# N-Type Organic Semiconductors

Subjects: Nanoscience & Nanotechnology | Physics, Condensed Matter
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This work was intended to enlarge the gates toward green organic technologies at room temperature, searching for new types of semiconductors with low toxicity and simple molecular organization. In our previous studies, para-aminobenzoic acid was used to construct a p-type green semiconductor. A non-toxic organic compound, acting as an electron donor, is sulpho-salicylic acid. SSA can be efficiently attached to the external shell of a ferrite ($Fe_3O_4$) nanocore, providing $Fe_3O_4$–SSA nanoparticles. This is a N-Type Organic Semiconductor - made by green technologies and used to construct a simple thin film transistor.

Keywords: Semiconductors ; Organic electronics ; Nano-core shell

## 1. Introduction

The latest advances in materials science successfully serve nanoelectronics' interests, such as flexible electronic devices with elastomeric substrates [1], field-effect transistors attached to a gold electrode sensing pad for deoxyribonucleic acid hybridization [2], carbon-related materials such as diamond [3], or nanocomposites serving as efficient hole-transporting layers for organic solar cells [4]. Some organic materials present superior performance than inorganic materials for thin-film transistors (TFTs) [5]. A convenient method for the deposition of organic materials is dip-coating [6]. Polymers such as pentacene are the most widely used organic semiconductors for p-type materials nowadays [7], as well as for n-type materials under special conditions [8]. The precursors of pentacene are polycyclic aromatic hydrocarbons (PAHs), and their toxicity comes from the ability of these PAHs to bind to deoxyribonucleic acid inside cells [9]. Therefore, the green technologies are much sought after for solar cells [10] and other electronic devices [11]. OLED for display purposes was eco-friendly defined in terms of low power consumption and long lifetime [12]. However, after carrying out a search, zero results were returned for green technologies for n-type organic transistors, except one regarding green solvents [13].

This work was intended to enlarge the gates toward green organic technologies at room temperature, searching for new types of semiconductors with low toxicity and simple molecular organization. In our previous studies, para-aminobenzoic acid was used to construct a p-type green semiconductor [14]. A non-toxic organic compound, acting as an electron donor, is sulpho-salicylic acid (SSA), the chemical structure of which is presented in Figure 1. SSA can be efficiently attached to the external shell of a ferrite ($Fe_3O_4$) nanocore, providing $Fe_3O_4$–SSA nanoparticles using self-assembling techniques [15]. Essentially, an $Fe_3O_4$ nanocore represents an intrinsic semiconductor and SSA is suitable for organic electronic devices due to its molecular conjugation [16]. The self-assembly of SSA onto the external shell of ferrite nanoparticles easily occurs during the synthesis step, yielding core–shell nanoparticles with a good dispersibility in water. To create a demonstrator, we used a low-cost technology to deposit $Fe_3O_4$–SSA onto a compatible insulator on indium tin oxide (ITO)-coated glass. Finally, we tested the n-type characteristics of the $Fe_3O_4$–SSA film using a point-contact transistor. The $Fe_3O_4$–SSA film was contacted by two probes, i.e., the source and drain, and the ITO film was contacted by a third probe, i.e., the gate. This point-contact transistor, also named pseudo-MOS (Metal Oxide Semiconductor) or Ψ-MOSFET (Metal Oxide Semiconductor Field Effect Transistor) transistor, is specifically used for the in-situ electrical characterization of the conduction in thin semiconductors on insulators [17][18], including organic biomaterials [19][20].

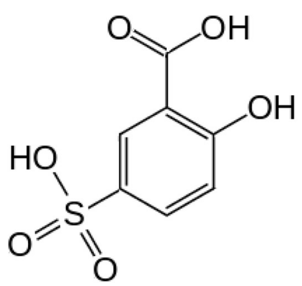


**Figure 1.** The chemical structure of sulpho-salicylic acid (SSA).

## 2. The n-Type Characteristics and the Low Toxicity of the $Fe_3O_4$–SSA Film

In this section, the n-type characteristics of the $Fe_3O_4$–SSA compound were discussed as the electron donor.

Some specific conduction mechanisms through the SSA molecules from the external shells may arise. For this purpose, an SSA molecule was simulated by HyperChem molecular modeling software, indicating the following electric charge distribution (Figure 2).

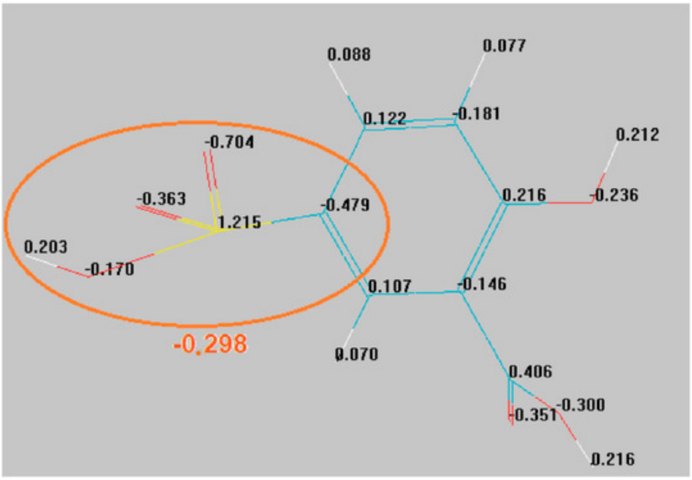


**Figure 2.** The simulation results of the electrical charge distribution inside the SSA molecule.

Inside the SSA molecule, the local electronic charge density, expressed by a normalized value at the elementary charge, was computed for each atom. The neutrality condition was fulfilled, because the global electrical charge of the SSA molecule was +2.932–2.93 ≅ 0. However, the sulphonate group, $SO_3H$, possessed a net negative electronic charge density of −0.298 (Figure 2). This augments the argument to consider the SSA molecule an electron donor, subsequently offering the n-type behavior of the $Fe_3O_4$–SSA film. On the other hand, the $Fe_3O_4$ film or magnetite was indexed as a semiconductor with a Fermi energy of 3.64 eV and band gap energy of 2.2 eV [21]. Hence, the $Fe_3O_4$ core–shell substrate plays a significant role as a matrix for an intrinsic semiconductor.

The second discussion concerns the low toxicity of the $Fe_3O_4$–SSA compound and its precursors during the technological flow. Ferrite has a low toxicity and by degradation, it can generate $Fe^+$, $O^-$ ions, usually encountered in the human body and the environment.

A quantitative parameter for the evaluation of toxicity is the lethal dose, defined as a given quantity for the studied toxic substance that is administered per kilogram of the body weight of rats, at which a given percentage of the treated test animals die. The median lethal dose, denoted $LD_{50}$, corresponds to a mortality of 50% from the tested animals after inoculation with the substance [22]. Previously, various studies were performed to evaluate the toxicity of SSA [23]. For rats, the $LD_{50}$ for SSA was established at 700 mg/kg [22]. This value indicates much lower toxicity of SSA than that of PAHs, such benzo[k]fluoranthene ($LD_{50}$ = 14 µg/kg) or other PAHs with an $LD_{50}$ below 90 µg/kg [24]. Even in recent studies, a high cytotoxicity of polyphenolic compounds has been revealed [25], while polyphenols are specifically used for organic semiconductors applied in flexible electronics [26]. On the other hand, the precursor of SSA is salicylic acid—a veritable green compound that acts as a plant hormone or vascular drug [27].

## 3. Conclusions

We demonstrated that an organic transistor with an $Fe_3O_4$–SSA film is operational. Obviously, many functional parameters have to be further optimized in the coming years to surpass the performance of the current OTFTs.

Herein, we investigated $Fe_3O_4$–SSA material as a candidate for green organic transistors. For this purpose, the synthesis of the $Fe_3O_4$–SSA material was based on co-precipitation. The FT-IR spectra confirmed the existence of SSA, while the TEM imaging captured the $Fe_3O_4$–SSA aggregates. The $Fe_3O_4$–SSA nanoparticles had good dispersion stability according to a zeta potential of +45.3 mV.

The point-contact OTFT transistor with an $Fe_3O_4$–SSA film presented an increasing drain current as the positive gate voltage increased, demonstrating the n-type character of the film. This was the main experimental argument for inducing an electron accumulation channel with a positive gate voltage. Compared to other OTFTs, our $Fe_3O_4$–SSA transistor presented a threshold voltage of approximately 5 V and an $I_{ON}/I_{OFF}$ ratio of 500, close to the parameters of a classical pentacene OTFT.

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