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Dr. Cigdem YUMUSAK

Yildiz Technical University
Faculty of Arts and Science
Physics Department
Istanbul, Turkey

Host: Prof. Dr. Niyazi Serdar SARICIFTCI

Johannes Kepler University
Linz Institute for Organic Solar Cells
Linz, Austria

Contents

Objective

In the context of organic based electronics the development of efficient and stable organic solar cells constitutes the next major leap in the development of said electronics. Indeed the complexity of the physics operating in these devices offers a major driving force for new developments. Mastering the physics and the device structure leading to it, will lead to major spin-offs in the development of the other device types. Originally, most of the attempts to realize organic solar cell devices were based on essentially the same concepts as thin-film pndevices. This resulted in energy conversion efficiencies of about 1% with the main limitation being the short exciton diffusion length and the insufficient exciton dissociation. The breakthrough for solar cells incorporating an organic part came with the advent of concepts, which were radically deviating, from the planar heterojunction solar cells. The generic idea behind these concepts is the existence of a bulk-distributed interface to capture the excited carrier and to increase the exciton dissociation rate. The *Graetzel cell* or *dye-sensitized cell* is a prominent example of this generic idea belonging to the class of hybrid cells. Within the pores of a porous TiO2-layer a monolayer of an organic sensitizer is adsorbed on the pore walls. After absorption of a photon, the excited electron within the sensitizer molecule is immediately transferred to the conduction band of TiO2, after which the electron diffuses through the porous network to the contact. The oxidized sensitizer molecule is reduced to the original state by supply of electrons through a liquid electrolyte within the pores. Cells based on this concept show confirmed energy conversion efficiencies up to 11% on small-area cells, whereas up-scaled modules exhibit efficiencies between 5 and 7%. Standing issues within this type of solar cells are the replacement of the sensitizer by a material with increased absorption in the red and infrared part of the spectrum, the replacement of the liquid electrolyte by a solid-state hole conductor and the improvement of the cell stability. Due to the mentioned issues, the Graetzel-cell concept is increasingly moving towards the development of solid state dye-sensitized solar cell employing organic hole conductors and the replacement of the sensitizer dye with quantum dot light absorbers.

The full-organic counterpart of the Graetzel-cell is the bulk donor-acceptor heterojunction concept that is based on blends of two organic compounds one with donor-character, the other with acceptor properties. The excitons dissociate very efficiently at the interfaces between donor and acceptor phases and flow through the percolated donor and

acceptor sub-networks to the contacts, which are carrier selective. A soluble C60 derivative, PCBM, is often used as acceptor component because exciton dissociation turns out to be extremely efficient with transfer times in the range of 100 fs. However, at the moment there is a clear call for alternatives that allow the replacement of PCBM by a polymer with acceptor characteristics. Some preliminary results in this direction start to appear (e.g. CN-PPV/MEH-PPV). For sure the progress made over the last years in organic photovoltaics is impressive, from an efficiency of only 0.04% around 1995, going to 1%, next to 2.5% in 2000, 2.9% in 2001 using MDMO-PPV and recently efficiencies of over 3% have been demonstrated in 2003 using poly(3-hexyl thiophene). Very promising is that these results are merely a consequence of optimization of the morphology of the bulk heterojunction. Furthermore such promising results were obtained mostly for materials that only absorb light in the blue light and UVrange of the solar spectrum. Work has been undertaken by many groups meanwhile to use socalled low band gap conjugated polymers with a stronger absorption in the main emission spectrum of the sun. Besides this issue of extension of the active layer absorbance towards the red and infrared range, other standing issues are the use of materials with higher mobilities and again the critical issue of stability of the morphology so obtained. In the frame of improving the red- and infrared sensitivity of the donors, the majority of the activities are directed towards thiophene derivatives, which could also improve stability. Improved ordering and enhanced mobilities within the acceptor part are also expected from the inclusion of nanotubes. However, it is to be expected that for large surface applications an absolute need for an alternative, acceptor material available on large-scale can be identified. Also controlling morphology in a rational manner by using principles of self-assembly and supra-molecular organization shows important potential.

Recent work shows that new developments are sought in the consideration of a broader scope of materials used as components in the composite layer, ranging from organic molecules to inorganic nano-structured compounds. This evolution is driven for example by the possibility of combining the low-cost thin-film fabrication of the polymers with the good electrical and optical properties of the inorganic semiconductors. The high surface tension at such inorganic nano-particles, compared to the nonpolar nature of the conjugated polymers used, brings new challenges to real control on morphology. It can be envisaged that use of amphiphilic or polar conjugated polymers is needed to reconcile the polarity differences between these two classes of materials. This would possibly lead to the use of environmentally more friendly solvents.

During the visit, we worked to gain a better comprehensive understanding of the electrooptical mechanisms occurring in the photoactive films, a significant improvement of the photovoltaic efficiency through the synthesis of new materials and the assembly of new materials systems.

Additionally, we have fabricated organic field-effect transistors with DNA gate. In organic field effect transistors (OFETs) the gate dielectric plays a crucial role - these highly insulating thin film polymer layers are key-components in state of the art organic transistor devices. When replacing the polymer layer by introducing solution-processed thin film modified biopolymer Desoxyribonucleic Acid (DNA) as gate insulator, transistor-characteristics are changed towards remanence-like hystheresis behaviours. The hysteresis-loops probed in bio-organic field effect transistors (BiOFETs) derived from DNA and fullerene derivatives form bistable states which can be used for memory devices at low operating voltage regime compared to similar organic thin film transistors using polymers as gate insulator.

Part I

1.1 Background

A property of a "free" electron gas is its capacity of collective plasma oscillations. These oscillations can occur in the bulk of the material or at the interface between a metal and a dielectric medium. The latter oscillations are therefore called surface plasmons (SP). The physical properties of these plasmons are reviewed in monographs [2,3].

The effect of excited surface plasmons in a *inorganic* semiconductor/metal-Schottky junction has been examined in detail [4-8]. Using the method of attenuated total reflection (ATR) a SP was excited at the metal/air interface. This excited Plasmon leads to an increased amount of photoexcited electrons in the metal which are capable to surmount the Schottky barrier and therefore increase the short circuit photocurrent.

The effect of SPs on the short circuit photocurrent (I_{SC}) of a Schottky-type *organic* solar cell based on copper phthalocyanine (CuPc) with the cell structure (glass/Al/CuPc/Ag) has also been investigated by several authors [9-13]. An excited surface plasmon in the aluminum interface to CuPc or in the silver interface to air increases (I_{SC}). This enhancement was explained with increased absorption of photons in the organic dye layer due to the high electric field strength in the vicinity of the excited SP.

The large enhancement of the electric field related to the oscillating electron plasma can also be used to increase the Raman scattering signal from molecules adsorbed on a metal surface. This surface enhanced Raman scattering (SERS) has also been used to study the Raman spectra of organic dyes [14-16].

In small metal clusters localized plasmon excitations can occur by direct light absorption due to the much simpler selection rules. Here no *k*-selection rule exists. In the system (ITO/metal-clusters/CuPc/In) it has been shown that the incorporation of copper or gold clusters between the ITO and CuPc increases the photocurrent originating from the Schottky-contact at the

CuPc/In-contact by a factor of more than two [1]. This effect was explained by an increased photovoltaic conversion efficiency due to resonant light absorption in the metal clusters.

While the performance of organic photovoltaics has been improving steadily, this technology still faces fundamental limitations in efficiency and stability that need to be overcome for it to be competitive with other solar cells. Innovative cell designs, such as stacked organic/inorganic heterojunctions with embedded nanostructured metal features, may enhance their overall performance. A stack design can increase light absorption efficiency through complementary absorption of separate portions of the solar spectrum by different layers with specifically designed bandgaps. This minimizes thermal losses and increases the overall photon conversion efficiency.
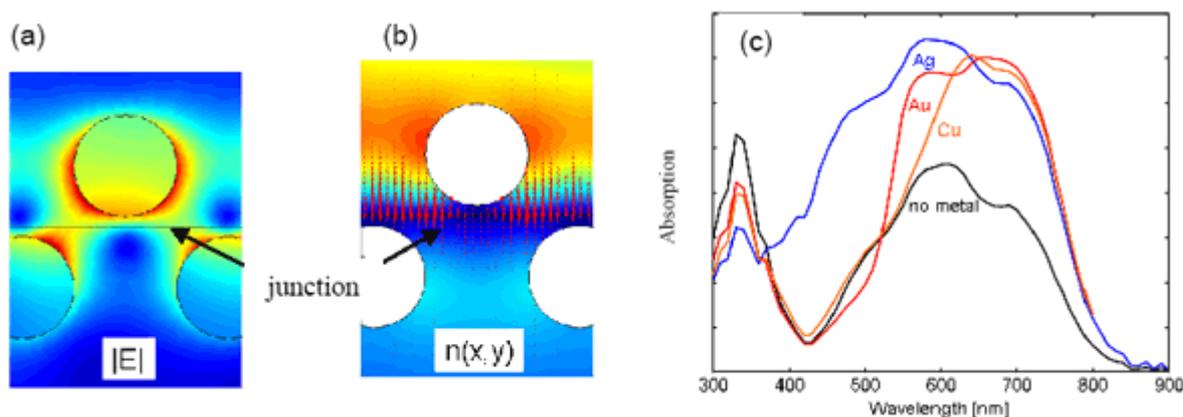
Figure 1 Simulation of a metal nanostructure enhanced organic solar cell. Interaction of an incident electromagnetic wave with metal nanoparticles at the junction between donor (top) and acceptor (bottom) materials leads to resonant effects resulting in an enhanced optical electric field between the particles (Figure 1a). This leads to an increased exciton density at the donor-acceptor junction shown by the red areas in Figure 1b. The absorption enhancement effect for the addition of different metal particles is shown in Figure 1c.

Nanoscale metal structures embedded in organic devices could also potentially be beneficial in improving the light absorption, as well as the charge separation and charge collection processes. When placed at the donor-acceptor interface of an organic heterojunction, electrically isolated metal nanoparticles may enhance photon absorption by concentrating the electromagnetic energy of incident radiation close to the junction (see Figure 1) and may also assist the exciton energy migration process, leading to

enhanced charge separation. Tuning of the spectral properties of the cells may also be achieved through the appropriate choice of metal type and nanostructure shape, size and organization.

In series-connected stacks, the absorption of light by single cells must be carefully designed for photocurrent matching. This constraint makes them intolerant to variations in the illumination spectrum. However, efficient lateral current extraction could be achieved by using high sheet-conductivity nanopatterned metal films that can theoretically transmit 80% of the incident radiation. The upper limit for the transmissivity of these metal junctions is unclear and will be studied in this project. These features would drop the requirement of current matching for multijunction stacks and reduce losses in large-area organic photovoltaics. Various pattern geometries will be explored, such as arrays of nanoscale holes or slits to achieve high radiation transmission through the excitation of sub-wavelength plasmon modes. Geometrical parameters such as the size, spacing, and in-plane symmetry of the nanoscale features will be tuned for optimal light transmission and spectral selectivity.

1.2 Experimental Results

In this part, relationships between molecular thin film structure and multiple surface plasmon (SP) excitations at nano-interfaces have been investigated for prism/metal thin film/molecular thin films in the attenuated total reflection Kretschmann configuration. Recently, emission light through the prism that strongly depended upon the emission angles was observed using the reverse irradiation, that is, direct irradiation of a laser beam from air to molecular thin films. Emission light in the reverse irradiation has investigated in detail for organic thin films with various structures. From the dispersion property of the emission spectra at various emission angles, it was estimated that the emission light was caused by excitation of multiple SPs at the nano-interfaces. The emission properties also depended upon the amount of dye molecules, nano-spacing between the metal and dyes, and polarizations of the laser beam. It is thought that the phenomenon is useful for application to new devices utilizing multiple SP excitations.
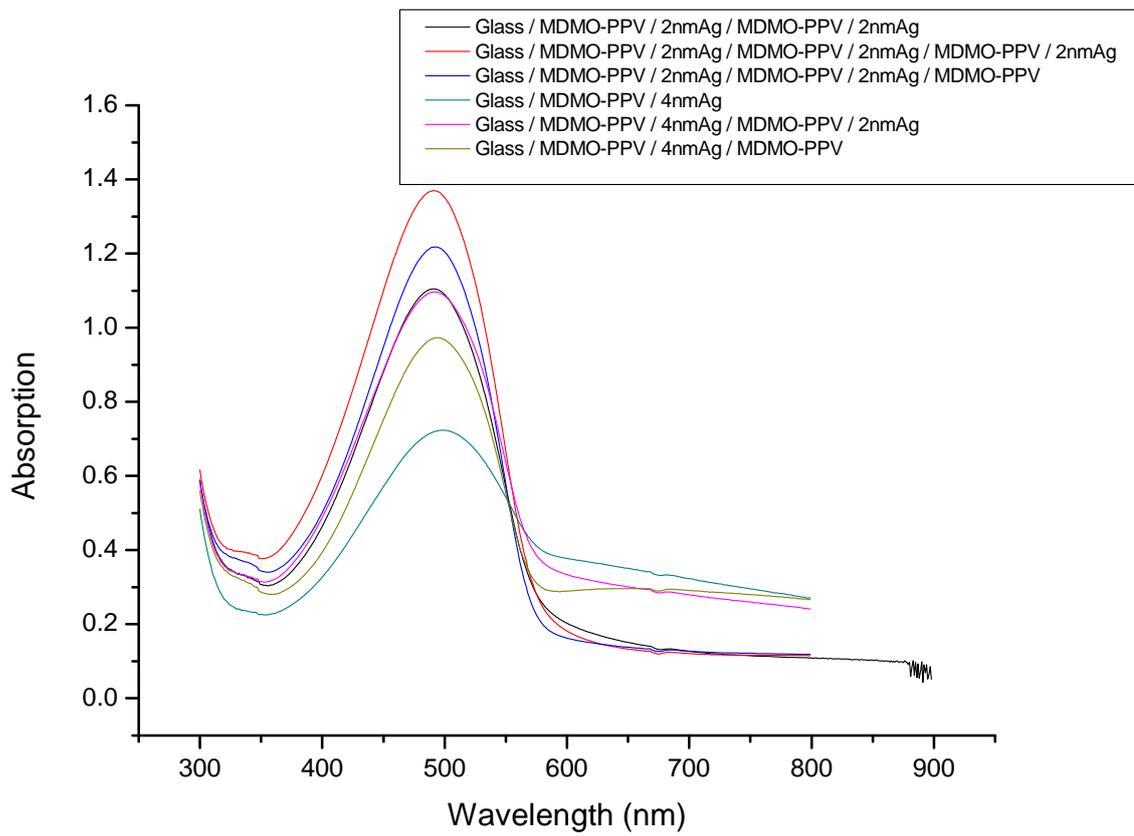
Figure 2 Absorption spectrum of MDMO-PPV / Ag thin films
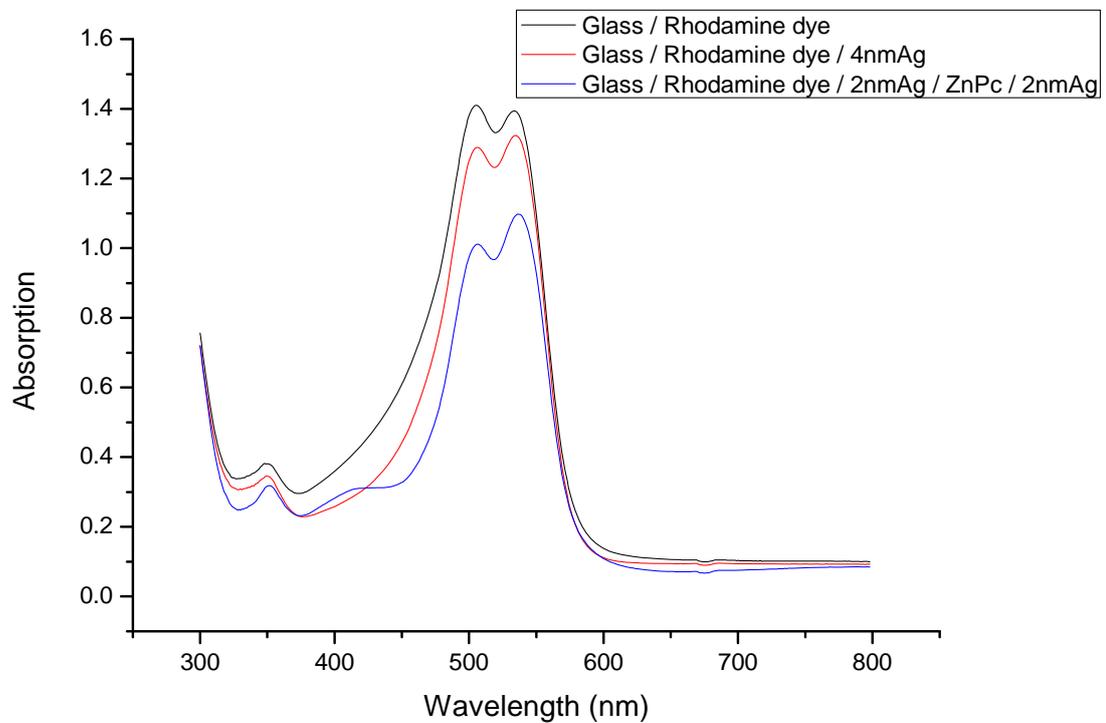
Figure 3 Absorption spectrum of Rhodamine dye / Ag thin films
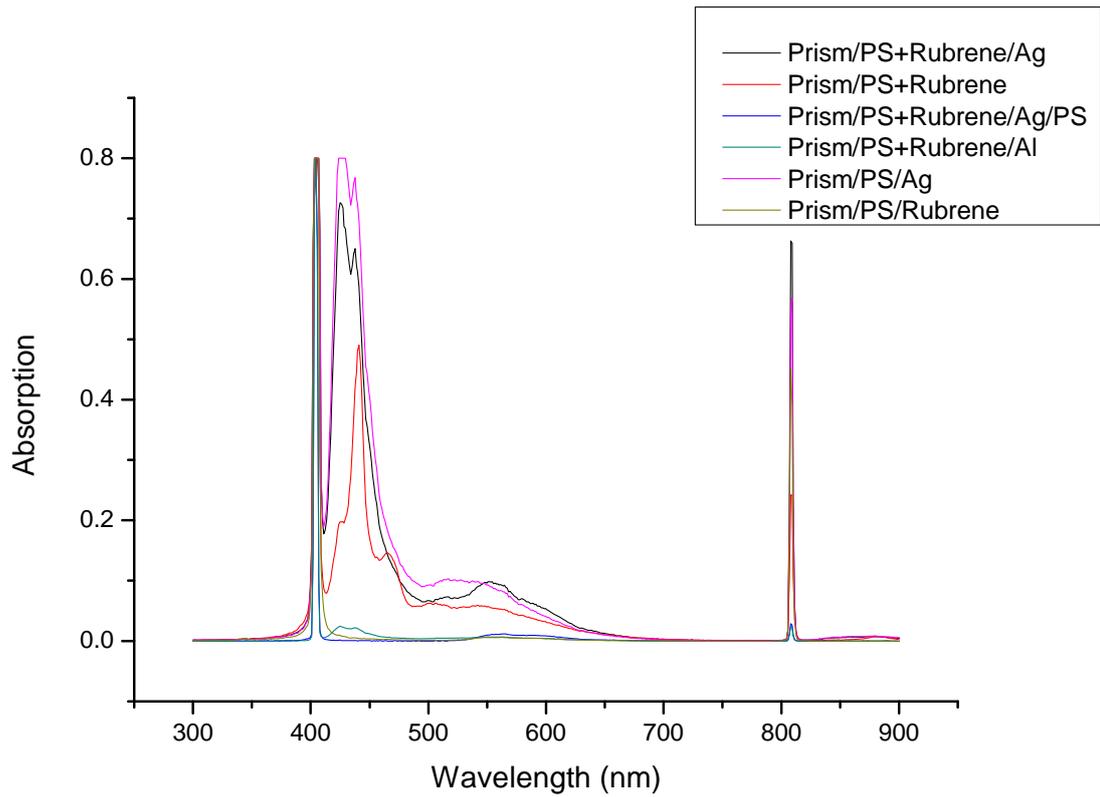
Figure 4 Absorption spectrum of Rubrene / thin metallic films
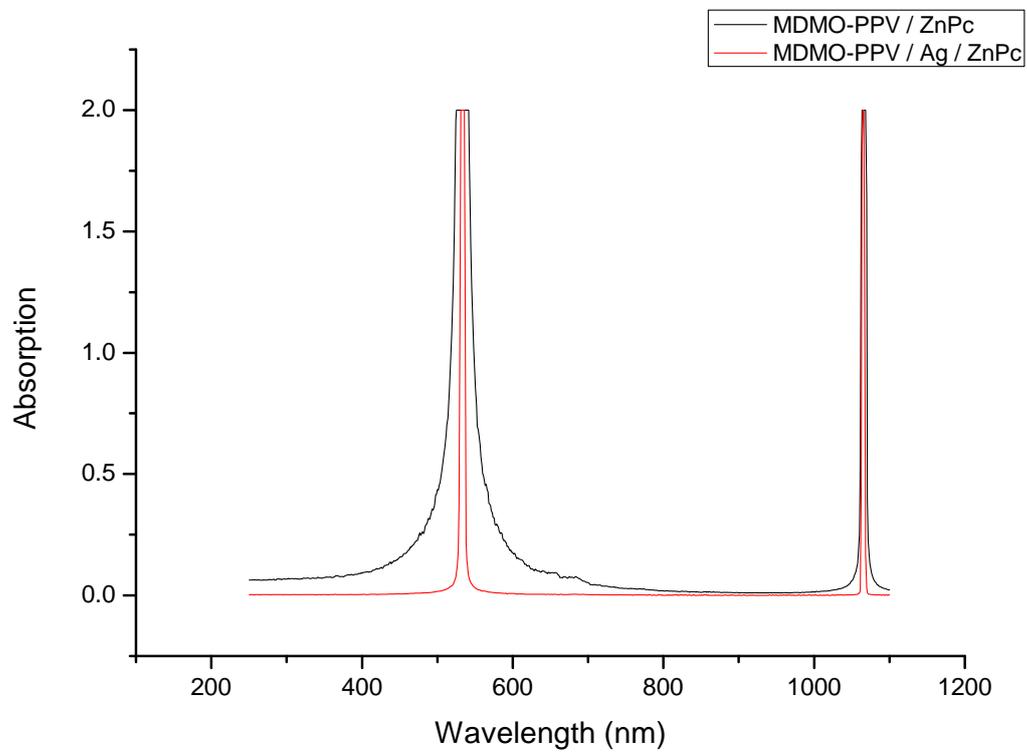
Figure 5 Absorption spectrum of MDMO-PPV with ZnPc

1.3 Conclusion

These results have been preparing and will be published soon. Also it will be presented in an international conference.

Future collaboration aims at realizing a high efficiency organic photovoltaic cell using metal nanoscale features in a multijunction device. In particular, transparent high-sheet-conductivity nanopatterned metal films will be developed to be used as conductors allowing parallel subcell connection, and metal nanostructures will be embedded in the active layers to enhance the photon absorption and charge separation efficiency.

Part II

2.1 Background

DNA – CTMA as Dielectric Insulator

DNA derived form marine waste products and modified with surfactant demonstrates excellent passive and active optical properties [17]. The suitability in electro-optic waveguide devices has been proofed – optical memory and optical amplifier applications make DNA-CTMA also interesting for electronic usage as insulating layers [18]. The film quality in terms of smothness and ability of self-assembling is a basic requirement in optical research too and the reproducable scientific work on DNA based films is the fundament of the idea using it for electronic insulator applications.

Origin of DNA – CTMA Complex

Based on the work of L. Wang et al. [19] it has been demonstrated that DNA is available in large scale for an applicable self-assembled bulk film material. As an anionic polyelectrolyte modification treatment of DNA is done with cationic lipid-like surfactants rendering a highly organised assembly and enhanced mechanical properties. Originally DNA is derived from salmon waste products such as milt and roe sacs [20]. After treatment with enzymes for protein elimination by protease, proteins are removed by controlling the pH level to 7.5. The material undergoes further cleaning steps such as freeze-drying and filtration after active carbon treatment for decolourisation.

Figure 2 Purified, dried salmon DNA dissolution ready for further treatment (blade-shearing, sonification, ion-exchange) [17].

Exhibited in Figure 2, the final product is a DNA dissolution, which is available for a bright assortment of different molecular weights starting from 8 000 kDa down to 200 kDa with a purity of 96%.
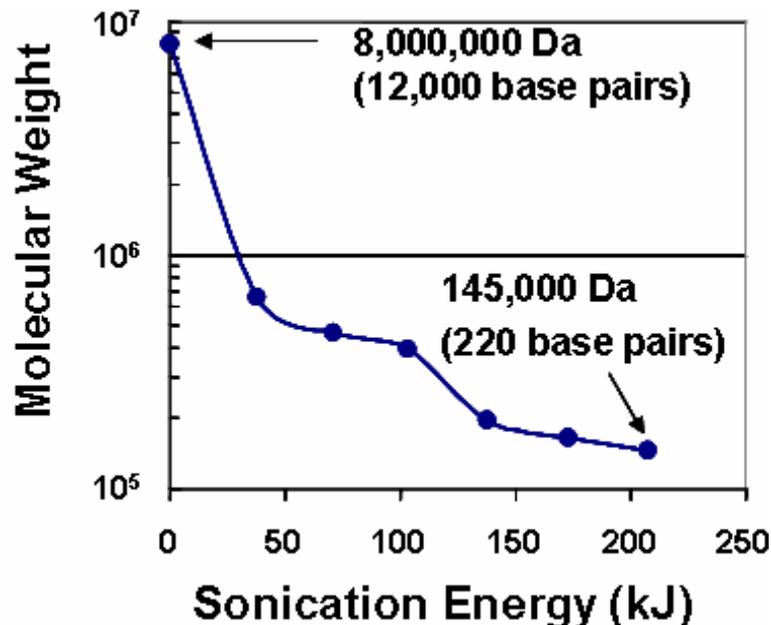
Figure 3 Mechanical modification ot the molecular weigth of DNA. By blade shearing and sonification relatively large batch sizes up to 4 g are obtained [18].

The molecular weight is measured using gel phase electrophoresis. 2 % of proteins still remain in the water-soluble dissolution. For processing the DNA dissolution with lipid surfactant CTMA it is first dissolved in deionised water and stirred for 6 hours. The desired concentration for ion exchange reaction is 6 g l-1. From the CTMA surfactant a solution with the same concentration is made and drop-wisely the same volume added to the DNA solution. The schematic of the ion-exchange reaction is illustrated in Figure 4. It continuous to stir for 6 hours, afterwards the precipitate is separated by filtering using a nylon filter 0.45 μm pore size. The last steps are to rinse the material with deionised water unless the water coming out is clear and bubble-free followed by drying over vacuum for a couple of hours.
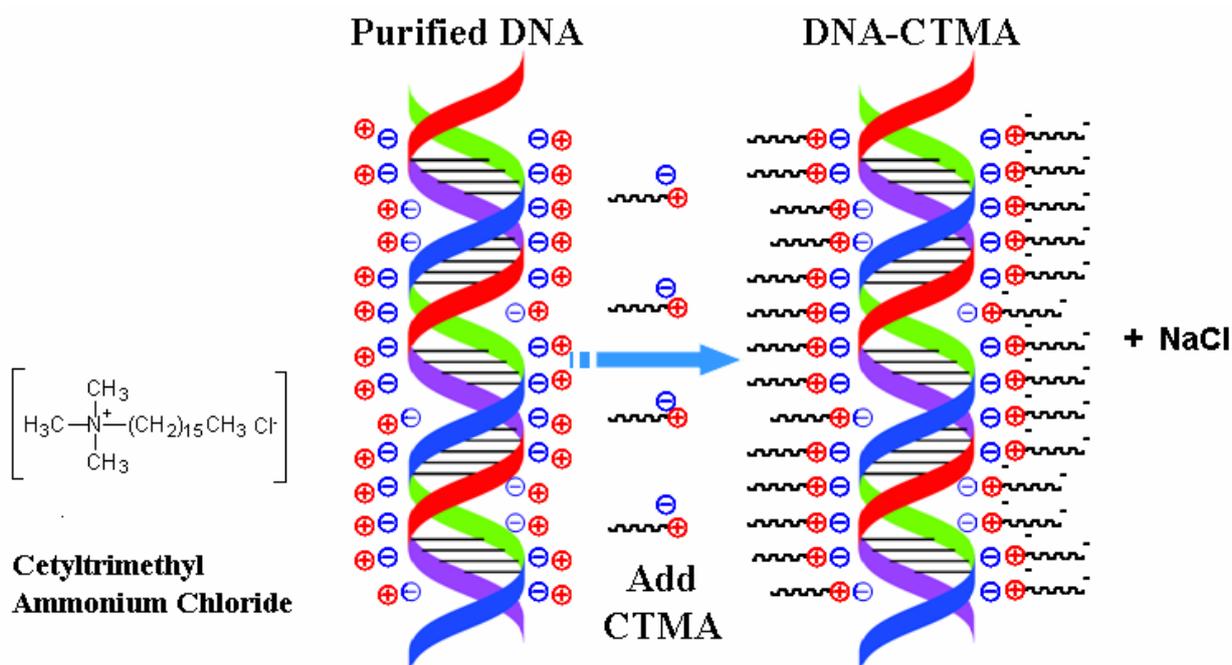
Figure 4 Ion exchange reaction in water of Na-DNA with cationic lipid CTMA surfactant forming a water-insoluble DNA-CTMA complex and sodium-chloride [17].

DNA-CTMA-PPIF Films

The resulting DNA-CTMA films, while of high optical quality, are soft and scratch easily (a visible mark is left on the film when scratched by a fingernail). This makes them incompatible with more aggressive processing techniques, such as sawing, that are often required to fabricate a photonic device. One solution to this problem is to crosslink the DNA-CTMA films. The crosslinker used in this work is poly(phenyl isocyanate)-co-formaldehyde (PPIF). The resulting crosslinked DNA-CTMA films are significantly harder (the films show no mark when scratched by a fingernail) than the noncrosslinked films and are also resistant to the solvents used to process the films [19].

To prepare a crosslinked DNA-CTMA film, the DNA-CTMA is dissolved in butanol at a concentration appropriate for its molecular weight. An amount of 81.2 mol % PPIF, with respect to DNA-CTMA, is dissolved separately in butanol at a concentration of 0.51 M. Both the DNA-CTMA-butanol and PPIF-butanol solutions are mixed in a 60°C oven for 1 to 2 h. Once fully dissolved, the DNA-CTMA-butanol solution is added to the PPIF-butanol solution

and the resulting solution is mixed for an additional 2 hours in the 60°C oven. The DNA-CTMA-PPIF solution is then filtered through a 0.2 μm pore size syringe filter and left to sit overnight in the 60°C oven. It is spin deposited on to a substrate using the same spin parameters as the non-crosslinked DNA-CTMA films. The substrates are baked in an 80°C oven for 5 min and then cured in a vacuum oven at 175°C for 15 min.

2.2 Experimental Results

Device Architecture and Fabrication

All organic field effect transistors here are fabricated using bottom-gate/top contact structure borrowed from TFT-structure.
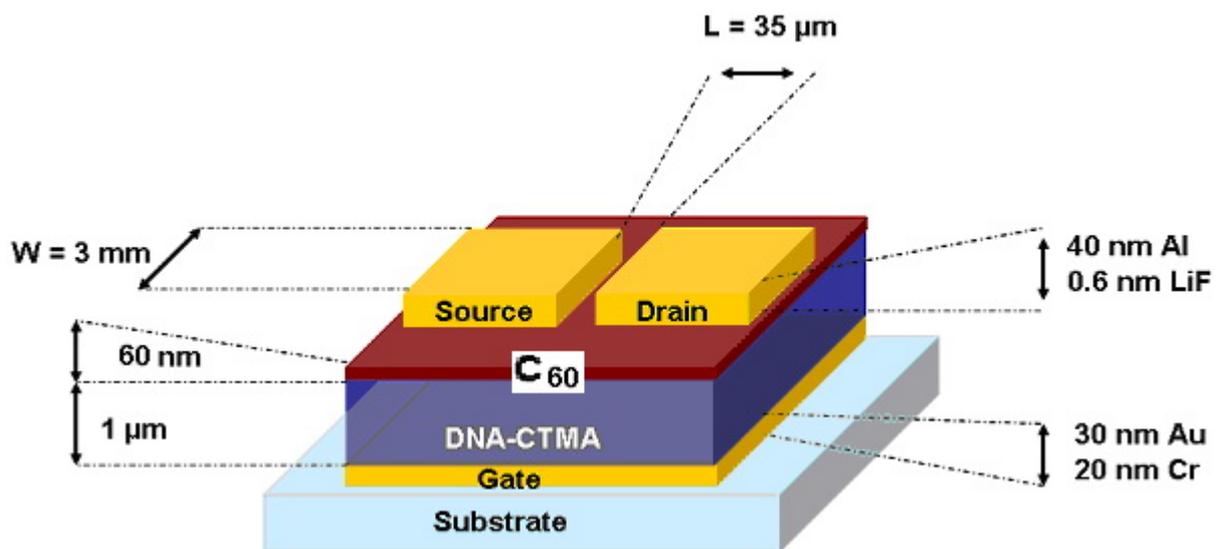
Figure 5 Top-contact/bottom-gate OFET structure including geometric device parameters

In Figure 5 the structure of a bio-organic field-effect transistor is presented. Dimensions of the channel lengh L, channel width W are provided as well as the z-cross section parameters including the 1 μm dielectric layer, a 60 nm C_{60} and top electrodes. Apart from OFETs also 2-terminal devices are fabricated namely metal-insulator-metal devices (MIM) and metal-insulator-semiconductor-metal (MIS) devices depiced in Figure 6.
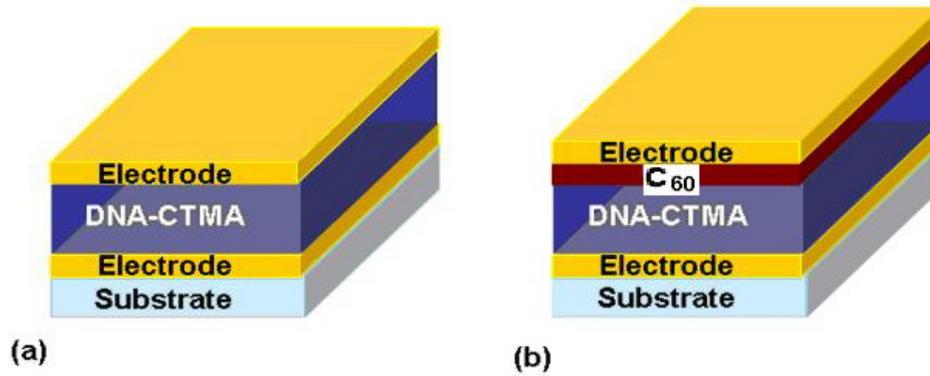
Figure 6 Two-electrode schematic "sandwich" device with both (*a*) a metal-insulator-metal (MIM) and (*b*) a metal-insulator-semiconductor-metal (MIS) device with embedded DNA-CTMA as dielectric layer.

The two-electrode devices use the same geometrical parameters as depicted in Figure 34 for the OFET structure. Except MIM top-electrodes on the C_{60} film are LiF/Al which guarantees a good contact to the semiconductor. In case of MIM gold is used as both bottom and top electrode as work-function differences in non-symmetric device structure would be a disadvantage in measurements.

The transfer and output characteristics of these devices are shown following figures.
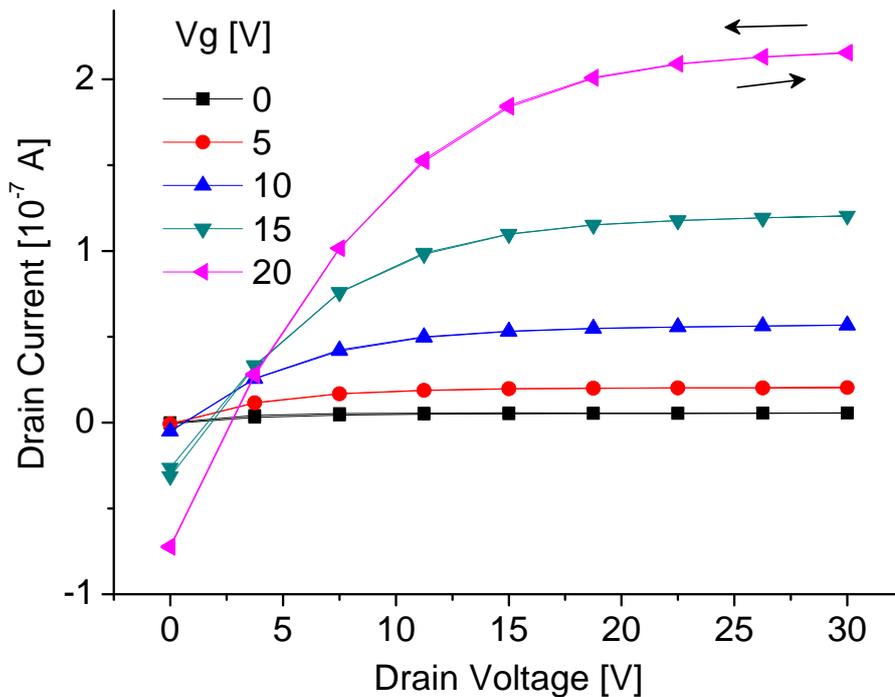
Figure 7 The output characteristic of C_{60} on DNA-CTMA-PPIF dielectric
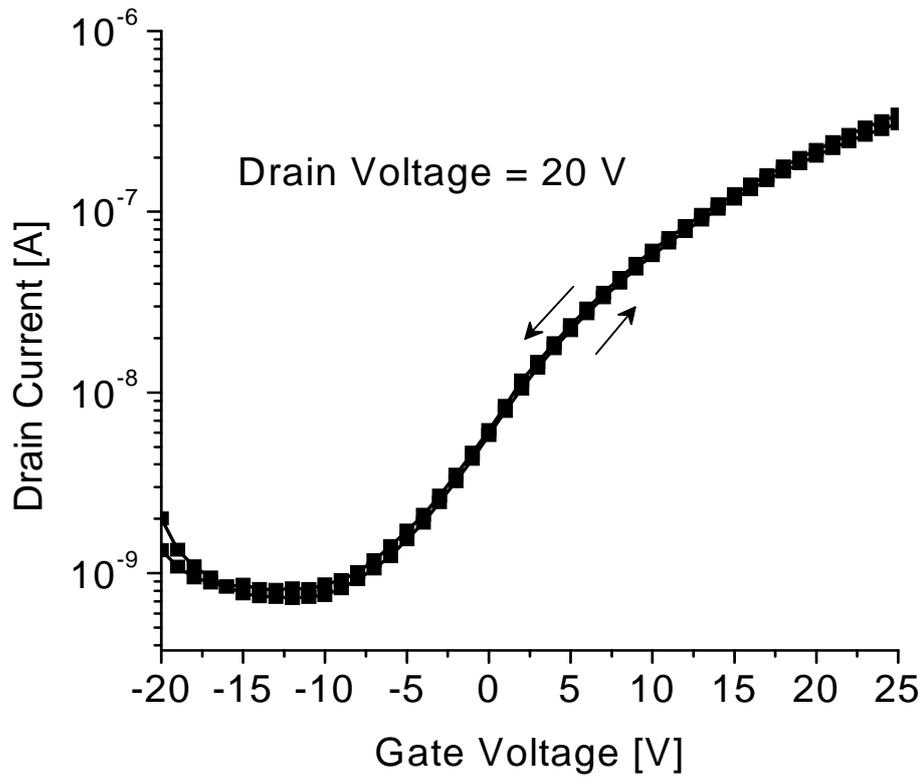
Figure 8 The transfer characteristic of C_{60} on DNA-CTMA-PPIF dielectric
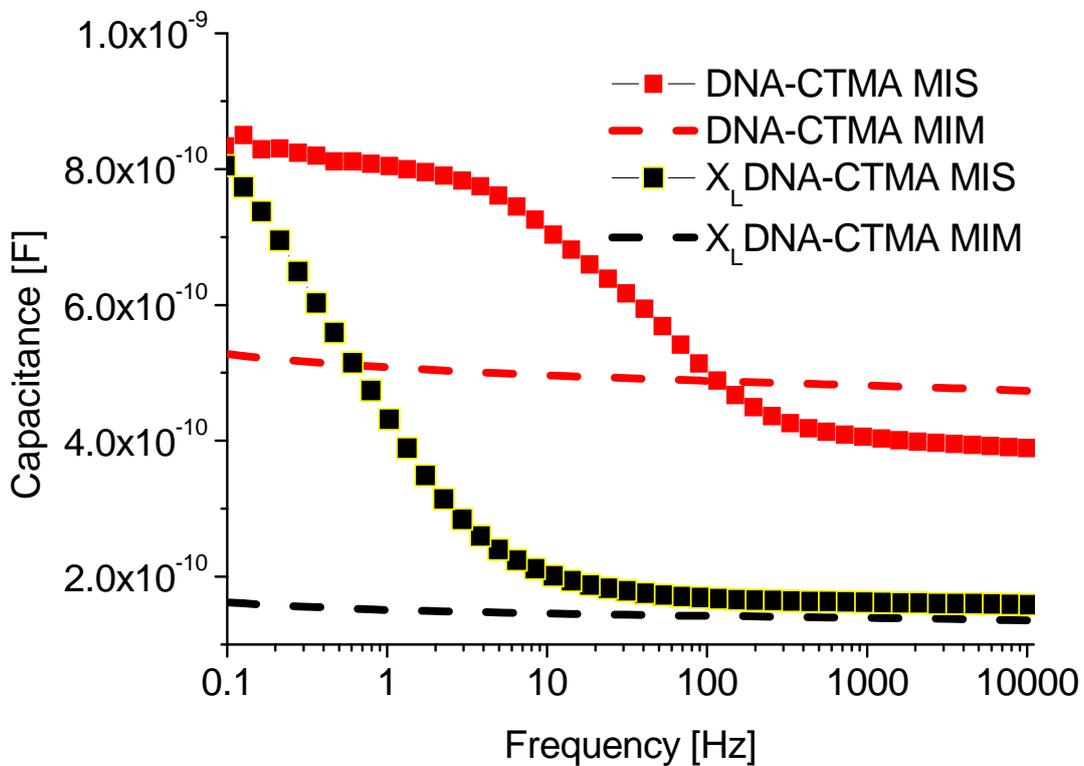
Figure 9 Quasi-static capacitance-electric field curves for the MIS and MIM structures

2.3 Conclusion

These results were presented as a invited talk; "DNA (Deoxyribonucleic Acid) as Dielectric in BioFETs" in *3rd International Symposium, Technologies for Polymer Electronics – TPE 08*. Optimization of these results have also been completed and then it will be used for the publication of a full article.

In future collaboration, we have been planning on fabricating OFETs with DNA gate using different semiconductor materials.

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