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Nobel Prize 2000: from conducting polymers to molecular electronics.

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It can be stated that conducting or more generally conjugated polymer science was born in 1977. In earlier times research efforts devoted to polyconjugated systems were extremely rare and not systematic. Neither molecular nor electronic structure of conjugated polymers in their undoped (semiconducting) state were elucidated. Moreover the chemical nature of the doping reactions which render these polymers conductive was not known similarly as the mechanism of their conductivity, despite the fact that few papers describing unusually high conductivity of some conjugated polymers were published. In 1977 Heeger, MacDiarmid and Shirakawa showed that poly(acetylene) **1**, which is the simplest polyconjugated system, can be rendered conductive by the reaction with bromine or iodine vapors. Spectroscopic studies that followed demonstrated without any ambiguity that this reaction is redox in nature and consists of the transformation of neutral polymer chains into polycarbocations with simultaneous insertion of the corresponding number of Br_3^- or I_3^- anions between the polymer chains in order to neutralize the positive charge imposed on the polymer chain in course of the doping reaction. This important discovery initiated an extensive and systematic research devoted to various aspects of the chemistry and physics of conjugated polymers both in their neutral (undoped) and charged (doped) states. According to SCIFINDER almost 40 thousands of scientific papers were published in this field of research since 1977. This previously underestimated family of macromolecular compounds turned out to be extremely interesting both from the basic research and application points of view.

Poly(acetylene) and a little later developed poly(*p*-phenylene) **2** were the 1st generation of conducting polymers. Although highly conductive (see Fig.1) and highly ordered they were insoluble and infusible and for this reason impossible to process. Moreover, in the doped state they

were unstable at ambient conditions undergoing irreversible oxidation in air with simultaneous loss of electrical conductivity.

Heterocyclic conjugated polymers such as poly(pyrrole) **3,** poly(thiophene) **4-5** and others developed in early 80 of 20th century, belonging to the 2nd generation of conducting polymers, were not processible either, although much more stable in the conducting form as compared to poly(acetylene). Polyaniline **6,** an interesting conducting polymer "rediscovered" in 1983 can also be included into this group.

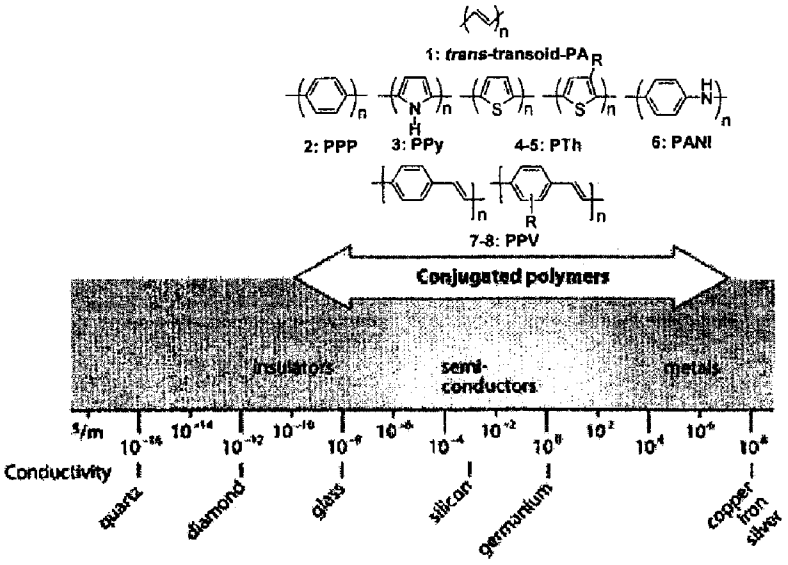
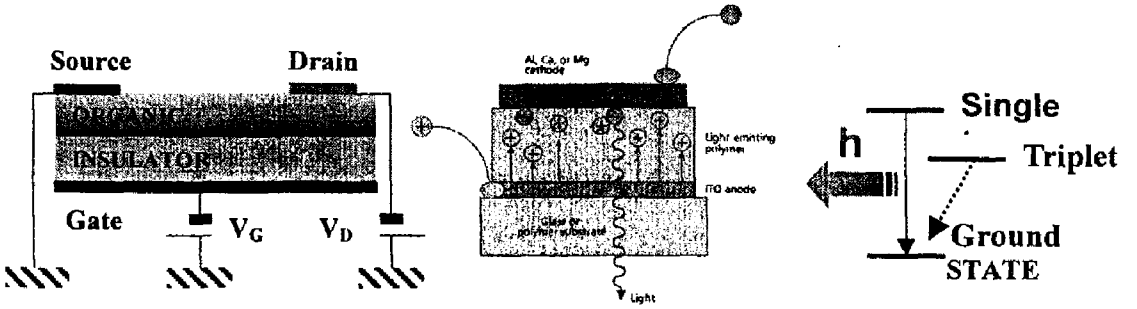


Fig.1: Representative derivatives of the intrinsically conducting polymers family and their electrical conductivity

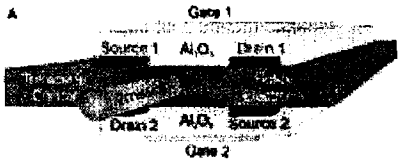
First solution processible conducting polymers (3rd generation), namely poly(3-alkylthiophenes) **5** were synthesized in 1986. Significant efforts to improve regioregularity of these polymers resulted in the synthesis of poly(3-alkylthiophenes) with the regioregularity exceeding 99%. These polymers are especially interesting because if used as a thin semiconducting layer in the field effect transistor (FET) configuration (Fig.2) they become superconducting at 2.35 K. This is the first example of the superconductivity of an organic polymer. Substitued poly(*p*-phenylene vinylene)s **7-8**, similarly as substituted poly(thiophene)s are also solution processible. The advantage of poly(thiophene) and poly(*p*-phenylene) families of conjugated polymers consists of the fact that their optical and electronic properties can be tuned in a precise manner by branching appropriate functional groups to the conjugated backbone.

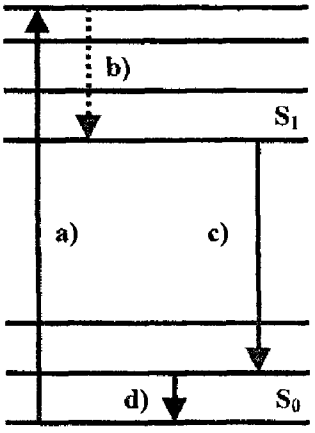
construction of polyconjugated molecules based optically-pumped or electrically-driven lasers or photovoltaic diodes.

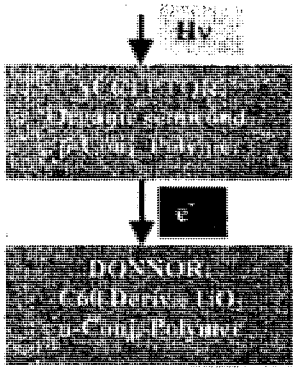


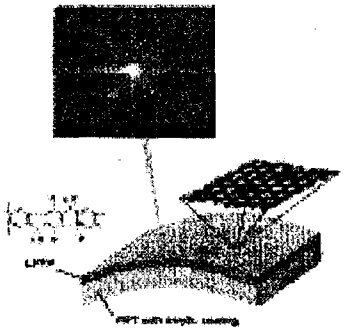
Schematic representation of a FET structure

Scheme of a single-layer LED and the electronic states describing the electroluminescence mechanism

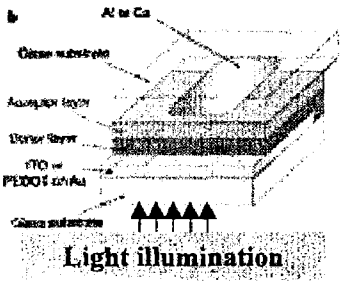








4-LEVEL LASER SCHEME
a) Photoabsorption
b) Internal conversion to the excited state
c) 0-1 laser transition
d) Ground state relaxation



bi-Layer Configuration D/A Heterojunctions

Electrically-driven and optically-pumped organic/plastic lasers and the electronic states describing the lasing

Scheme of a bi-layer photovoltaic diode and principle of D/A heterojunction

Fig 3: Organic and plastic electronic/optoelectronic devices using conjugated materials as active components: Field-Effect Transistor (FET), Light-Emitting Diode (LED), Laser, and Photovoltaic Diodes