roll fabrication of printed electronics.

Flexible OLEDs may be used in the production of rollable displays, electronic paper, or bendable displays which can be integrated into clothing, wallpaper or other curved surfaces. Prototype displays have been exhibited by companies such as Sony, which are capable of being rolled around the width of a pencil.

Disadvantages

Both the flexible substrate itself as well as the process of bending the device introduce stress into the materials. There may be residual stress from the deposition of layers onto a flexible substrate, thermal stresses due to the different coefficient of thermal expansion of materials in the device, in addition to the external stress from the bending of the device.

Stress introduced into the organic layers may lower the efficiency or brightness of the device as it is deformed, or cause complete breakdown of the device altogether. Indium tin oxide (ITO), the material most commonly used as the transparent anode, is brittle. Fracture of the anode can occur which can increase the sheet resistance of the ITO or disrupt the layered structure of the OLED. Although ITO is the most common and best understood anode material used in OLEDs, research has been undertaken into alternative materials that are better suited for flexible applications including carbon nanotubes.

Encapsulation is another challenge for flexible OLED devices. While the common method of encapsulation for regular OLEDs is to seal the organic layer between glass, this is inappropriate for flexible OLEDs. The materials in an OLED are sensitive to air and moisture which lead to degradation of the materials themselves as well as quenching of excited states within the molecule. Flexible encapsulation methods are generally not as effective a barrier to air and moisture as glass, and current research aims to improve the encapsulation of flexible organic light emitting diodes.

Source (edited): "http://en.wikipedia.org/wiki/Flexible_organic_light-emitting_diode"

John McGinness

John Edward McGinness (November 19, 1943), is an American physicist and physician. McGinness worked as a in the field of Organic electronics and Nanotechnology.

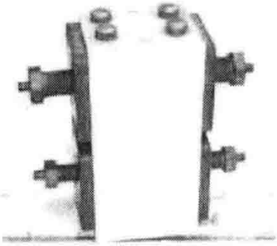
Education

McGinness studied physics at the University of Houston and after his B.S. in 1966 he received his PhD for Physics at the Rice University in 1970.

He became assistant professor for Biophysics at the University of Texas (Tumor Institute).He received his MD from University of Texas Medical School at Houston in 1985 and worked in Internal Medicine for one year, changing to psychiatry and working at the Department of Psychiatry, University of Texas Health Science Center at Houston from 1989 till 1992 Author of roughly 40 research publications, book chapters, and presentations.

Work

John McGinness pioneered much of the modern field of organic electronics.



An organic polymer voltage-controlled switch from 1974. Now in the Smithsonian Chip collection

In 1972, while working at the Metallurgy department at Youngstown State University, Dr. McGinness suggested that electronic conduction in melanins (polyacetylene, polypyrrole, and polyaniline "blacks" and their copolymers) is analogous to conduction in amorphous solids such as the chalcogenide glasses. This area was originally pioneered by Neville Mott, among others. That is, it involves such things as mobility gaps, phonon-assisted hopping, polarons, Quantum tunneling, and so forth. This report anticipated the later Nobel-prize-winning work of Shirakawa *et al.* on conduction mechanisms in other oxidized polyacetylenes.

From Youngstown, Dr McGinness moved to the Physics Department of The University of Texas M. D. Anderson Cancer Center. The department had an interest in the physical properties of Melanin as a possible hook to treating melanoma. While of enormous importance now, this was a research backwater at the time. With the notable exception of Bolto *et al.*, who had reported high conductivity in iodine-doped polypyrrole, few but melanoma researchers had much reason to look at the electronic properties of such rigid-backbone polymer "blacks". This is why the putative first molecular electronic device came from a cancer hospital.

The chalcogenide glasses show "switching", in which an applied "threshold voltage" reversibly switches a material from a low-conductivity "OFF" state to a high-conductivity "ON' state. The similarity of conduction mechanisms suggested that the melanins might also demonstrate voltage-controlled switching. Following this lead, Dr McGinness and his MD Anderson coworkers constructed a voltage-controlled switch incorporating melanin as its active element . They also further characterized its electronic behavior.

This device was a "proof of concept" for McGinness' model for electronic conduction in such materials. In many ways, this work directly anticipated that leading to the 2000 Nobel Prize in Chemistry "For the Discovery and Development of Conductive Polymers", but with some differences. First, McGinness built an actual device with a high conductivity "ON" state, while they looked at passive high conductivity in another of the same class of polymer. Similarly, the Nobel winners worked in reverse—they stumbled upon passive high conductivity in another oxidized polyacetylene, unknowingly repeating the work of Bolto *et al.* with similarly iodine-doped polypyrrole. They then developed a model to explain high conductivity in such materials. This model was rather similar to Dr McGinness', with the addition of solitons for the special case of pure polyacetylene.

The pictured device represents several putative "firsts" in organic electronics. E.g., this voltage-controlled switch is apparently the first identifiable "active" organic semiconductor device. (An active device is one in which a current or voltage controls current flow.) As such, it is arguably parent to many later developments in organic electronics. In fact, only in the last decade or so have similar devices reappeared. Moreover, organic electronics is part of Nanotechnology. So this gadget is the putative first nanotech device. As such, it is now in the Smithsonians Institution's National Museum of American History collection of early electronic devices.

Similarly, while high-conductivity had been observed decades before in Charge transfer complex-type organic semiconductors and in polypyrrole , the "ON" state of the pictured device was the demonstration of a high "metallic" conductivity state in the linear-backbone conductive polymers. Thus, a subsequent news article in the journal *Nature* makes much of this materials "strikingly large conductivity", "high conductivity", and "large conduction".

At present, such oxidized polyacetylenes and their derivatives are the most commonly-used commercial conductive polymers. Further, the pictured device exhibited negative differential resistance, now a well-recognized property of electronically-active conductive polymers.

Interestingly, For further perspective concerning where this device fits in the history of Organic Electronics, see reference 9. A sample quote:

- "Also in 1974 came **the first experimental demonstration of an operating molecular electronic device** *(emphasis-added)* that functions along the lines of the biopolymer conduction ideas of Szent-Györgi. This advance was made by McGinness, Corry, and Proctor who examined conduction through artificial and biological melanin oligomers. They observed semiconductor properties of the organic material and demonstrated strong negative differential resistance, a hallmark of modern advances in molecular electronics.58 Like many early advances, the significance of the results obtained was not fully appreciated until decades later...(p 14)"

Since he was at a cancer research institute, McGinness' other interests included the role of free radicals in the action and toxicity of the anticancer drugs cisplatin, adriamycin, and bleomycin. E.g., he was the first to show (10) that the kidney toxicity of cisplatin involves reactive oxygen species. Some of this work was done with Harry Demopoulos, famous as the doctor in Clint Eastwood's *Dirty Harry* movies and as the person who resolved the Doris Duke will dispute. McGinness was also involved in the dielectic spectroscopy of water bound to membranes. This was related to the future development of Magnetic Resonance Imaging

John and his coworkers also obtained two US patents for organic-polymer-based energy storage devices (batteries),US patents# #4,366,216 and #4,504,557

Source (edited): "http://en.wikipedia.org/wiki/John_McGinness"

Light-emitting Electrochemical Cell

A **light-emitting electrochemical cell** (**LEC** or **LEEC**) is a solid-state device that generates light from an electric current (electroluminescence). LEC's are usually composed of two metal electrodes connected by (e.g. sandwiching) an organic semiconductor containing mobile ions. Aside from the mobile ions, their structure is very similar to that of an organic light-emitting diode (OLED).

LECs have most of the advantages of OLEDs, as well as additional ones:

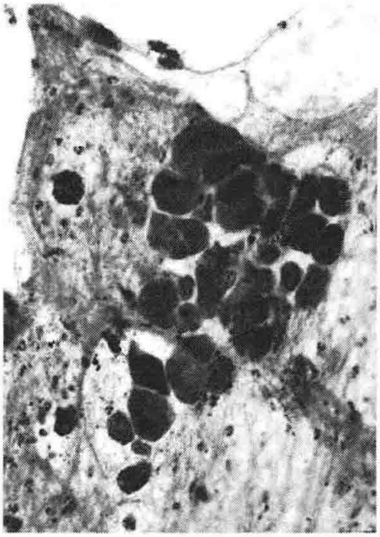
- The device does not depend on the difference in work function of the electrodes. Consequently, the electrodes can be made of the same material (e.g., gold). Similarly, the device can still be operated at low voltages.
  - Recently developed materials such as graphene or a blend of carbon nanotubes and polymers have been used as electrodes, eliminating the need for using indium tin oxide for a transparent electrode.
- The thickness of the active electroluminescent layer is not critical for the device to operate. This means that:
  - LECs can be printed with relatively inexpensive printing processes (where control over film thicknesses can be difficult).
  - Internal device operation can be observed directly.

History

While electroluminescence had been seen previously in similar devices, the invention of the polymer LEC is attributed to Pei et al. Since then, numerous research groups, and even a few companies, have worked on improving and commercializing the devices.

Source (edited): "http://en.wikipedia.org/wiki/Light-emitting_Electrochemical_Cell"

Melanin



Melanin pigment (dark granular material - center of image) in a pigmented melanoma. Pap stain.

Melanin (🔊 /ˈmɛlənɪn/; Greek: μέλας, *black*) is a pigment that is ubiquitous in nature, being found in most organisms (spiders are one of the few groups in which it has not been detected). In animals melanin pigments are derivatives of the amino acid tyrosine. The most common form of biological melanin is **eumelanin**, a brown-black polymer of dihydroxyindole carboxylic acids, and their reduced forms. All melanins are derivatives of polyacetylene. The most common melanin – dopamelanin – is a mixed copolymer of polyacetylene, polyaniline, and polypyrrole. Another common form of melanin is pheomelanin, a red-brown polymer of benzothiazine units largely responsible for red hair and freckles. The presence of melanin in the archaea and bacteria kingdoms is an issue of ongoing debate among researchers in the field.

The increased production of melanin in human skin is called melanogenesis. Production of melanin is stimulated by DNA damage induced by UVB-radiation, and it leads to a delayed development of a tan. This melanogenesis-based tan takes more time to develop, but it is long lasting.

The photochemical properties of melanin make it an excellent photoprotectant. It absorbs harmful UV-radiation and transforms the energy into harmless heat through a process called "ultrafast internal conversion". This property enables melanin to dissipate more than 99.9% of the absorbed UV radiation as heat (see photoprotection). This prevents the indirect DNA damage that is responsible for the formation of malignant melanoma and other skin cancers.

In humans

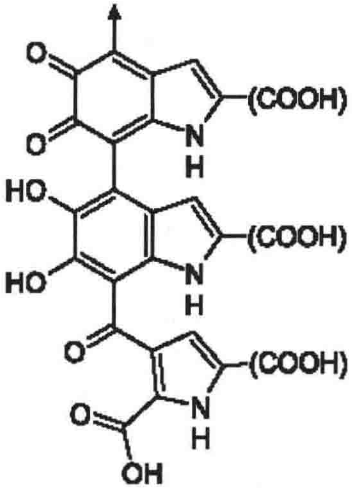
Albinism occurs when melanocytes produce little or no melanin. This albino girl is from Papua New Guinea.

In humans, melanin is the primary determinant of skin color. It is also found in hair, the pigmented tissue underlying the iris of the eye, and the stria vascularis of the inner ear. In the brain, tissues with melanin include the medulla and zona reticularis of the adrenal gland, and pigment-bearing neurons within areas of the brainstem, such as the locus coeruleus and the substantia nigra.

The melanin in the skin is produced by melanocytes, which are found in the basal layer of the epidermis. Although, in general, human beings possess a similar concentration of melanocytes in their skin, the melanocytes in some individuals and ethnic groups more frequently or less frequently express the melanin-producing genes, thereby conferring a greater or lesser concentration of skin melanin. Some individual animals and humans have very little or no melanin in their bodies, a condition known as albinism.

Because melanin is an aggregate of smaller component molecules, there are many different types of melanin with differing proportions and bonding patterns of these component molecules. Both pheomelanin and eumelanin are found in human skin and hair, but eumelanin is the most abundant melanin in humans, as well as the form most likely to be deficient in albinism.

Eumelanin



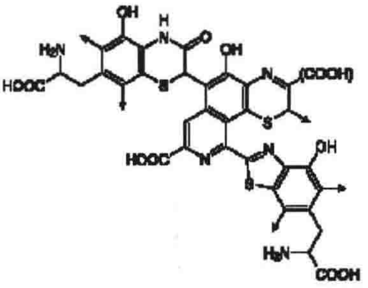
Part of the structural formula of eumelanin. "(COOH)" can be COOH or H, or (more rarely) other substituents. The arrows denotes where the polymer continues.

Eumelanin polymers have long been thought to comprise numerous cross-linked 5,6-dihydroxyindole (DHI) and 5,6-dihydroxyindole-2-carboxylic acid (DHICA) polymers. However, recent research into the electrical properties of eumelanin has indicated that it may consist of more basic oligomers adhering to one another by some other mechanism. Eumelanin is found in hair, areola, and skin, and the hair colors grey, black, yellow, and brown. In humans, it is more abundant in people with dark skin.

There are two different types of eumelanin. The two types are black eumelanin and brown eumelanin, with black melanin being darker than brown. Black eumelanin is mostly in non-Europeans and aged Europeans, while brown eumelanin is in mostly young Europeans.

A small amount of black eumelanin in the absence of other pigments causes grey hair. A small amount of brown eumelanin in the absence of other pigments causes yellow (blond) color hair.

Pheomelanin



Part of the structural formula of pheomelanin. "(COOH)" can be COOH or H, or (more rarely) other substituents. The arrows denotes where the polymer continues.

Pheomelanin is also found in hair and skin and is both in lighter-skinned humans and darker skinned humans. Pheomelanin imparts a pink to red hue and, thus is found in particularly large quantities in red hair. Pheomelanin also may become carcinogenic when exposed to the ultraviolet rays of the sun. In chemical terms, pheomelanin differs from eumelanin in that its oligomer structure incorporates benzothiazine and benzothiazole units that are produced, instead of DHI and DHICA, when the amino acid L-cysteine is present.

Neuromelanin

Neuromelanin is the dark pigment present in pigment bearing neurons of four deep brain nuclei: the substantia nigra (from the Latin *black substance*) - Pars Compacta part, the locus coeruleus (*blue spot*), the dorsal motor nucleus of the vagus nerve (cranial nerve X), and the median raphe nucleus of the pons. Both the substantia nigra and locus coeruleus can be easily identified grossly at the time of autopsy because of their dark pigmentation. In humans, these nuclei are not pigmented at the time of birth, but develop pigmentation during maturation to adulthood.

Although the functional nature of neuromelanin is unknown in the brain, the pigment is made from oxyradical metabolites of monoamine neurotransmitters including dopamine and norepinephrine. Luigi Zecca and David Sulzer demonstrated that neuromelanin pigment is an autophagy product that accumulates in lysosomes, which are unable to effectively degrade it . In this way, the synthesis of neuromelanin, is protective as its encapsulation within the autophagic organelle removes it from reacting with sites in the neuronal cytosol that could lead to neurtoxicity.

While neuromelanin becomes higher throughout life in most people, the loss of pigmented neurons from specific nuclei is seen in a variety of neurodegenerative diseases. In Parkinson's disease there is massive loss of dopamine-producing pigmented neurons in the substantia nigra. High levels of neuromelanin are also detected in primates and in carnivores such as cats and dogs.

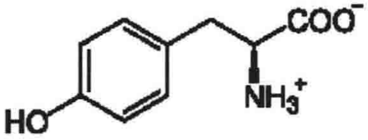
In other organisms

Melanins have very diverse roles and functions in various organisms. A form of melanin makes up the ink used by many cephalopods (see cephalopod ink) as a defense mechanism against predators. Melanins also protect microorganisms, such as bacteria and fungi, against stresses that involve cell damage such as UV radiation from the sun and reactive oxygen species. Melanin also protects against damage from high temperatures, chemical stresses (such as heavy metals and oxidizing agents), and biochemical threats (such as host defenses against invading microbes). Therefore, in many pathogenic microbes (for example, in *Cryptococcus neoformans*, a fungus) melanins appear to play important roles in virulence and pathogenicity by protecting the microbe against immune responses of its host. In invertebrates, a major aspect of the innate immune defense system against invading pathogens involves melanin. Within minutes after infection, the microbe is encapsulated within melanin (melanization), and the generation of free radical byproducts during the formation of this capsule is thought to aid in killing them. Some types of fungi, called radiotrophic fungi, appear to be able to use melanin as a photosynthetic pigment that enables them to capture gamma rays and harness its energy for growth.

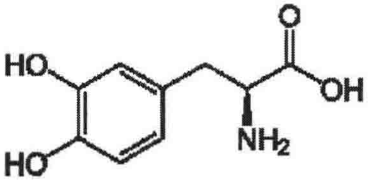
The black feathers of birds owe their color to melanin; they are much more readily degraded by bacteria than white feathers, or those containing other pigments such as carotenes.

Catechol melanins are plant melanins.

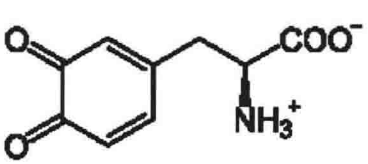
Biosynthetic pathways



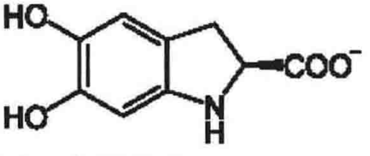
L-tyrosine



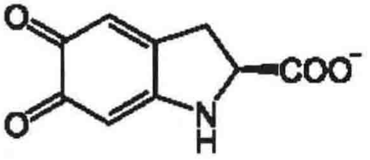
L-DOPA



L-dopaquinone



L-leucodopachrome



L-dopachrome

The first step of the biosynthetic pathway for both eumelanins and pheomelanins is catalysed by tyrosinase:

Tyrosine → DOPA → dopaquinone

Dopaquinone can combine with cysteine by two pathways to benzothiazines and pheomelanins

Dopaquinone + cysteine → 5-S-cysteinyldopa → benzothiazine intermediate → pheomelanin

Dopaquinone + cysteine → 2-S-cysteinyldopa → benzothiazine intermediate → pheomelanin

Alternatively, dopaquinone can be converted to leucodopachrome and follow two more pathways to the eumelanins

Dopaquinone → leucodopachrome → dopachrome → 5,6-dihydroxyindole-2-carboxylic acid → quinone → eumelanin

Dopaquinone → leucodopachrome → dopachrome → 5,6-dihydroxyindole → quinone → eumelanin

Microscopic appearance

Melanin is brown, non-refractile, and finely granular with individual granules having a diameter of less than 800 nanometers. This differentiates melanin from common blood breakdown pigments, which are larger, chunky, and refractile, and range in color from green to yellow or red-brown. In heavily pigmented lesions, dense aggregates of melanin can obscure histologic detail. A dilute solution of potassium permanganate is an effective melanin bleach.

Genetic disorders and disease states

Melanin deficiency has been connected for some time with various genetic abnormalities and disease states.

There are approximately ten different types of oculocutaneous albinism, which is mostly an autosomal recessive disorder. Certain ethnicities have higher incidences of different forms. For example, the most common type, called oculocutaneous albinism type 2 (OCA2), is especially frequent among people of black African descent. It is an autosomal recessive disorder characterized by a congenital reduction or absence of melanin pigment in the skin, hair, and eyes. The estimated frequency of OCA2 among African-Americans is 1 in 10,000, which contrasts with a frequency of 1 in 36,000 in white Americans. In some African nations, the frequency of the disorder is even higher, ranging from 1 in 2,000 to 1 in 5,000. Another form of Albinism, the "yellow oculocutaneous albinism", appears to be more prevalent among the Amish, who are of primarily Swiss and German ancestry. People with this IB variant of the disorder commonly have white hair and skin at birth, but rapidly develop normal skin pigmentation in infancy.

Ocular albinism affects not only eye pigmentation, but visual acuity, as well. People with albinism typically test poorly, within the 20/60 to 20/400 range. In addition, two forms of albinism, with approximately 1 in 2700 most prevalent among people of Puerto Rican origin, are associated with mortality beyond melanoma-related deaths.

Mortality also is increased in patients with Hermansky-Pudlak syndrome and Chediak-Higashi syndrome. Patients with Hermansky-Pudlak syndrome have a bleeding diathesis secondary to platelet dysfunction and also experience restrictive lung disease (pulmonary fibrosis), inflammatory bowel disease, cardiomyopathy, and renal disease. Patients with Chediak-Higashi syndrome are susceptible to infection and also can develop lymphofollicular malignancy.

The role that melanin deficiency plays in such disorders remains under study.

The connection between albinism and deafness is well known, though poorly understood. E.g., in his 1859 treatise *On the Origin of Species*, Charles Darwin observed that "cats which are entirely white and have blue eyes are generally deaf". In humans, hypopigmentation and deafness occur together in the rare Waardenburg's syndrome, predominantly observed among the Hopi in North America. The incidence of albinism in Hopi Indians has been estimated as approximately 1 in 200 individuals. It is interesting to note that similar patterns of albinism and deafness have been found in other mammals, including dogs and rodents. However, a lack of melanin *per se* does not appear to be directly responsible for deafness associated with hypopigmentation, as most individuals lacking the enzymes required to synthesize melanin have normal auditory function. Instead the absence of melanocytes in the stria vascularis of the inner ear results in cochlear impairment, though why this is, is not fully understood. It may be that melanin, the best sound-absorbing material known, plays some protective function. in alternate fashion, melanin may affect development, as Darwin suggests.

In Parkinson's disease, a disorder that affects neuromotor functioning, there is decreased neuromelanin in the substantia nigra as consequence of specific dropping out of dopaminergic pigmented neurons. This results in diminished dopamine synthesis. While no correlation between race and the level of neuromelanin in the substantia nigra has been reported, the significantly lower incidence of Parkinson's in blacks than in whites has "prompt[ed] some to suggest that cutaneous melanin might somehow serve to protect the neuromelanin in substantia nigra from external toxins.". Also see Nicolaus review article on the function of neuromelanins

In addition to melanin deficiency, the molecular weight of the melanin polymer may be decreased by various factors such as oxidative stress, exposure to light, perturbation in its association with melanosomal matrix proteins, changes in pH or in local concentrations of metal ions. A decreased molecular weight or a decrease in the degree of polymerization of **ocular melanin** has been proposed to turn the normally anti-oxidant polymer into a pro-oxidant. In its pro-oxidant state, melanin has been suggested to be involved in the causation and progression of macular degeneration and melanoma.

Higher eumelanin levels also can be a disadvantage, however, beyond a higher disposition toward vitamin D deficiency. Dark skin is a complicating factor in the laser removal of port-wine stains. Effective in treating white skin, in general, lasers are less successful in removing port-wine stains in people of Asian or African descent. Higher concentrations of melanin in darker-skinned individuals simply diffuse and absorb the laser radiation, inhibiting light absorption by the targeted tissue. In similar manner, melanin can complicate laser treatment of other dermatological conditions in people with darker skin.

Freckles and moles are formed where there is a localized concentration of melanin in the skin. They are highly associated with pale skin.

Nicotine has an affinity for melanin-containing tissues because of its precursor function in melanin synthesis or its irreversible binding of melanin and nicotine. This has been suggested to underlie the increased nicotine dependence and lower smoking cessation rates in darker pigmented individuals.

Human adaptation

Melanocytes insert granules of melanin into specialized cellular vesicles called melanosomes. These are then transferred into the other skin cells of the human epidermis. The melanosomes in each recipient cell accumulate atop the cell nucleus, where they protect the nuclear DNA from mutations caused by the ionizing radiation of the sun's ultraviolet rays. In general, people whose ancestors lived for long periods in the regions of the globe near the equator have larger quantities of eumelanin in their skins. This makes their skins brown or black and protects them against high levels of exposure to the sun, which more frequently results in melanomas in lighter-skinned people.

With humans, exposure to sunlight stimulates the skin to produce vitamin D. Because high levels of cutaneous melanin act as a natural sun screen, dark skin can be a risk factor for vitamin D deficiency in regions of the Earth known as cool temperate zones, i.e., above 36 degrees latitude in the Northern hemisphere and below 36 degrees in the Southern hemisphere. As a result of this, health authorities in Canada and the USA have issued recommendations for people with darker complexions (including people of southern European descent) to consume between 1000-2000 IU (International Units) of vitamin D, daily, through Autumn to Spring.

The most recent scientific evidence indicates that all humans evolved in Africa, then populated the rest of the world through successive radiations. It seems likely that the first modern humans had relatively large numbers of eumelanin-producing melanocytes. In accordance, they had darker skin as with the indigenous people of Africa today. As some of these original peoples migrated and settled in areas of Asia and Europe, the selective pressure for eumelanin production decreased in climates where radiation from the sun was less intense. Of the two common gene variants known to be associated with pale human skin, *Mc1r* does not appear to have undergone positive selection, while *SLC24A5* has.

As with peoples having migrated northward, those with light skin migrating toward the equator acclimatize to the much stronger solar radiation. Most people's skin darkens when exposed to UV light, giving them more protection when it is needed. This is the physiological purpose of sun tanning. Dark-skinned people, who produce more skin-protecting eumelanin, have a greater protection against sunburn and the development of melanoma, a potentially deadly form of skin cancer, as well as other health problems related to exposure to strong solar radiation, including the photodegradation of certain vitamins such as riboflavins, carotenoids, tocopherol, and folate.

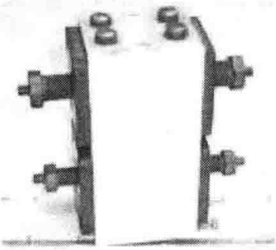
Melanin in the eyes, in the iris and choroid, helps protect them from ultraviolet and high-frequency visible light; people with gray, blue, and green eyes are more at risk for sun-related eye problems. Further, the ocular lens yellows with age, providing added protection. However, the lens also becomes more rigid with age, losing most of its accommodation — the ability to change shape to focus from far to near — a detriment due probably to protein crosslinking caused by UV exposure.

Recent research by J.D. Simon *et al.* suggests that melanin may serve a protective role other than photoprotection. Melanin is able to effectively ligate metal ions through its carboxylate and phenolic hydroxyl groups, in many cases much more efficiently than the powerful chelating ligand ethylenediaminetetraacetate (EDTA). Thus, it may serve to sequester potentially toxic metal ions, protecting the rest of the cell. This hypothesis is supported by the fact that the loss of neuromelanin observed in Parkinson's disease is accompanied by an increase in iron levels in the brain.

Physical properties and technological applications

In terms of structure and electronics, melanins are "rigid-backbone" conductive polymers composed of polyacetylene, polypyrrole, and polyaniline "Blacks" and their mixed copolymers. The simplest melanin is polyacetylene, and some fungal melanins are pure polyacetylene.

In 1963, D.E Weiss and coworkers reported high electrical conductivity in a melanin, iodine-doped and oxidized polypyrrole "Black". They achieved the quite high conductivity of 1 Ohm/cm. A decade later, John McGinness, and coworkers reported a high conductivity "ON" state in a voltage-controlled solid-state threshold switch made with DOPA melanin. Further, this material emitted a flash of light—electroluminescence—when it switched. Melanin also shows negative resistance, a classic property of electronically-active conductive polymers. Likewise, melanin is the best sound-absorbing material known, because of its strong electron-phonon coupling. This might explain part of the reason behind melanin's presence in the inner ear.



Melanin voltage-controlled switch, an "active" organic polymer electronic device from 1974. Smithsonian Chip collection.

These early discoveries were "lost" until the recent emergence of such melanins in device applications, in particular, electroluminescent displays. In 2000, the Nobel Prize in Chemistry was awarded to three scientists for their subsequent 1977 (re)discovery and development of such conductive organic polymers. In an essential reprise of the work by Weiss *et al.*, these polymers were oxidized, iodine-doped "polyacetylene black" melanins. There is no evidence that the Nobel committee was aware of the almost identical prior report by Weiss *et al.* of passive high conductivity in iodinated polypyrrole black or of switching and high electrical conductivity in DOPA melanin and related organic semiconductors. The melanin organic electronic device is now in the Smithsonian Institution's National Museum of American History's "Smithsonian Chips" , collection of historic solid-state electronic devices.

Although *synthetic* melanin (commonly referred to as BSM, or "black synthetic matter") is made up of 3-6 oligomeric units linked together — the so-called "protomolecule" — there is no evidence that *naturally occurring* biopolymer (BCM, for "black cell matter") mimics this structure. However, since there is no reason to believe that natural melanin does not belong to the category of the polyarenes and polycationic polyenes, like pyrrol black and acetylene black, it is necessary to review all the chemical and biological analytic data gathered to date in the study of natural melanins (eumelanins, pheomelanins, allomelanins)."

Evidence exists in support of a highly cross-linked heteropolymer bound covalently to matrix scaffolding melanoproteins. It has been proposed that the ability of melanin to act as an antioxidant is directly proportional to its degree of polymerization or molecular weight. Suboptimal conditions for the effective polymerization of melanin monomers may lead to formation of lower-molecular-weight, pro-oxidant melanin that has been implicated in the causation and progression of macular degeneration and melanoma. Signaling pathways that upregulate melanization in the retinal pigment epithelium (RPE) also may be implicated in the downregulation of rod outer segment phagocytosis by the RPE. This phenomenon has been attributed in part to foveal sparing in macular degeneration. `

Source (edited): "http://en.wikipedia.org/wiki/Melanin"

Metal Rubber

Metal Rubber is a broad, informal name for several conductive plastic polymers with metal ions produced by NanoSonic, Inc, in cooperation with Virginia Tech. This self-assembling nanocomposite is ultra flexible and durable to high and low pressures, temperatures, tensions, most chemical reactions, and retains all of its physical and chemical properties upon being returned to a ground state. NanoSonic's Metal Rubber™ is a highly electrically conductive and highly flexible elastomer. It can be mechanically strained to greater than 1000 percent of its original dimensions while remaining electrically conductive. As Metal Rubber can carry data and electrical power and is environmentally rugged, it opens up a new world of applications requiring robust, flexible and stretchable electrical conductors in the aerospace/defense, electronics and bioengineering markets.

TECHNOLOGY DESCRIPTION Metal Rubber is made through a modified molecular-level self-assembly production process using precursors NanoSonic produces in-house. Materials are manufactured in a variety of sizes and geometries.The possible uses of such a product include superior body armor, durable electronic sensors, various aerospace-building materials, and alternate commercial building materials.

Source (edited): "http://en.wikipedia.org/wiki/Metal_Rubber"

Molecular electronics

For quantum mechanical study of the electron distribution in a molecule, see stereoelectronics.

Molecular electronics (sometimes called *moletronics*) involves the study and application of molecular building blocks for the fabrication of electronic components. This includes both bulk applications of conductive polymers, and single-molecule electronic components for nanotechnology.

An interdisciplinary pursuit, molecular electronics spans physics, chemistry, and materials science. The unifying feature is the use of molecular building blocks for the fabrication of electronic components. This includes both passive (e.g. resistive wires) and active components such as transistors and molecular-scale switches. Due to the prospect of size reduction in electronics offered by molecular-level control of properties, molecular electronics has aroused much excitement both in science fiction and among scientists. Molecular electronics provides means to extend Moore's Law beyond the foreseen limits of small-scale conventional silicon integrated circuits.

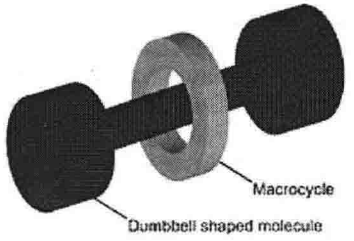
Molecular electronics is split into two related but separate subdisciplines: *molecular materials for electronics* utilizes the properties of the molecules to affect the bulk properties of a material, while *molecular scale electronics* focuses on single-molecule applications.

Molecular scale electronics, also called single molecule electronics, is a branch of nanotechnology that uses single molecules, or nanoscale collections of single molecules, as electronic components. Because single molecules constitute the smallest stable structures imaginable this miniaturization is the ultimate goal for shrinking electrical circuits.

Conventional electronics have traditionally been made from bulk materials. With the bulk approach having inherent limitations in addition to becoming increasingly demanding and expensive, the idea was born that the components could instead be built up atom for atom in a chemistry lab (bottom up) as opposed to carving them out of bulk material (top down). In single molecule electronics, the bulk material is replaced by single molecules. That is, instead of creating structures by removing or applying material after a pattern scaffold, the atoms are put together in a chemistry lab. The molecules utilized have properties that resemble traditional electronic components such as a wire, transistor or rectifier.

Single molecule electronics is an emerging field, and entire electronic circuits consisting exclusively of molecular sized compounds are still very far from being realized. However, the continuous demand for more computing power together with the inherent limitations of the present day lithographic methods make the transition seem unavoidable. Currently, the focus is on discovering molecules with interesting properties and on finding ways to obtaining reliable and reproducible contacts between the molecular components and the bulk material of the electrodes.

Molecular electronics operates in the quantum realm of distances less than 100 nanometers. The miniaturization down to single molecules brings the scale down to a regime where quantum effects are important. As opposed to the case in conventional electronic components, where electrons can be filled in or drawn out more or less like a continuous flow of charge, the transfer of a single electron alters the system significantly. The significant amount of energy due to charging has to be taken into account when making calculations about the electronic properties of the setup and is highly sensitive to distances to conducting surfaces nearby.

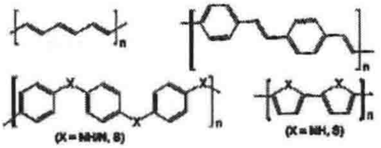


Graphical representation of a rotaxane, useful as a molecular switch.

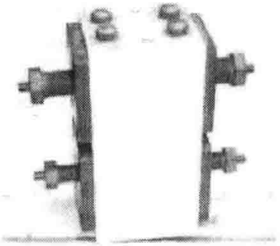
One of the biggest problems with measuring on single molecules is to establish reproducible electrical contact with only one molecule and doing so without shortcutting the electrodes. Because the current photolithographic technology is unable to produce electrode gaps small enough to contact both ends of the molecules tested (in the order of nanometers) alternative strategies are put into use. These include molecular-sized gaps called break junctions, in which a thin electrode is stretched until it breaks. Another method is to use the tip of a scanning tunneling microscope (STM) to contact molecules adhered at the other end to a metal substrate. Another popular way to anchor molecules to the electrodes is to make use of sulfur's high affinity to gold; though useful, the anchoring is non-specific and thus anchors the molecules randomly to all gold surfaces, and the contact resistance is highly dependent on the precise atomic geometry around the site of anchoring and thereby inherently compromises the reproducibility of the connection. To circumvent the latter issue, experiments has shown that fullerenes could be a good candidate for use instead of sulfur because of the large conjugated π-system that can electrically contact many more atoms at once than a single atom of sulfur.

One of the biggest hindrances for single molecule electronics to be commercially exploited is the lack of techniques to connect a molecular sized circuit to bulk electrodes in a way that gives reproducible results. Also problematic is the fact that some measurements on single molecules are carried out in cryogenic temperatures (close to absolute zero) which is very energy consuming.

Molecular materials for electronics



Chemical structures of some conductive polymers. From top left clockwise: polyacetylene; polyphenylene vinylene; polypyrrole (X = NH) and polythiophene (X = S); and polyaniline (X = NH/N) and polyphenylene sulfide (X = S).



Voltage-controlled switch, a molecular electronic device from 1974. From Smithsonian Chip collection.

Molecular materials for electronics is a term used to refer to bulk applications of conductive polymers. Conductive polymers or, more precisely, intrinsically conducting polymers (ICPs) are organic polymers that conduct electricity in their bulk state. Such compounds may have metallic conductivity or can be semiconductors. The biggest advantage of conductive polymers is their processability, mainly by dispersion. Conductive polymers are not plastics, i.e., they are not thermoformable, but they are organic polymers, like (insulating) polymers. They can offer high electrical conductivity but do not show mechanical properties as other commercially used polymers do. The electrical properties can be fine-tuned using the methods of organic synthesis and by advanced dispersion techniques.

The linear-backbone "polymer blacks" (polyacetylene, polypyrrole, and polyaniline) and their copolymers are the main class of conductive polymers. Historically, these are known as melanins. PPV and its soluble derivatives have similarly emerged as the prototypical electroluminescent semiconducting polymers. Today, poly(3-alkylthiophenes) are the archetypical materials for solar cells and transistors.

Conducting polymers have backbones of contiguous sp hybridized carbon centers. One valence electron on each center resides in a p orbital, which is orthogonal to the other three sigma-bonds. The electrons in these delocalized orbitals have high mobility when the material is "doped" by oxidation, which removes some of these delocalized electrons. Thus the conjugated p-orbitals form a one-dimensional electronic band, and the electrons within this band become mobile when it is partially emptied. Despite intensive research, the relationship between morphology, chain structure and conductivity is poorly understood yet.

Conductive polymers enjoy few large-scale applications due to their poor processability. They have been known to have promise in antistatic materials and they have been incorporated into commercial displays and batteries, but there have had limitations due to the manufacturing costs, material inconsistencies, toxicity, poor solubility in solvents, and inability to directly melt process. Nevertheless, conducting polymers are rapidly gaining attraction in new applications with increasingly processable materials with better electrical and physical properties and lower costs. With the availability of stable and reproducible dispersions, PEDOT and polyaniline have gained some large scale applications. While PEDOT (poly(3,4-ethylenedioxythiophene)) is mainly used in antistatic applications and as a transparent conductive layer in form of PEDOT:PSS dispersions (PSS=polystyrene sulfonic acid), polyaniline is widely used for printed circuit board manufacturing – in the final finish, for protecting copper from corrosion and preventing its solderability. The new nanostructured forms of conducting polymers particularly, provide fresh air to this field with their higher surface area and better dispersability.

Source (edited): "http://en.wikipedia.org/wiki/Molecular_electronics"

Negative resistance

Negative resistance is a property of some electric circuits where an increase in the current entering a port results in a decreased voltage across the same port. This is in contrast to a simple ohmic resistor, which exhibits an increase in voltage under the same conditions. Negative resistors are theoretical and do not exist as a discrete component. However, some types of diodes (e.g., tunnel diodes) can be built that exhibit negative resistance in some part of their operating range. Such a differential negative resistance is illustrated in Figure 1 with a resonant tunneling diode. Similarly, some chalcogenide glasses, organic semiconductors, and conductive polymers exhibit a similar region of negative resistance as a bulk property.