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Research Summary

Within the six-month exchange grant, two areas of research were actively pursued: Electron Spin resonance (ESR) of organic semiconducting materials and fabrication and testing of organic field-effect transistors (OFETs) based on natural and biocompatible materials. Experiments using electron spin resonance were successfully applied to show the mechanisms responsible for electrical contact modification when lithium fluoride is deposited along with aluminium onto fullerene C_{60}, and some preliminary studies have been applied to understand the formation of non-geminate charge carriers in donor:acceptor organic films. Work with purification and processing of natural semiconductors, dielectrics, and substrate materials proved fruitful in providing devices performing at the state-of-the-art level made from biocompatible materials. Impressive results were achieved with the natural dye indigo, which demonstrates ambipolar transport with mobilities in the $10^{-3} – 10^{-2}$ cm^2/V·s range. Indigo transistors were successfully processed onto substrates made from shellac, a natural resin. Both these research directions, explored in the past six months, have provided a successful start for continuing research projects.

Electron Spin Resonance (ESR) Studies

Interfaces of metal contacts and organic semiconductors play a crucial role in the physics of organic electronic devices. Fabricating efficient electroluminescent and photovoltaic devices relies on matching the anode and cathode work functions to optimize both hole and electron injection and extraction. Metals routinely used as cathode materials in organic electronic devices have high work functions relative to most semiconducting organic materials, resulting in a Schottky contact with significant barrier to electron injection. For this reason, research efforts in many organic devices focus on effectively limiting contact resistance. Improved electron injection can be achieved by employing a commonly used technique of depositing a thin (0.5- to 2-nm) layer of LiF onto the semiconducting thin film prior to depositing aluminum as the cathode metal.[1] Ohmic contact behavior has been reported in the case of C_{60} with LiF|Al.[2] Several mechanisms that explain improved injection have been proposed: efficient electron tunneling through insulating LiF,[3] a chemical reaction to cause n-doping of the semiconductor,[4,5] dipole alignment at the cathode–semiconductor interface,[6] and shielding of the organic layer from detrimental reactions with the cathode metal,[3] among others. Here we present evidence showing that in the case of C_{60}|LiF|Al, LiF dissociates upon deposition of Al, releasing lithium and consequently forming a $C_{60}^-Li^+$ charge-transfer complex. This species acts as a donor-type dopant and accounts for the improvement of electron injection by creating a substantial concentration of donor states near the interface, thereby lowering the barrier width for injection. Electron spin resonance (ESR) proved to clarify the mechanism of dissociation of LiF.

Several paramagnetic species that occur in organic electronic devices can be detected by using ESR, including charge carriers in the form of hopping radical anions and cations, triplet excitons, and permanently charged paramagnetic impurities.[7] Knowing that many paramagnetic species related to fullerenes have been reported, we evaluated C_{60} films with Al and Al/LiF to test if doping reactions were occurring. Films of neat C_{60}, C_{60} with Al or LiF/Al deposited on top, as well as the opposite deposition order of C_{60} onto the cathode materials, were investigated. In total, two types of paramagnetic species were observed. In neat films of C_{60}, or when Al is deposited onto C_{60}, an ESR signal at $g = 2.001$ is observed. The same 2.001 signal is observed in samples of C_{60} deposited onto Al and LiF/Al. Annealing at 120°C in either case causes an increase in the population of the 2.001 signal by about 25%. Annealing at higher temperatures up to 280°C does not appreciably affect this concentration. Figure 1 shows the ESR signals obtained for samples with both deposition orders. Assuming that this paramagnetic species resides in the C_{60} layer, the $g = 2.001$ spin population corresponded to 0.005 to 0.01 mol% of the total C_{60} film in both cases. This radical signal has been reported in powder fullerene samples under vacuum and was found to increase reversibly with the presence of oxygen.[8] A g-value of 2.001 is characteristic of a weakly bound carbon-centered radical and is too low for an oxygen-centered radical,[9] suggesting a fullerene–oxygen adduct with a fullerene cage-centered radical. Deposition of LiF followed by Al onto C_{60} films, however, resulted in the appearance of an ESR signal with $g = 1.998$ corresponding to the C_{60} radical anion with a concentration of 1 to 2×10^{19} cm^{-3} (1 mol% doping). This g-value is in excellent agreement with prior ESR studies of photoexcited fullerene films.[10] The data strongly suggest that deposition of LiF onto C_{60} followed by Al results in the dissociation of lithium that generates a $C_{60}^-Li^+$ charge-transfer complex. Annealing does not change the amount of signal, showing that the LiF dissociation reaction is complete upon deposition. This observation, combined with the fact that annealing up to 280°C of Al|LiF|C_{60} films never generates any $g = 1.998$ signal, shows that the thermal deposition process is integral for LiF to dissociate and $C_{60}^-Li^+$ to form. Only about 0.5% of the LiF dissociates, indicating that most of the deposited LiF remains intact. Over a dozen measured sample sets, standard deviation in the population of the g=2.001 species was small, $\pm 2.3 \times 10^{17}$ cm^{-3} for samples with C_{60} as the upper (exposed) layer, and $\pm 2.0 \times 10^{16}$ cm^{-3} for samples with C_{60} covered with Al. Standard deviation for the population of the fulleride anion (g = 1.998) was higher, $\pm 1.9 \times 10^{19}$ cm^{-3}.
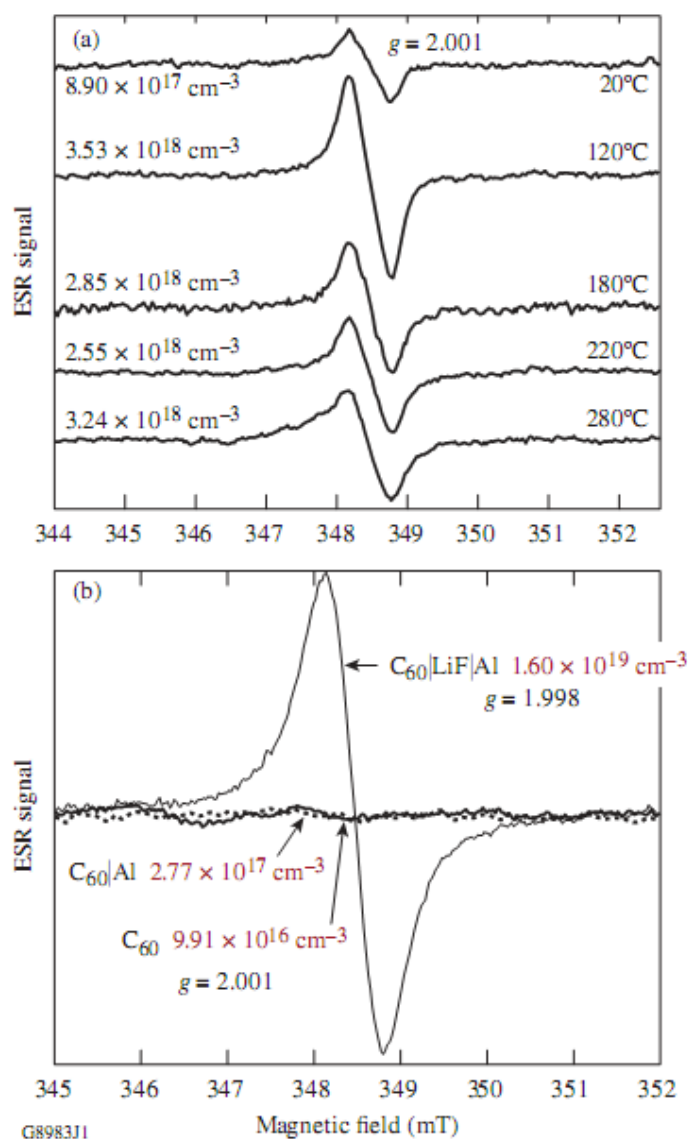
Figure 1. (a) Electron spin resonance (ESR) of Al|LiF|C_{60} (inverted deposition sequence) samples annealed at different temperatures. Only a signal for $g = 2.001$ is detected. (b) ESR signal of 35-nm C_{60} neat film, and with Al and LiF/Al cathodes deposited on top. Films with LiF demonstrate a strong signal with a g-value of 1.998, corresponding to C_{60}^- radical anion, while the remaining samples show a $g = 2.001$ signal.

Besides evaluating doping, light-induced electron spin resonance (L-ESR) experiments were conducted. Through L-ESR, generation of positive and negative polarons, in the form of non-geminate carriers, can be observed at low temperatures. As a model system 3-hexyl thiophene (P3HT) and the acceptor material [6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM) were chosen. As an example, we can take the model system P3HT/PCBM. A heterojunction film (co-cast) in the dark shows no ESR signal at any temperature between room temperature and 4K, however irradiation at temperatures below 77K produces a light-induced ESR signal corresponding to the paramagnetic positive polaron on the P3HT and the characteristically-narrow negative anion of the fullerene [11]. As temperature is lowered to 4K, illumination must be more intense to generate the same signal. Further, the lower the temperature, the longer the signal persists after the irradiation has been switched off. The latter is due to the fact that at very low temperatures the transport required for anions and cations to recombine is inhibited (according to previous studies in amorphous systems, at very low temperatures recombination is dominated by a tunneling process, which is slow) [12]. However, the observation that generation of an ESR signal requires more irradiation at lower temperatures could contain a great deal of information about the nature of charge separation on the D-A scale and the subsequent separation of carriers that

produce a persistent ESR signal. The distinction between these two regimes has been called geminate ('*just-born*') and non-geminate 'carriers'. In principle, geminate carriers will recombine rapidly, while non-geminate carriers are the only ones that, in a solar cell, can contribute to a photocurrent [13]. In typical ESR, due to the limits imposed by the modulation frequency and the magnetic sweep speed, only species with lifetimes in the seconds regime will show up in a 'swept out' first-derivative signal. Thus, in this heterojunction system, presumably only non-geminate carriers contribute to an ESR signal. By measuring at different temperatures activation energies for the generation of non-geminate charge carriers can be determined. Our current experiments are focused on studying thin planar structures, in order to elucidate the factors responsible for effective transition from the geminate to non-geminate regime. Understanding these factors is integral for designing effective heterojunctions for photovoltaic devices. As part of this ESF-funded project, an effective L-ESR platform for measurements from room temperature down to 4K has been set up.
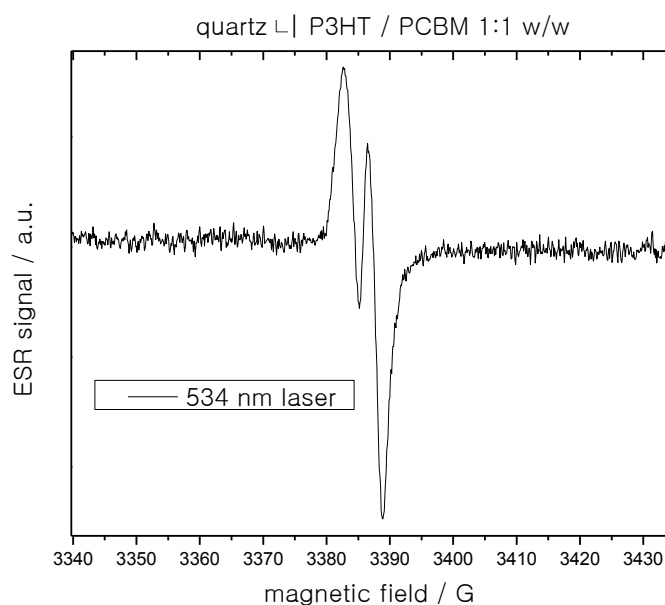

Figure 2. L-ESR of a P3HT/PCBM blend at 4K after 60 s of irradiation.

**Organic Field Effect Transistors (OFETs) based on biocompatible materials**

Though research in organic electronics based on OFETs continues to flourish, especially in the field of developing novel materials, the factor of environmental sustainability of the materials and processes employed is often not considered. Further, surprisingly few investigations have been done on materials from or inspired by nature. Nature offers a diversity of materials, for example organics with electrical properties ranging from insulators to semiconductors. Natural insulators and semiconductors can be used for novel optical and electrical applications to develop electronic items that are biocompatible, bioresorbable, biodegradable or bio-metabolisable. In our recent work, we have shown the promise of several natural materials in OFET devices – in particular the dye indigo and the natural resin Shellac.

Figure 3 shows the structure of indigo and the transfer characteristics of an OFET device with indigo as the semiconducting material and shellac resin as the substrate material. The gate dielectric is a layer of aluminum oxide (AlO_x) passivated with a thin layer of tetratetracontane ($C_{44}H_{90}$). Indigo, despite its relatively small π-conjugated network, shows substantial absorption in the red part of the visible spectrum as well as good charge transport properties. Indigo demonstrates ambipolar transport with electron and hole mobilities in the $10^{-3} - 10^{-2}$ cm^2/V·s range. The ambipolar OFET behaviour of indigo places it among the best and most promising ambipolar organic semiconductors used today. From solution electrochemistry (cyclic voltammetry), it is apparent that thin films of indigo deposited on ITO can readily be reduced and oxidized reversibly (figure 4, left). Thin films of indigo display a large bathochromic shift in UV-Vis absorption of about 100 nm relative to [14] dilute indigo (figure 5). This clearly shows that aggregation between indigo molecules in the solid state is strong. Most likely it is the strength of these interactions that results in the

good charge transport properties. The substrate material used is shellac, a natural resin produced by the lac beetle and utilized for centuries as a natural thermoplastic [15]. Shellac was also shown to be a very effective dielectric material, with stabile relative permittivity (≈ 3.9) over a frequency range for 1×10^{-3} Hz to 1×10^{4} Hz (figure 4). Current work is in progress to explore indigo in photovoltaic devices, as well as for using shellac in other OFET architectures, as well as an encapsulation material.
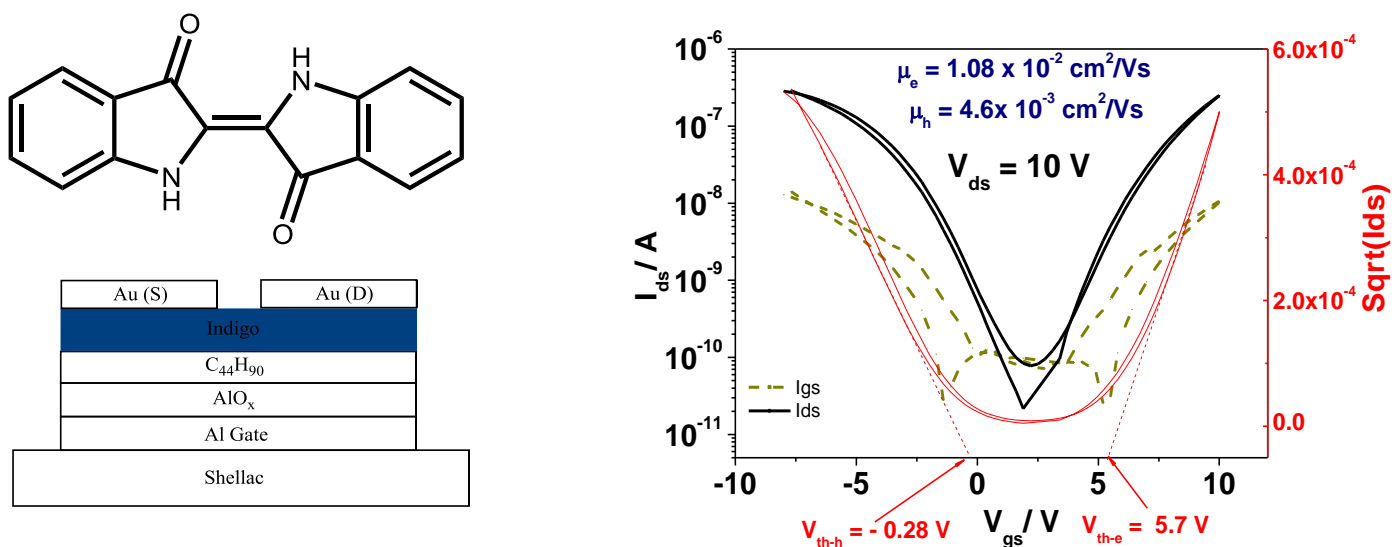
Figure 3. (Left) Structure of the indigo molecule and indigo-based transistor (Right) Transfer characteristics of OFET device fabricated on a shellac substrate with indigo as semiconductor, AlO_x passivated with 5 nm of tetratetracontane.
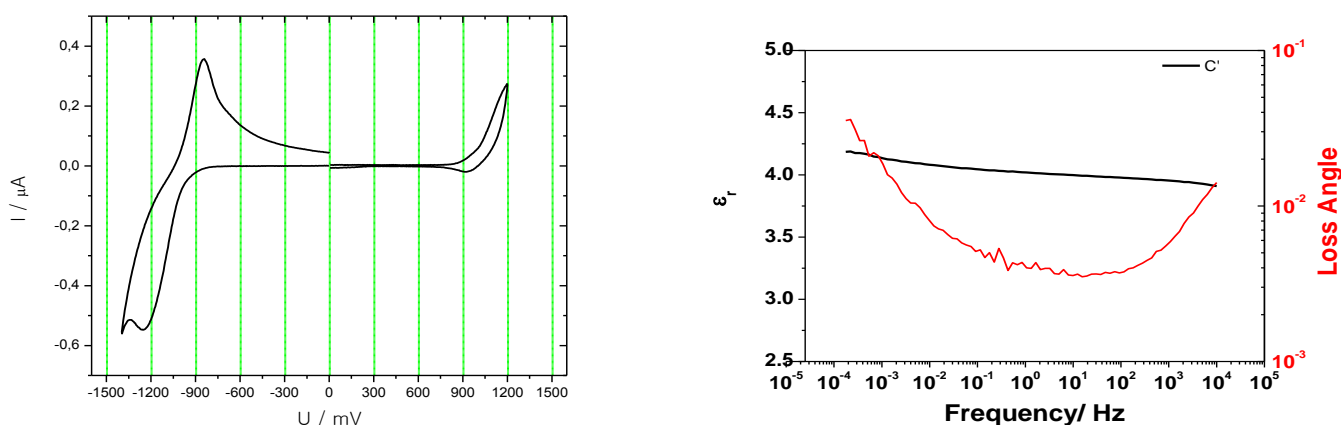
Figure 4. (left) Cyclic voltammogram of indigo film on ITO working electrode, 50 mV/s scan rate, 0,1 tetrabutylammonium phosphorus hexafluoride in acetonitrile supporting electrolyte. (right) Frequency-dependent relative permittivity measured using small-signal technique. A breakdown field of 5 MV/cm was found for shellac.
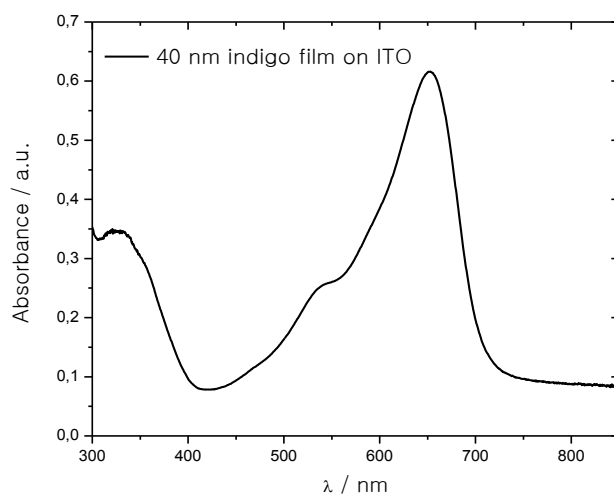
Figure 5. UV-Visible spectrum of a 40 nm thin film of indigo on ITO.

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Publications and Conference Presentations

Two manuscripts are currently in preparation on the subject of natural semiconductors and dielectric materials. A third manuscript concerning ESR doping-studies has been submitted to *Applied Physics Letters*. The support of this ESF exchange grant is credited in each.

ESF support is also credited in the following Presentations and Conference Proceedings:

- SPIE Photonics West 2011

C_{60}/LiF/Al cathodes studied by electron spin resonance, infrared reflection-absorption, and impedance spectroscopy **Eric D. Glowacki** (Johannes Kepler Univ. Linz), et al. (Proc. SPIE 7935-17)

- Two Presentations at the MRS 2011 Spring Meeting

Nonvolatile Organic Field-effect Transistor Memory Elements and Circuits from Biodegradable and Biocompatible Materials Mihai Irimia-Vladu[1,3], Pavel A. Troshin[2], **Eric D. Glowacki[3]**, Yasin Kanbur[4], Melanie Reisinger[1], Guenther Schwabegger[5], Alexander Mumyatov[2], Reinhard Schwoediauer[1], Vladimir Razumov[2], Helmut Sitter[5], Siegfried Bauer[1] and Niyazi S. Sariciftci[3]; [1]Soft Matter Physics, Johannes Kepler University, Linz, Austria; [2]Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Russian Federation; [3]Linz Institute for Organic Solar Cells, Johannes Kepler University, Linz, Austria; [4]Polymer Science and Technology, Middle East Technical University, Ankara, Turkey; [5]Institute of Semiconductor and Solid State Physics, Johannes Kepler University, Linz, Austria.

Natural Products and Biodegradable Dyes as Semiconducting Materials - Fully Sustainable and Biodegradable Organic Photovoltaic Devices. **Eric D. Glowacki**[1], Mihai Irimia-Vladu[2,1], Siegfried Bauer[2] and Niyazi Serdar Sariciftci[1]; [1]Linz Institute for Organic Solar Cells, Johannes Kepler University, Linz, Austria; [2]Soft Matter Physics, Johannes Kepler University, Linz, Austria.