

Unexpected electromechanical actuation in conjugated polymer based diodes

Gilles Dennler,^{*a} Niyazi Serdar Sariciftci,^a Reinhard Schwödiauer,^b Siegfried Bauer^b and Howard Reiss^c

DOI: 10.1039/b516318h

Conjugated polymers are widely used as electroactive materials because of their morphological changes induced by redox cycling. But this type of materials was recently shown to induce several other electromechanical actuations. While undoped conjugated polymer based diodes undergo common Maxwell stress and electro-thermal actuation under reverse and forward polarization, respectively, devices based on doped active material exhibit an unusual type of electromechanical strain. This strain, in between piezoelectricity and electrostriction, opens new routes for material investigation and potential applications in "smart" actuators.

^aLinz Institute for Organic Solar Cells (LIOS), Johannes Kepler University, Linz, Austria.
E-mail: gilles.dennler@jku.at

^bInstitute of Experimental Physics, Department of Soft-Matter Physics, Johannes Kepler University, Linz, Austria

^cUniversity of California, Department of Chemistry and Biochemistry, Los Angeles, USA

Conducting and semiconducting conjugated polymers¹ are today widely investigated and technologically implemented as electroluminescent light emitters² in organic light emitting diodes (OLED),³ and as active semiconductors in organic field effect transistors (OFET),^{4,5}

non-volatile memories,⁶ photodiodes⁷ and solar cells.^{8,9} But beyond showing interesting electronic properties, conjugated polymers are also soft materials with a Young modulus in the range of GPa and even below. Thus, conjugated polymers are exploited in transducers:



Gilles Dennler

Gilles Dennler received a Ph.D. degree in Plasma Physics at the University of Toulouse, France, and a Ph.D. degree in Experimental Physics at the Ecole Polytechnique of Montréal, Canada in 2002. He is currently Assistant Professor in the Linz Institute for Organic Solar Cells directed by Prof. N. S. Sariciftci.



Niyazi Serdar Sariciftci

Niyazi Serdar Sariciftci received a doctorate degree in Semiconductor Physics at the University of Vienna in 1989. After four years spent in the Institute of Polymer and Organic Solids at the University of California, Santa Barbara, with Prof Alan Heeger (Nobel laureate 2000 for Chemistry), he was appointed Chair Professor in Physical Chemistry at the Johannes Kepler University of Linz in 1996.



Reinhard Schwödiauer

Reinhard Schwödiauer started his career as a precision mechanic in the industry. He later reoriented his interests to more academic issues and studied physics in Linz (Austria). He received his Ph.D. in 2002. After a research stay at Ecole Polytechnique in Montréal where he worked in thin film optics he returned to Linz and joined the Soft Matter Physics group of Prof. S. Bauer.



Siegfried Bauer

Siegfried Bauer studied Physics at the Technical University in Karlsruhe, where he received a Ph. D. degree in 1990. He is currently the Head of the Soft Matter Physics Department at the Johannes Kepler University of Linz. His work was awarded by the Information Technology Society in the VDE, the Berlin-Brandenburg Society of Polymer Research, and the Physical Society of Berlin.

mechanical motion in macroscopic devices has been shown to arise from (i) redox reactions during which the incorporation/release of bulky ions induces conformational change^{10–13} and (ii) Joule heating when an electrical current flows through the material.¹⁴

We aim in this short Highlight to focus on new electromechanical actuation possibilities recently reported.

Converse piezoelectricity and electrostriction are fundamental electro-mechanical responses, commonly considered as a mechanical deformation with an applied electric stimulus at zero stress.^{15,16}

$$S_{ij} = d_{ijk}E_k + M_{ijkl}E_kE_l + A_{ijklm}E_kE_lE_m + B_{ijklmn}E_kE_lE_mE_n + \dots \quad (1)$$

where S_{ij} denotes the mechanical strain tensor, d_{ijk} the piezoelectric d -tensor, M the electrostrictive tensor, and A and B are tensors describing nonlinear piezoelectric and higher order electrostrictive effects, respectively. Experimentally, the converse piezoelectric and electrostrictive responses are usually observed in samples where the electric stimulus is provided by an applied voltage V , leading to an electric field $E = V/l$ within the material, where l is the appropriate sample dimension. In practical experiments, eqn (1) is expressed with the experimentally controlled, and therefore easily accessible, applied voltage V , leading to a linear and quadratic relationship between the electromechanically induced strain and the applied voltage for the piezoelectric and electrostrictive response, respectively.¹⁷ However, replacing the electric field E in eqn (1) with the applied voltage V via $E = V/l$ is only

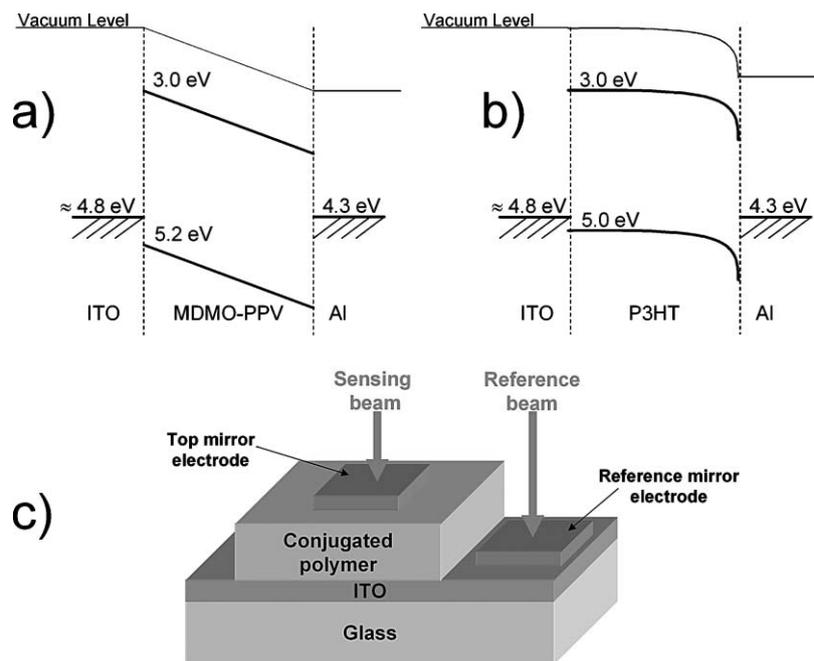
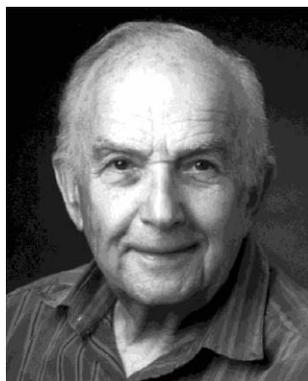


Fig. 1 Energetic diagram of (a) undoped MDMO-PPV and (b) p-doped P3HT sandwiched between ITO and Al. In (a), the electric field is homogeneous throughout the entire device thickness while in (b), the field drops linearly in the depletion zone present in the polymer on the Al side. (c) Schematic cross-section of a diode designed to allow Nomarsky interferometer measurements.

permitted when the electric field within the material is uniform. In materials where the electric field is strongly non-uniform across the thickness, one might expect different laws governing the electromechanical response *versus* the applied voltage stimulus. Fig. 1 illustrates this statement. Poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylene-vinylene) (MDMO-PPV) is commonly used in its intrinsic form (Fig. 1a). Due to its large band gap (2.2 eV), undoped MDMO-PPV behaves like a fully depleted semiconductor: When sandwiched between

indium tin oxide (ITO) and aluminium (Al) electrodes, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are straight lines (at least in the non injecting regime) indicating a homogeneous electric field throughout the entire device. On the other hand, poly(3-hexylthiophene) (P3HT) is a conjugated polymer slightly p-doped by exposure to ambient air.^{18,19} It has been previously reported that P3HT deposited on ITO, coated with Al, and exposed to air forms an ohmic contact with ITO^{20,21} and a Schottky contact with Al,²² as illustrated in Fig. 1b. In this case, the electric field drops linearly in the depletion region, and therefore is strongly non-uniform.

The electromechanical strain of the diodes can be investigated with a two-beam Nomarski interferometer,²³ described in detailed elsewhere.²⁴ This type of interferometer is based on a laser (He–Ne) which beam is split into a reference and a sensing beam. The former one is reflected by a reference mirror, while the latter one impinges on a mirror present on the top surface of the device. The relative displacement between the two mirrors is probed by



Howard Reiss

Howard Reiss was appointed Full Professor in the Department of Chemistry and Biochemistry at the University of California in Los Angeles (UCLA) in 1968. He is currently Professor Emeritus at UCLA, member of the National Academy of Sciences (1977), and fellow of both the American Physical Society and the American Association for the Advancement of Sciences.

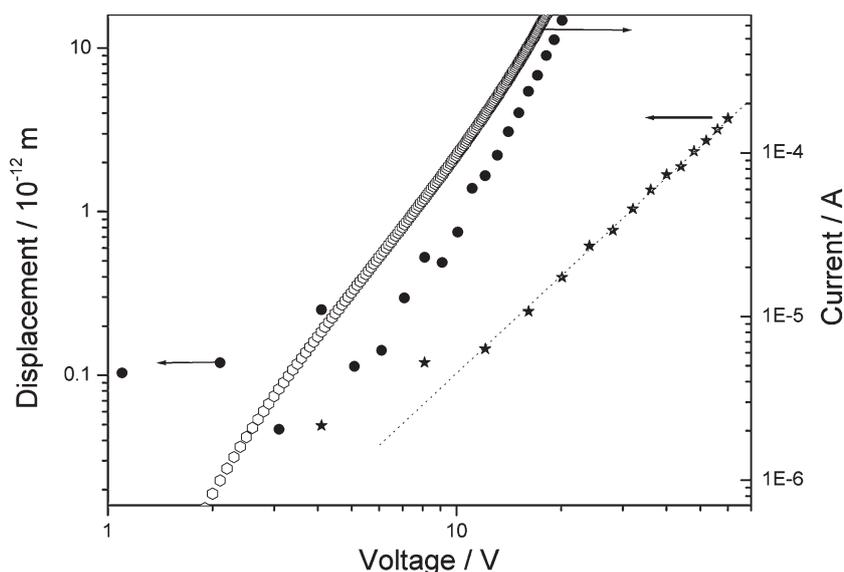


Fig. 2 Electromechanical displacement of the upper surface of a ITO/MDMO-PPV/Al device versus the amplitude of the sinusoidal voltage (at a frequency of 33.3 Hz) in forward (●) and reverse direction (★). Each curve is fitted by a power law: The exponents found are respectively 4.4 (●) and 2 (★). Right axis: Current through the diode (○) in forward direction.

measuring the phase shift $\Delta\phi$ between the two reflected beams. Thus, strains from several tenths of nanometres down to the sub-picometre regime can be detected over a wide range of frequencies (in our case, from 0.1 up to 10 kHz).²⁴ As depicted in Fig. 1c, our diodes have been designed so that one of the beams is reflected by an Al reference mirror evaporated on the ITO coated glass substrate while the other beam hits the top Al electrode of the diode.

Fig. 2 shows the displacement of the surface of an ITO/MDMO-PPV/Al with respect to the substrate surface versus the amplitude V_0 of the applied sinusoidal voltage $V = V_0(1 + \sin 2\pi ft)$ at a frequency $f = 33.3$ Hz.²⁴ The amplitude of the electromechanical strain shows a power law dependence versus the amplitude of the applied voltage under both forward and reverse bias conditions ($\propto V_0^\alpha$): Under reverse bias the exponent is $\alpha \approx 2.0$, whereas under forward bias it reaches $\alpha \approx 4.4$.

The strains appearing under reverse bias are induced by Maxwell force.²⁵ When a voltage is applied to the diode structure, the opposite charges on the electrodes attract each other, leading to a compressive stress and a corresponding compressive strain on the material between the electrodes. The effective compressive stress p , is expressed by $p = \epsilon\epsilon_0 E^2$, where ϵ is the relative dielectric

constant of the material, ϵ_0 the vacuum permittivity and E the constant electric field in the material. For small stress the strain along the z -axis, s_{33} , is given by $s_{33} = -p/Y = \epsilon\epsilon_0 E^2/Y$ where Y is the Young modulus of the conjugated polymer. This type of strain is expected to occur in the forward direction as well, but only if the electric field is not screened by a space charge region. However, the power law with an exponent $\alpha \approx 4.4$ suggests another type of actuation. Indeed, as shown in Fig. 2, the voltage dependence of the strain does follow quite closely the voltage dependence of the current flowing in the device. It has been proposed that this electro-thermal actuation originates in the associated high current density in the diode:²⁶ The power dissipated in the resistance of the device induces Joule heating of the surface of the substrate. This local heating creates an “*in situ* bimorph” in the temperature gradient through the cross section of the substrate. This bimorph structure causes deflection and bending of the substrate. The thermal actuation mechanism was confirmed by fixing the device on one side, leaving the rest free to move and deform. Profilometer based measurements show that a 1 mm thick 1.5 cm \times 1.5 cm glass substrate “cantilever” experiences a bending strain: For an applied voltage of 35 V (corresponding

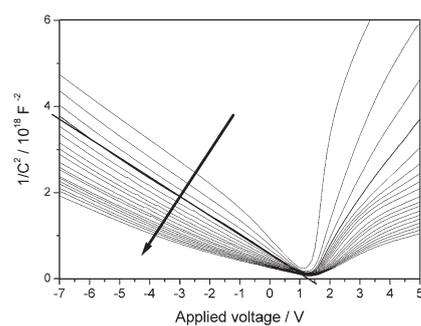


Fig. 3 $1/C^2$ of an ITO/P3HT/Al diode recorded at 1 kHz every 2 min in air versus the applied voltage V . The arrows indicate increasing time. The thick solid line is a linear fit of one intermediate curve.

to a current of about 5 mA and a dissipated power of 175 mW) the free edge of the sample moved with an amplitude of more than 170 nm. Changing the substrate from glass ($Y \approx 65$ GPa and $CTE \approx 9 \times 10^{-6} \text{ K}^{-1}$) to poly(ethylene-terephthalate) (PET, $Y \approx 4$ GPa and $CTE \approx 120 \times 10^{-6} \text{ K}^{-1}$), the displacement attains several micrometres for voltages as low as 5 V.²⁶

In contrast to MDMO-PPV, P3HT is doped by exposure to ambient air, and forms a Schottky contact with Al. Fig. 3 displays the $1/C^2$ plot versus voltage, where C is the capacitance of the ITO/P3HT/Al structure. The curves have been recorded successively every 2 min, just after moving the sample out of the evaporation chamber for Al deposition.²⁷ The arrow indicates the increasing time direction. Although the first and the last scans cannot be perfectly fitted by a linear function line, the linearity of intermediate scans prove the existence of a Schottky contact. The concentration of impurities is estimated according to:²⁸

$$\frac{1}{C^2} = \frac{2(V_{bi} - V)}{A^2 q \epsilon \epsilon_0 N_A}, \quad (2)$$

where V_{bi} is the built-in potential, V the applied voltage, A the active surface area of the device, q the charge of the impurities, ϵ the relative dielectric constant of the semiconductor, ϵ_0 the permittivity of vacuum, and N_A the concentration of impurities. N_A is found to evolve from 5×10^{16} to $1 \times 10^{17} \text{ cm}^{-3}$ with increasing time. Thus, the characteristics of the P3HT based Schottky contacts evolve with time due to the diffusion of doping impurities into the active P3HT layer.

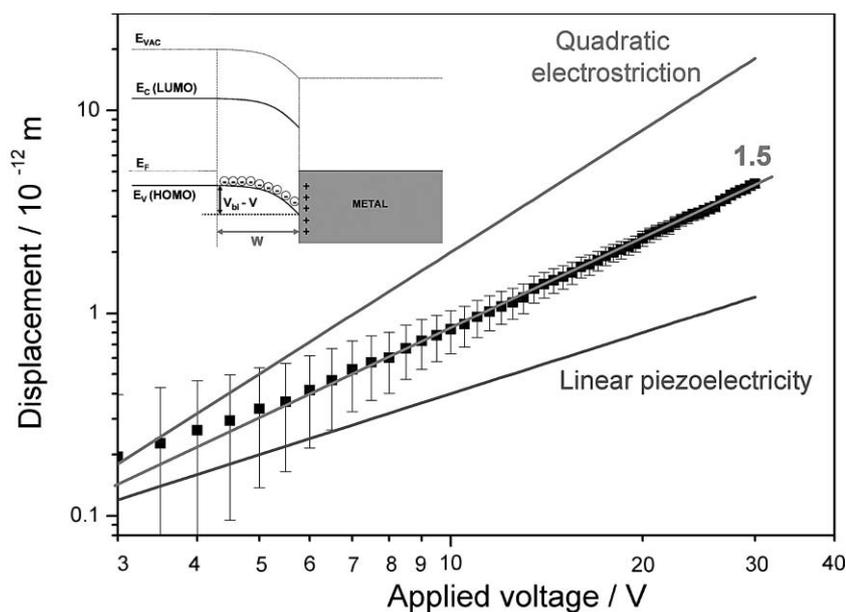


Fig. 4 Displacements recorded with a Nomarski interferometer on a Schottky ITO/P3HT/Al diode for reverse applied voltages (at 1555 Hz).

These P3HT based devices, showing a rectification ratio of several orders of magnitude at ± 10 V, have been observed to undergo the same electro-thermal actuation in the forward direction than the diodes based on MDMO-PPV. However, in the reverse direction, an unusual electromechanical strain is observed. As shown in Fig. 4, the actuation does not follow the electrostrictive force quadratic dependence of the voltage, but follows a power law with an exponent $\alpha = 1.5$.²⁷ This strain *versus* voltage dependence is exactly in between pure electrostriction and converse piezoelectricity. The electromechanical actuation of the diode is explained with a model, which is based on the coulombic attraction of charges present in the Schottky contact, and the resulting strongly non-uniform electric field distribution. As depicted in the inset of Fig. 4, the junction between the doped P3HT and Al involves positive charges stored in the metal at the interface with the semiconductor, and negative doping ions present in the conjugated polymer (assumed to be firmly bound to the semiconductor). These charges of opposite sign attract each other and therefore induce compressive strains. Based on this model, the calculation for the strain–voltage relation gives:²⁷

$$S = \frac{1}{Y} \left(-\frac{2qN_A\epsilon\epsilon_0}{9} \right)^{1/2} (V_{bi} - V)^{3/2} \quad (3)$$

where Y is the Young modulus of the active material, q the charge of an electron, ϵ the relative dielectric constant of the semiconductor, ϵ_0 the permittivity of vacuum, N_A the concentration of acceptor impurities, V_{bi} is the built-in potential, and V the applied voltage. It has to be noted here that this model is valid for all kinds of semiconductors. It means that it does predict the same type of actuation in inorganic (*i.e.*, silicon) junction too, yet the strain might in this case be much smaller due to the large Young modulus of inorganic materials.

The two electromechanical actuations observed in undoped conjugated polymer based diodes, namely Maxwell stress and electro-thermo actuation have already been reported to occur separately in polymers. However, in the diodes shown here, both mechanisms are active, by simply choosing reverse or forward bias voltage. Such electromechanical properties, correlated with the semiconducting properties of conjugated polymers might open a route to “smart actuators”. Anticipated devices may be able to actuate and perform logic operations simultaneously and monolithically. Although the displacements reported so far are too small to be exploited, several ways can be envisaged to enhance them: Foaming the active material²⁹ or mixing it with low Young modulus elastomeric material (*i.e.*, polyurethane) in order to

increase the softness; mixing the active material with high dielectric constant materials to increase the strength of the Maxwell stress; and tuning the substrate properties and geometry to optimize the electro-thermo bending. Besides, the movement reported herein might have direct consequences for the reliability of OLEDs and OFETs, suggesting for example potential delamination of electrode/active materials.

On the other hand, the unexpected and unusual electromechanical actuation observed in Schottky contact, yet potentially exploitable in actuators too, offers tremendous opportunities for basic material science. The model that leads to eqn (3) relies on several assumptions. First of all, it has been assumed that N_A is homogeneous throughout the entire device thickness. When this condition is relaxed, the power law exponent deviates from its 1.5 value, potentially covering the entire range from linear piezoelectricity to quadratic electrostriction. Therefore, the investigation of the electromechanical properties of organic semiconductor may potentially allow the determination of the doping profile and the resulting inhomogeneous electric field distribution. Moreover, the model assumes that ions are firmly bound to the semiconductor. This is certainly the case in inorganic semiconductors, but might differ in conjugated polymers, where ions can more easily diffuse or drift. Thus, eqn (3) will be verified only for frequencies high enough to prevent migration of ions and consequent modification of the Schottky junction, inducing a frequency dependent electromechanical effect. Finally, the presence of doping species is mandatory for the creation of a Schottky contact. Interestingly enough, conjugated polymers can in certain cases undergo a photodoping process, largely exploited in conjugated polymer based solar cells.³⁰ Therefore, one can imagine tuning the electromechanical behavior of conjugated polymer based active materials simply by using light.

We have presented the electromechanical actuation properties of conjugated polymer based diodes. The three distinct electromechanical effects are observed in such devices, namely Maxwell stress, electro-thermo actuation, and the unusual actuation in Schottky contacts (“H. Reiss effect”). These effects may

pave a way for a new type of “smart, monolithic actuators”. Further investigations might disclose entirely new and even more exotic material properties.

Acknowledgements

We gratefully acknowledge the financial support of the Austrian Foundation for the Advancement of Science (FWF NANORAC Contract No: FWF-N00103000). We thank Attila Mozer, Helmut Neugebauer and Christoph Lungenschmied for fruitful discussions.

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