Highly sensitive multi-layer pressure sensor with an active nanostructured layer of an organic molecular metal

V Laukhin1,2,4, V Lebedev2, E Laukhina2,3, C Rovira2,3 and J Veciana2,3
1 Institució Catalana de Recerca i Estudis Avançats (ICREA), Barcelona, Spain
2 CIBER de Bioingeniería, Biomateriales y Nanomedicina (CIBER-BBN), Spain
3 Institut de Ciencia de Materials de Barcelona (ICMAB-CSIC), Campus UAB, Bellaterra, Spain

E-mail: vladimir@icmab.es

Abstract: This work addresses to the modern technologies that need to be instrumented with lightweight highly sensitive pressure sensors. The paper presents the development of a new plain flexible thin pressure sensor using a nanostructured layer of the highly sensitive organic piezoresistive metal $\beta$-(BEDT-TTF)$_2$I$_3$ as an active component; BEDT-TTF = bis (ethylenedithio)tetrathiafulvalene. The original construction approach permits one to operate the developed sensor on the principle of electrical resistance variations when its piezoresistive layer is elongated under a pressure increase. The pressure sensing element and a set of gold electrodes were integrated into one compact multi-layer design. The construction was optimized to enable one generic design for pressure ranges from 1 to 400 bar. The pressure tests showed that the sensor is able to control a small pressure change as a well definite electrical signal. So the developed type of the sensors is very attractive as a new generation of compact, lightweight, low-cost sensors that might monitor pressure with a good level of measurement accuracy.

1. Introduction

Engineering flexible all-organic sensing materials with electrical detection principle brings great opportunities in the field of physical sensors for their applications in hi-techs [1-3]. A need for flexible pressure sensors that can be easily located at the body tissue, synthetic and natural textiles, artificial skins, catheters, etc. is constantly on the rise across many hi-techs and industries [2, 4]. In this context, our interest in the use of piezo-resistive organic molecular metals as active polycrystalline layers in sensor engineering has grown steadily over the last decade due to their important material properties, such as electrical conductivity, high strain (pressure) resistance sensitivity, long-term stability, and weightless [5a, 6]. Additionally, it is worthwhile mentioning that the covering process of polymeric films with the oriented highly piezo-resistive polycrystalline layer of the molecular conductor $\beta$-
(ET)$_2$I$_3$ (ET=BEDT-TTF=bis(ethylenedithio)tetrathiafulvalene, figure 1) is a simple two step procedure carried out at moderated temperature [7, 8].

The polycrystalline conductive covering layer reveals attractive mechanical properties such as excellent adhesion to a polymeric substrate and high fracture toughness. We showed that the electro-mechanical behaviour of these films is conditioned by the softness of the lattice of the BEDT-TTF-based molecular conductors [5]. The maximum strain ($\varepsilon_{\text{max}}$) before the fracture of the conductive layer is about 1 % [9] that is much greater than the same characteristic for conventional metals and semiconductors, in which very little deformation ($\varepsilon_{\text{max}} \approx 0.2$ %) occurs before the point, at which the stress is sufficient to induce failure [10]. The tests demonstrated that BL (bi-layered) films are able to control very small strain (relative strain 10-3 %) in a wide range of deformation. Haematoxylin-Eosin staining of the tissues adjacent to the sensing BL film and to the silicon band showed the less inflammatory reaction to the above mentioned BL film as compared with the reaction to a silicone band [11]. So, the developed sensing BL films have a higher biocompatibility than standard silicone-based materials used in surgery. The BL film-based membranes with sensitivity to pressure changes being 13.3 $\Omega$/mmHg have been developed and the first simple prototypes of devices for monitoring the body movements (breathing rhythms [5a], blood pulse [12], and intraocular pressure [11]) have been designed and fabricated. It should be note that all developed prototypes operated on the principle of electrical resistance variations when the plans of sensitive BL films were elongated/deformed under load. The BL film dilatation results in stretching the conductive crystallographic $ab$ plane of the “c” oriented sensing crystallites of the $\beta$-(BEDT-TTF)$_2$I$_3$ molecular metal and in its turn increases the distances between the BEDT-TTF molecules layered along the $ab$-plane (figure 2). This leads to a decrease of the intra- and inter- BEDT-TTF molecular stack transfer integrals with an enormous increase of the BL film resistance [6].

The tests of devices [5a, 11, 12] demonstrated that the BL film-based sensors are able to replace conventional sensors in biomedical technologies that need to control any very delicate bending as well
as quite large deformation. However, it remains a challenge to develop film sensors being capable of measuring quite large pressure values. In this connection we focus our study on the development of design approaches enable the use of delicate highly strain sensing BL films for monitoring hundreds of bars with a high level of measurement accuracy.

Here we demonstrate two design approaches permitting the use of the above mentioned piezo-resistive BL films for monitoring pressure changes in a range from ambient conditions up to a few hundred bars. One of the developed pressure sensors (sensor 1) operates on the principle of electrical resistance decrease when the lattice of the piezo-resistive molecular metal $\beta$-(BEDT-TTF)$_2$I$_3$ is compressed under quasi-hydrostatic conditions. The other one (sensor 2) operates on the principal of electrical resistance increase when the conductive crystallographic ab plane of the $\beta$-(BEDT-TTF)$_2$I$_3$ crystallites is stretched in all directions due to the pressure induced deformation.

2. Fabricating compact flexible multi-layer pressure sensors with the $\beta$-(BEDT-TTF)$_2$I$_3$ as a piezo-resistive component

2.1. Preparing flexible piezo-resistive BL-based gauge

In line with the early reported method [7, 8] we first prepared a 25 $\mu$m thick polycarbonate (PC) films that contain a 2 wt. % of BEDT-TTF which is a precursor for the molecular metal $\beta$-(BEDT-TTF)$_2$I$_3$. The films were cast on glass supports at 130 °C from a 1,2-dichlorobenzene solution of PC and BEDT-TTF.

In order to cover the film with the (BEDT-TTF)$_2$I$_3$-based layer, we exposed the film surface to the vapors of a solution of iodine in dichloromethane. The surface of a polycarbonate film easily swells under its exposure to dichloromethane vapors; this swelling facilitates a migration of BEDT-TTF molecules from the film bulk to the swollen film surface where the part of donor molecules are oxidized to radical cations by I$_2$, which penetrates in the film surface together with dichloromethane vapors. This redox process induces the rapid nucleation of the highly insoluble (BEDT-TTF)$_2$I$_3$ molecular metal and the metallic facing layer is formed. The treatment of the film surface with iodine/dichloromethane vapors resulted in the formation of the covering layer of the $\alpha$-phase of (BEDT-TTF)$_2$I$_3$. The prepared polycarbonate/\textalpha-(BEDT-TTF)$_2$I$_3$ BL film was annealed at 150°C during 30 min; this annealing permitted us to prepare the highly piezo-resistive polycarbonate/\textbeta-(BEDT-TTF)$_2$I$_3$ BL film with gauge factor 20 [5, 8].

The surface analysis on a micro scale, performed using “Quanta FEI 200 FEG-ESEM” scanning electron microscope (SEM) showed that the crystallites are of submicron sizes (Figure 3).

![Figure 3. SEM image of the conductive covering layer based on $\beta$-(BEDT-TTF)$_2$I$_3$.](image-url)
The formation of the β-(BEDT-TTF)$_2$I$_3$-based sensing layer was confirmed by the X-ray analysis. As figure 4 shows, the X-ray diffraction pattern presents the family of $(00l)$ reflections of β-(BEDT-TTF)$_2$I$_3$ [5a,b]; therefore, the β-(BEDT-TTF)$_2$I$_3$-based layer of the polycarbonate/β-(BEDT-TTF)$_2$I$_3$ BL film is formed by c* oriented crystals that is in a good agreement with early reported data [7, 8]. At this orientation the c* axis of the linked crystals is mainly perpendicular to the film surface and, consequently, their conductive crystallographic ab plans are parallel to it.

![Figure 4. X–ray powder diffraction pattern of the piezoresistive covering layer of β-(BEDT)$_2$I$_3$](image)

The BL film-based gauges with an area of ca. 12 × 5 mm$^2$ were cut and then mounted as a pressure sensing component in two different compact flexible multi-layer pressure sensors (hereafter 1 and 2).

2.2. Setting up pressure sensor 1

Pressure sensor 1 was packaged using a two-step process (figure 5) in which the BL film-based gauge was integrated with 4 gold electrodes into a compact flexible two layer structure (figure 6). This design involves the use of the electrical response of the lattice of β-(BEDT-TTF)$_2$I$_3$ to pressure when it is compressed under quasi hydrostatic conditions; high surface friction of polycarbonate layers permits their use as a pressure-transmitting medium.

![First step: fabrication of the flexible piezo-resistive unit (BL-film)](image)

![Second step: fabrication of the two layer pressure sensor](image)

![Figure 5. Scheme of the fabrication of pressure sensor 1](image)

To fabricate pressure sensor 1, the BL film-based gauge of 25 μm thick with an area of ca. 12 × 5
mm² was glued with the conductive side up to a polycarbonate-based supporting film of 400 μm thick and the area 30 × 30 mm² as it is schematically shown in figure 6, top. Then, another polycarbonate film of 200 μm thick with the plan area of 30 × 50 mm² on which surface the four gold electrodes of 1 μm thick were preliminarily deposited was placed over the BL film-based gauge to make electrical contacts with the sensing part of the piezo-resistive unit; the film with gold electrodes was fixed using glue as it is shown in figure 6, bottom. To complete pressure sensor 1, four Cu wires were attached to the gold electrodes using graphite paste; to remove any stress from the gold electrodes, Cu wires were additionally attached (using glue) to the polycarbonate film with the plan area of 30 × 50 mm² as it is shown in figure 6, bottom.

![Figure 6. Schematic representation of the pressure sensor 1: (top) a piezo-resistive unit showing the BL film-based gauge location on the centre of the polycarbonate supporting film; (bottom) the piezo-resistive measuring element: (1) polycarbonate film, on which surface the gold electrical electrodes (2) were deposited; (3) four Cu wires attached to the gold electrodes using graphite paste; (4) BL film-based gauge between the polycarbonate films of 200 and 400 μm thick with a plane areas 30×50 and 30×30 mm², respectively (5).]

2.3. Setting up pressure sensor 1.
Pressure sensor 2 was packaged using a three-step process (figure 7), in which the BL film-based gauge was integrated with 4 gold electrodes into a compact flexible six layer structure.

![Figure 7. Scheme of the fabrication of multi layer pressure sensor 2]
A key design issue for pressure sensor 2 is the use of two layers of a double sided film tape that characterized with small surface friction. This design proposes the dilatation of the plan of the flexible pressure measuring element shown in figure 6, top due to small surface friction when pressure is load perpendicularly to its plane. The piezo-resistive unit and flexible two layer pressure measuring element were manufactured in series as it was described in the previous section (figure 6). At the final step, the flexible pressure measuring element was sandwiched between two Kapton layers of 130 μm thick using a double sided film tape (figure 8).

![Figure 7. Schematic view of the multi-layer pressure sensor 2: (1) polycarbonate film on which the gold electrical contacts (2) were deposited; (3) four Cu wires attached to the gold contacts using graphite paste; (4) piezo-resistive BL film-based gauge; (5) polycarbonate film of 400 μm thick with a plane area 30x30 mm; (6) two Kapton films of 130 μm thick with a plane area 30x30 mm glued to the polycarbonate films with a double sided film tape (7)](image)

3. Pressure tests
To study the effect of pressure on the electrical resistance of the developed multi-layer pressure sensors, the sensors 1 and 2 were placed on the piston of the hydraulic press (“Unipress”, Poland) in turn. Sensors were subjected to different pressure load cycles by hydraulic press that pushes the piston with the pressure sensor against the stationary disc; the electrical response of the sensor was simultaneously measured by Multimeter Agilent 34970A in a four contacts configuration. Here it should be noted that the developed design permits 1-D pressure load on the area 30x30 mm² of the multi-layer sensors excluding the area were Cu wires are attached to the gold electrodes (figure 9).

![Figure 9. Schematic representation of pressure loading at cyclic pressure load tests of developed multi layer sensors](image)
3.1. Electrical response of sensor 1 to pressure

As figure 10 shows that the electrical response of sensor 1 to the multi-step cyclic load is a reversible well-detected signal; the maximum pressure loading was 545 bars.

![Graph showing electrical response of sensor 1 to pressure](image)

**Figure 10.** Electrical resistance response of sensor 1 to the pressure variation in the range 0-545-0 bar; each step up and down is 55 bars.

For better visualization of the electro-mechanical behaviour of sensor 1, its electrical resistance response to step-like cyclic pressure loading is plotted as relative resistance changes versus pressure in figure 11. With reference to this figure it can be seen that the resistance of sensor 1 significantly decreases when pressure increases from 0 up to 545 bars.

![Graph showing electrical resistance response](image)

**Figure 11.** Electrical resistance response of sensor 1 to pressure loading.

Therefore, as it was suggested in section 2.2., this design approach allowed us to operate the sensor on the principle of electrical resistance variations when the lattice of piezo-resistive crystallites of β-(BEDT-TTF)$_2$I$_3$ is compressed under load. Under compression of the β-(BEDT-TTF)$_2$I$_3$ lattice the
distances between the BEDT-TTF molecules decreases (figure 12) that in turn increases the intra- and inter- BEDT-TTF molecular stack transfer integrals that results in decreasing of the BL film resistance. As the pressure-dependent compression of the lattice parameters monotonically slows down when pressure increased from 0 up to 545 bars, the sensor electrical response to pressure significantly deviates from the linearity. This nonlinear behavior is one of the disadvantages of sensor 1 that is able to impose significant restrictions for sensor applications.

![Figure 12. Schematic representation of the crystallographic ab plan of the sensing crystallites of the piezo-resistive metal β-(BEDT-TTF)$_2$I$_3$ under quasi hydrostatic compression.](image)

### 3.2. Electrical response of sensor 2 to pressure

In this section we will show that the optimized multi layer construction of the sensor 2, whose operated principle is based on the expansion of the piezo-resistive β-(BEDT-TTF)$_2$I$_3$ layer under pressure load is able to overcome the above mentioned problem.

Multi-layer pressure sensor 2 was subjected to different pressure load cycles using the hydraulic press as it is schematically shown in figure 9. The pressure tests reveal that electrical response of the multi-layer sensor 2 to pressure is very strong and well reproducible (figure 13).

![Figure 13. Illustration of repeatability of the respond of the sensor 2 at different pressure cycles: 0–275-0 bar, 0-325-0 bar and 0–380-0 bar.](image)

For better visualization, the electrical resistance data, which were collected for the second loop of multi cyclic pressure load in the range 0-275 bar, are plotted as relative resistance changes versus
pressure in figure 14. The figure shows that in contrast to sensor 1 the electrical response of sensor 2 to pressure does not deviate essentially from the linearity.

![Figure 13. Normalized resistance change of sensor 2 vs applied pressure for the pressure range 0-275 bar.](image)

The presence of two layers of a double sided film tape is one of the key solutions in this sensor construction that permits the sensor to solve the problem of the non linear pressure-dependent compression of the lattice parameters. Due to low surface friction of the tape layers, the plane of the piezo-resistive BL film-based gauge is stretched when pressure is applied. Under extension, the distances between the BEDT-TTF molecules in the lattice of the \( \beta-(\text{BEDT-TTF})_2\text{I}_3 \) crystallites increases (figure 2) that in turn decreases the intra- and inter- BEDT-TTF molecular stack transfer integrals and as a result the resistance of the \( \beta-(\text{BEDT-TTF})_2\text{I}_3 \) layer increases (figure 13, 14). The sensitivity of the sensor, calculated as the ratio between the relative resistance change and pressure change was found to be around 0.3%/bar. Taking into account the initial resistance value of the sensor (7.6 kOhms), it is easy to estimate that the sensor sensitivity corresponds to 23 Ohms/bar. Thus, the developed multi-layer design allows the use of thin BL film-based gauges for fabricating compact flat pressure sensors which are able to control small pressure changes in the wide pressure range (0-400 bar) as a well defined electrical signal.

4. Summary
This study showed that the BL films: polycarbonate/(001) oriented \( \beta-(\text{BEDT-TTF})_2\text{I}_3 \) layer may be easily mounted in pressure sensors as a flexible pressure measuring element.

The construction of a compact flexible multi-layer pressure sensor was designed and optimized to enable one generic design for pressure ranges at least up to 400 bars.

The pressure tests demonstrated that the developed type of the sensors is very attractive as a new generation of durable, low-cost, all-organic pressure sensors that could monitor quite large pressure values with a good level of measurement accuracy.

5. Acknowledgements
The authors acknowledge the financial support from Instituto de Salud Carlos III, through “Acciones CIBER.” The Networking Research Center on Bioengineering, Biomaterials and Nanomedicine (CIBER-BBN), an initiative funded by the VINational R&D&I Plan 2008–2011, Iniciativa Ingenio 2010, Consolidar Program, CIBER Actions and financed by the Instituto de Salud Carlos IIIwith assistance from the European Regional Development Fund. The authors also appreciate the financial support through the projects: BE-WELL (CTQ2013–40480-R) granted by DGI (Spain), and GenCat
(2014-SGR-17) financed by DGR (Catalunya), the European Commission’s Seventh Framework Programme for Research under contracts FP7-OCEAN-2013-614155.

6. References
[1] Yirish S, Kirinaki N V, Myshkin I L 2005 World Sensors and MEMS Markets: Analysis and Trends Sensors & Traducers Magazine (S&T e-Digest) 62 Issue 12 456-461
[2] Jacobs I S, Axisa F, Schmitt P M, Gehin C, Delhomme G, McAdams E, Dittmar A 2005 Flexible technologies and smart clothing for citizen medicine, home healthcare and disease prevention IEEE Transactions on Information Technology in Biomedicine 9 (3) 325-336
[3] Someya T, Sekitani T, Iba S, Kato Y, Kawaguchi H, Sakurai T 2004 Conformable, flexible, large-area networks of pressure and thermal sensors with organic transistor active matrixes, Proc. Natl. Acad. Sci. USA 101 9966–9970
[4] Leonardi M., Pitchon E M, Bertsch A, Renaud Ph, Mermoud A 2009 Wireless contact lens sensor for intraocular pressure monitoring: assessment on enucleated pig eyes Acta Ophthalmol. 87 433–437
[5] (a) Laukhina E, Pfattner R, Ferreras L R, Galli S, Mas-Torrent M, Masciocchi N, Laukhin V, Rovira C, Veciana J 2010 Ultrasensitive Piezoresistive All-Organic Flexible Thin films, Adv. Mater. 22 977-991; (b) Laukhina E 1997 Systematic Study of the (ET)2I3 Reticulate Doped Polycarbonate Film: Structure, ESR, Transport Properties and Superconductivity J. Phys. I France 7 1665-1675
[6] Kondo Y R, Higa M, Kagoshima S, Hoshino H, Mori T, Mori H 2006 Electrical and Structural Properties of 0-type BEDT-TTF Organic Conductors under Uniaxial Strain J. Phys. Soc. Jpn. 75 044716-7
[7] . Jeszka J K, Tracz A 1992 A new method of growing crystalline networks in polymer matrices by simultaneous CT complex formation and in situ crystallization Polym. Adv. Technol. 3 139–142
[8] Laukhina E, Rovira C, Ulanski J 2001 Organic metals as active components in surface conducting semi-transparent films Synth. Met. 21 1407-8
[9] Laukhina E, Pfattner R, Mas-Torrent M, Rovira C, Veciana J, Laukhin V 2011 Film-based Sensors with Piezoresistive Molecular Conductors as Active Components: Strain Damage and Thermal Regeneration Sensors & Transducers Journal 10 1-12
[10] a) Bridgman P W 1952 Physics of High Pressure G. Bell & Sons Ltd., London, 257, b) Hoffmann K 1987 Einführung in die Technik des Messens mit Dehnungsmessstreifen Hottinger Baldwin Messtechnik GmbH, Darmstadt 62
[11] Laukhin V et al 2011 Prototype for Noninvasive IOP Monitoring with a Nanostructured Polymeric Sensor Embedded in a Contact Lens Sensors and Actuators A 170 36-43
[12] Laukhina E, Lebedev V, Laukhin V, Oncins G, Pfattner R, Rovira C, Veciana J 2011 Lightweight biocompatible physical sensors: polymeric films self-metallized with organic molecular conductors Transducers ’11 Beijing 1978-1981