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Wireless dual stimuli actuation of dye sensitized conducting polymer hybrids

Ambrose Ashwin Melvin#, Bhavana Gupta#, Kostiantyn Tieriekhov, Wojciech Nogala, Patrick Garrigue, Stephane Reculosa, Alexander Kuhn*

Dr. A. A. Melvin, Dr. B. Gupta, K. Tieriekhov, P. Garrigue, Dr. S. Reculosa, Prof. A. Kuhn

Univ. Bordeaux, ISM, CNRS UMR 5255, Bordeaux INP, ENSCBP, 16 Avenue Pey Berland, 33607 Pessac, France.

E-mail: kuhn@enscbp.fr

Dr. B. Gupta, Dr. Wojciech Nogala

Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

#A. A. Melvin and B. Gupta contributed equally to this work

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Actuators controlled by external stimuli have received a lot of attention in recent years. Herein we report a polymer based dual stimuli actuator, triggered by light and an electric field. This allows a better control of actuation, enlarging the field of potential applications, like e.g. in the frame of soft robotics. The actuator is composed of polypyrrole (PPy) and TiO₂ modified with methylene blue (MB). In aqueous solution, the resulting freestanding hybrid film shows reversible actuation due to the synergy of light and an applied electric field. Illumination with light produces electron-hole pairs in the TiO₂ layer, which are shuttled to the opposite ends of the actuator by the potential gradient present in solution. This results in electrochemical oxidation and reduction reactions at the two extremities and consequently in site selective swelling of the polymer, which finally leads to a controlled motion of the actuator, following the principles of logic gate operations. Such synergistically induced switching allows developing original actuation schemes for performing complex mechanical tasks triggered by more than one stimulus.

1. Introduction

Actuation of soft materials triggered by external stimuli is a highly relevant and straight forward approach for carrying out mechanical tasks in a controllable way. [1] The actuation mechanism generally relies on some external stimuli such as magnetic or electric fields, light, or the presence of certain (bio)chemical compounds. [2] Among these different stimuli, magnetic fields and optics provide the possibility of a completely wireless mode of action. However, for electric fields, typically a wired connection with a power supply is required, which might severely limit the actuator's degree of freedom. [3] Wireless induction of actuation via electric fields is therefore an interesting challenge in the frame of stimulating the motion of soft materials. Moreover, actuators that can be triggered by more than one stimulus might further increase the control of motion e.g. in the context of soft robotics. However, this requires systems with dual functionality, a feature that is difficult to achieve with a single material. Consequently, there is a need for designing hybrid materials, able to respond simultaneously to more than one stimulus.

Among all the different soft materials, conducting polymers allow straightforward electrochemical actuation in form of bi-layer and tri-layer systems, or structures with differential roughness, leading to an artificial muscle type behavior.[4] Recent reports have demonstrated the possibility of electrochemical actuation of these polymers in a wireless mode, based on the concept of bipolar electrochemistry, opening up various potential applications.[1d, 3a, 5] In this approach, an electric field is generated in an electrolyte by two feeder electrodes, inducing a polarization potential difference along the polymer object, eventually causing electrochemical reactions at its extremities. At one end of such a bipolar object, electrons are collected by an oxidation reaction and can be used at the other end for carrying out an electrochemical reduction reaction. Depending on the initial oxidation state of the polymer, one or the other extremity starts shrinking or swelling due to the release or incorporation of counter ions. This induces a deformation of the polymer, constituting the basis for the electromechanical actuation. The initial trigger is still of physical nature (electric field), but leads finally to a chemical effect, via spatially separated reduction and oxidation reactions occurring on one and the same object. This breaking of symmetry of the chemical system finally results in the observed actuation. Since this concept of bipolar actuation depends on charge generation and separation, it is interesting to integrate a second material in the system, which allows formation of additional charge carriers in the polymer in the presence of light. This not only decreases the energy required for bipolar actuation, but also helps with the recovery of the initial actuator position when switching off the electric field, and thus enables its reversible cyclic operation.

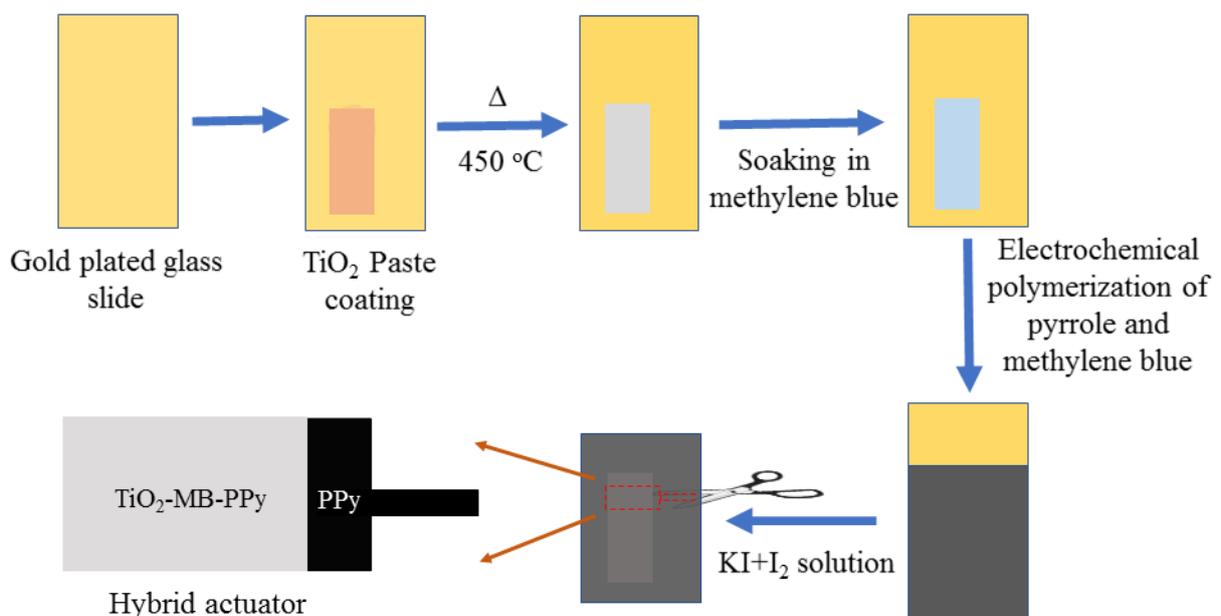
Light induced charge separation is widely known in the case of semiconductors, and is e.g. used in the context of photocatalysis with materials such as TiO₂, ZnO and BiVO₄. [6] Among these materials, TiO₂ is highly robust and often adopted due to its easy synthesis, stable nature and efficient charge separation, but its activity spectrum is limited to UV light. [7] Combinations of such inorganic semiconductors with conducting polymers in the form of nanocomposites have been examined for various applications, especially for photo- and electrocatalysis. [8] However, it is still a challenge to incorporate such semiconductors in a freestanding thin film of conducting polymer, which is a key requirement for designing actuators that can respond simultaneously to an electric field and light. In order to further increase charge generation and to extend the wavelength range, impregnation of such semiconductors with dyes has been intensively studied. [9]

In this contribution we report the synthesis of a freestanding TiO₂-methylene blue-polypyrrole (TiO₂-MB-PPy) hybrid film by electrochemical polymerization of pyrrole on a pre-annealed thin TiO₂ film. The hybrid film can then be used for wireless actuation, triggered by the synergy between an external electric field and light, based on the concept of bipolar electrochemistry. Efficient actuation

only occurs when both stimuli cooperate, whereas electric field or light alone do not induce a response. Thus, the bipolar operating principle can be considered as an analog of a logic AND gate with an electromechanical readout signal.[10]

2. Results and discussion

The main challenge of the work is to design a flexible material which is simultaneously sensitive to light and to the presence of an electric field. In order to synthesize such a hybrid structure in which TiO₂ is strongly linked to the polypyrrole matrix, we followed the strategy illustrated in Scheme 1. After casting TiO₂ paste on a gold coated glass slide and subsequent annealing, polypyrrole is electrogenerated inside the pores of the methylene blue impregnated TiO₂ surface. As methylene blue also polymerizes by oxidative polymerization, there is the possibility of poly(methylene blue) formation along with polypyrrole formation ($E_{ox}(Py) = 0.6 \text{ V vs Ag/AgCl}$ $E_{ox}(MB) = 0.65 \text{ V vs Ag/AgCl}$). [11] After complete polymerization, the hybrid system is immersed into a solution containing a mixture of KI and I₂ which allows dissolving the gold layer. [12] This liberates a free standing hybrid film which is sensitized with methylene blue.



Scheme 1. Illustration of the sequential steps for the synthesis of a freestanding hybrid TiO₂-MB-PPy actuator.

The surface morphology of the hybrid TiO₂-MB-PPy film was characterized by Scanning Electron Microscopy (SEM). At the border between the TiO₂-methylene blue modified part and the pure PPy (Figure 1a) one can distinguish two different morphologies. The brighter left part corresponds to the semiconductor having a rather rough surface (Figure 1b), whereas the darker region on the right is the PPy film with a very smooth morphology (Figure 1c).

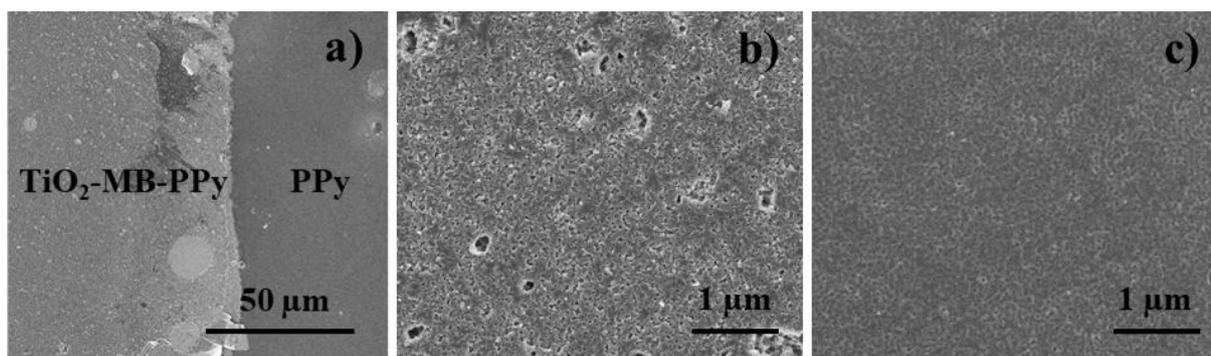
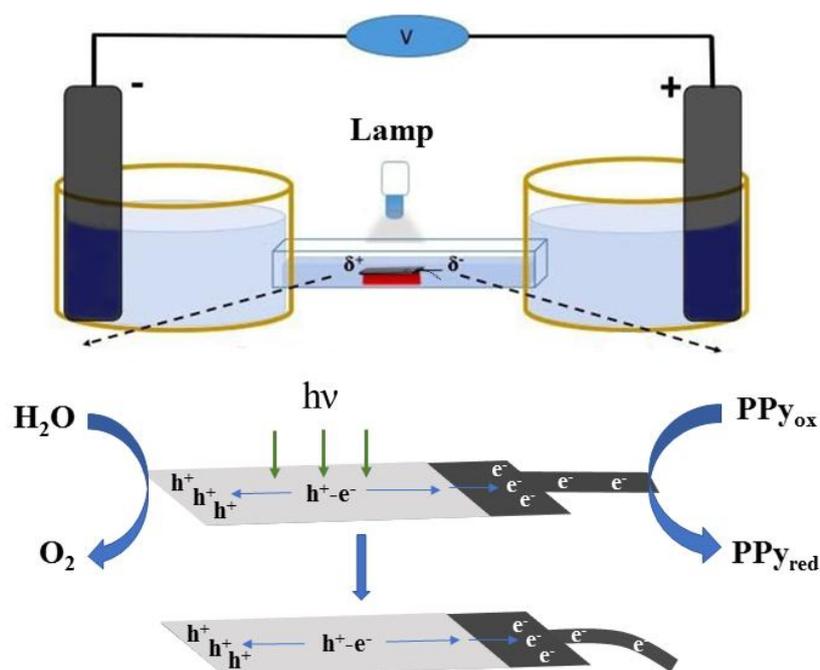


Figure 1. Top view SEM images of a TiO₂-MB-PPy actuator a) Junction between TiO₂-MB-PPy (left) and PPy (right); zoom on the b) TiO₂-MB-PPy and c) PPy domains.

The resulting hybrid film can then be integrated in a bipolar electrochemical cell as shown in Scheme 2. It is acting as a bipolar electrode when placed in the center of the cell with the TiO₂-MB-PPy surface facing upwards, while the bottom side is fixed on an inert support (indicated in red). The extremity of the bipolar electrode, which is only composed of PPy, is not fixed on any support, so that it can undergo mechanical deformation and act as a kind of cantilever. The opposite TiO₂-MB-PPy extremity is about five times broader, which helps concentrating the excited electrons from the conduction band of the semiconductor in the smaller actuating PPy part, and thus amplifies the electromechanical deformation. As soon as an electric field is applied, the polymer gets polarized with respect to the solution potential, leading to a δ^+ and δ^- extremity. This can in principle already trigger an oxidation and reduction reaction at the respective ends of the polymer strip, if the magnitude of the polarization potential difference is high enough.[1d] However, simultaneous illumination of the semiconductor with light allows enhancing this effect in such a way that electric fields of much lower magnitude can already trigger redox reactions at the opposite ends. The impact of light generates an electron-hole pair in the TiO₂-MB-PPy matrix, and these charge carriers are separated under the influence of the electric field and are driven to the respective extremities where they can induce redox reactions.[13]

Initially, the synthesized PPy film is in a fully oxidized state and loaded with dodecylbenzene sulfonate (DBS) and iodide ions as a result of the electrosynthesis and the treatment with KI/I₂ solution. Consequently, the reduction of the polymer strip at the δ^- extremity leads to a preferential release of iodide ions, due to their smaller size compared to DBS anions, in order to maintain charge neutrality in the film.



Scheme 2. Schematic illustration of TiO₂-MB-PPy actuation in a bipolar electrochemical cell under the influence of electric field and light. The electric field is imposed by two graphite feeder electrodes and generates a δ^+ and δ^- polarization at the two extremities of the hybrid actuator. The simultaneous impact of light facilitates the generation of charge carriers which are then separated by the electric field. The induced redox reactions at the two extremities lead to electromechanical bending.

The two faces of the polymer are not identical in terms of surface roughness. The face which was in contact with the gold electrode during the electrosynthesis is rather smooth, whereas the face which was growing towards the electrolyte has a rougher morphology.[1d] This is a key factor for the directional bending of the actuator because iodide release is more pronounced on the rough face. As the release of anions is accompanied with a volume decrease of the polymer, the rough face starts to shrink much more than the smooth face. Hence, the overall deflection is from the smooth towards the rough face, which means in the present case that the actuator is bending downwards.

Under the simultaneous influence of light, additional charge carriers are generated, which can be used for the bipolar electrochemical reactions at the two extremities of the actuator (Figure 2). The first and most important advantage of these additional charges is a decrease in the amplitude of electric field required for bipolar electromechanical actuation. A similar effect has been reported in the case of actuation induced by chemical and enzymatic reactions.[3a] In comparison to an actuator made out of pure PPy, the TiO₂-MB-PPy device starts actuating at a significantly lower electric field (Supporting information Video S1), i.e. at already 1.2 V/cm (Figure 2d), whereas an actuator purely based on PPy does not show any deformation for the same electric field (Figure 2b). Electric fields of at least 1.5 V/cm are necessary in the latter case to observe significant bending. Furthermore, the magnitude of deformation of a TiO₂-PPy based actuator is much smaller (one third) (Figure 2c) compared to its methylene blue modified analog (Figure 2d). This illustrates the importance of MB for efficient light collection and an increase of the charge separation in TiO₂. [14] As shown in Figure S1, actually in the presence of MB it is possible to extend the spectrum of light wavelength that can be collected by the hybrid material. TiO₂ alone only produces photocurrent at rather short

wavelengths, whereas once MB is present, even quite long wavelengths (>600nm) still contribute to a significant generation of charge carriers. This allows their subsequent transfer to PPy, where they are collected and used for the electrochemical reactions under the influence of the external electric field, analog to what has been reported also for other systems.[13] Such a charge separation, where charges move to their respective extremities due to the polarization by the global electric field is absolutely crucial for efficient actuation. This is supported by the fact that when only electric field (input I) is applied, without irradiation, the TiO₂-MB-PPy hybrid is completely inactive (Figure 2e). On the other hand, applying only light (input II), doesn't lead to actuation either (Figure 2f). This means that efficient actuation is the result of the synergy of both, electric field and light. Therefore, the functionality of this system follows the operation principles of a logic "AND" gate.

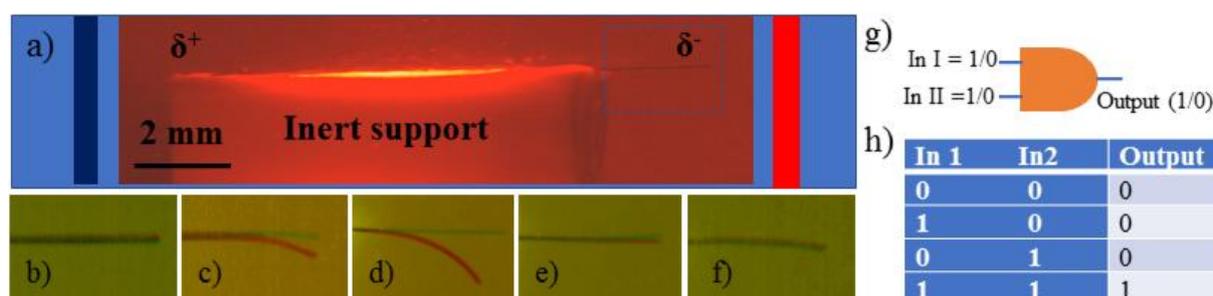


Figure 2. a) Experimental set up of wireless electromechanical actuation under the influence of an electric field and light. The actuator is positioned on an inert support in a solution between two feeder electrodes (red: anode; blue: cathode) and exposed to light; b) Pure PPy actuator c) TiO₂-PPy actuator d) TiO₂-MB-PPy actuator; e) the TiO₂-MB-PPy actuator only exposed to the electric field f) or only irradiated with light. The electrolyte is 0.5 M Na₂SO₄ with an electric field of 1.2 V/cm. The dotted rectangle indicates the area of the zoom made for images b)-f); green and red indicate the initial position of the actuator and after bending, respectively. All images were recorded after 60 sec of exposure. g) and h) are the AND logic gate and the truth table respectively, summarizing the results obtained for the TiO₂-MB-PPy actuator. Input I and Input II are the electric field and light and the resulting output is the actuation.

In order to further understand this dual stimulus effect, we studied in more detail the influence of the light intensity, keeping all other experimental conditions constant (shape and composition of the bipolar electrode, light source distance, electrolyte concentration, readout time and electric field). As illustrated in Figure 3 a-d, the light intensity has a strong impact on the degree of deflection, and actually seems to follow an almost linear correlation (Figure 3e).

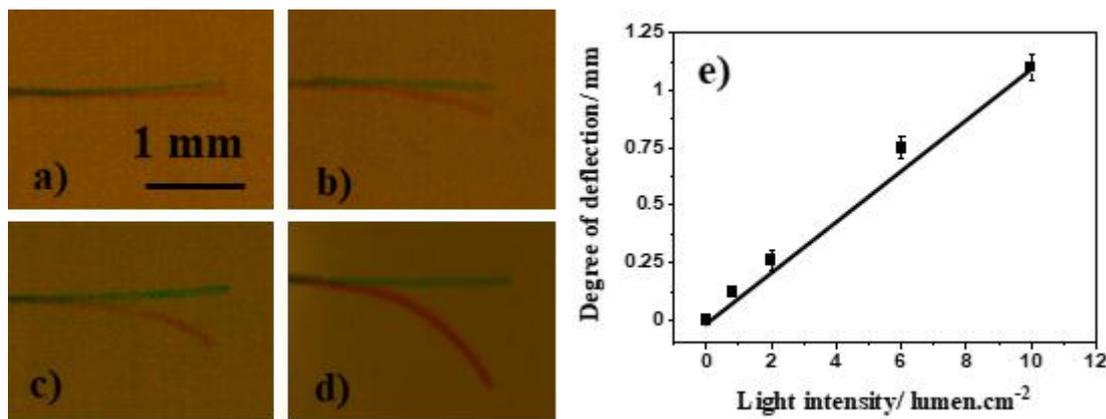


Figure 3. Effect of light intensity on electromechanical deformation of a TiO₂-MB-PPy actuator a) 0.8 b) 2 c) 6 and d) 10 lumen.cm⁻² light intensity; e) Calibration curve of the degree of deflection as a function of light intensity. The electrolyte is 0.5 M Na₂SO₄ with an electric field of 1.2 V/cm for all the experiment. All images were recorded after 60 sec of exposure.

A higher light intensity increases the amount of charge carriers,[15] which then get separated under the influence of the electric field. The overall time required to reach maximum bending under these conditions is 60 sec. After 60 sec the shape of the polymer remains stable or only shows insignificant actuation. When slightly decreasing the electric field, the polymer can reach almost the same degree of bending, but the required time increases significantly. Applying 1.0 V/cm, doesn't lead to significant actuation, even after more than 2 min. We conclude that there is a threshold value for the electric field in order to ensure efficient charge separation, most likely related to the internal resistance of the hybrid actuator.

In order to investigate the reversibility of actuation, the polarity of the feeder electrodes was switched. During electrochemical reduction the polymer tends to bend downwards, while during oxidation the actuator tries to recover its original position after switching the polarity of the feeder electrodes. The reduced state of polypyrrole is an unstable state. Therefore, the recovery process, involving oxidation of the reduced polymer, is easier from an energetic point of view, because the oxidized state is thermodynamically more favorable. In contrast, the energy which is required to reduce it back from its oxidized state is higher.[16] Consequently, polypyrrole bends downwards at 1.2 V/cm as an effect of reduction in the presence of both, electric field and light. However, during recovery, only an electric field of 1.2 V/cm with inverted polarity of the feeder electrodes without light is sufficient, as shown in Figure 4a and 4b (Supporting information Video S2). At the opposite extremity, where oxygen was produced in the forward cycle, there needs to be now a reduction reaction. This can involve either oxygen, which is anyway dissolved in the surrounding solution, or also reduction of protons to hydrogen. However, it is rather difficult to estimate the relative contribution of both reactions.

Importantly, reversible actuation was found to be possible for multiple cycles. Consequently, this reversibility might be interesting for switching functions. Redox changes in conducting polymers have already been exploited for using them as electrochemical switches in electrical circuits.[17] In contrast to these interesting previous approaches, the polymer composite can be used in the present work as a wireless switch. In order to illustrate this feature we integrated the actuator in an electronic circuit comprising a light emitting diode (LED). For this the actuator is placed in the bipolar

cell and the cell is filled with electrolyte up to a level where the surface of the polymer is just slightly immersed. The cantilever size is slightly bigger in comparison to the previous experiments i.e. 5 mm. Two needles acting as the contact terminals of the electronic circuit are positioned at the respective extremities of the actuator (Figure 4c). Needle 1 is immersed in the liquid and touches the broader section of the bipolar object, while needle 2 is kept just above the polymer cantilever, not touching the liquid in order to avoid short-circuiting.

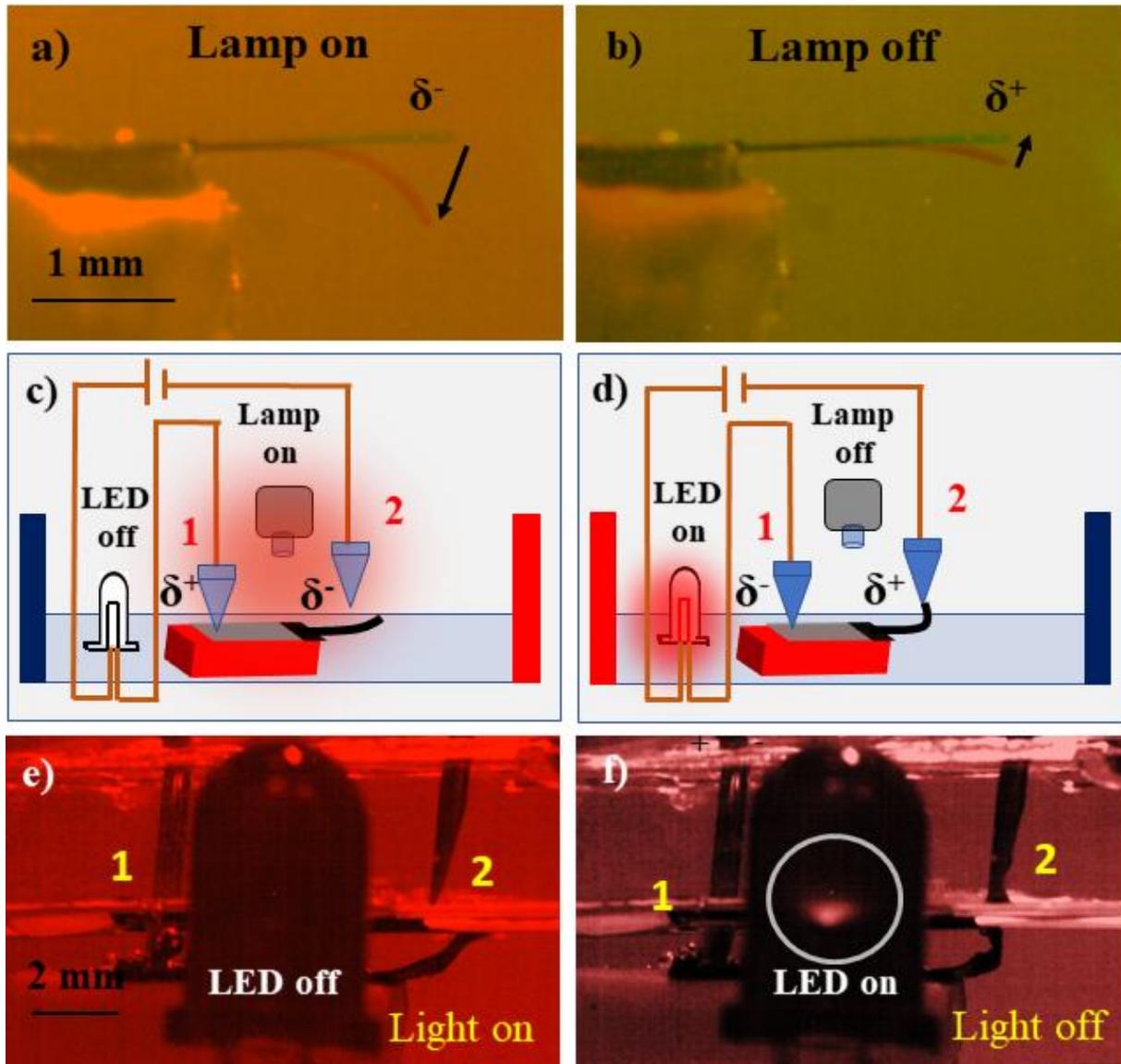


Figure 4. Reversible actuation and its use as a switch. a) and b) reversible actuation of TiO₂-MB-PPy by changing the polarity of the feeder electrodes under illumination and in the dark. Arrows represent the direction of bending. Schematic illustration of the set-up using the hybrid polymer as a wireless electric switch c) in the “off” state in the presence of an electric field combined with illumination and d) in the “on” state in the presence of an external electric field of opposite polarity in the dark; e) and f) are the corresponding pictures of the experiment. 1 and 2 indicate the positions of the two needles acting as connectors of the electric circuit.

The right extremity of the cantilever has been slightly folded mechanically before the experiment in order to facilitate its crossing of the air/water interface during actuation (Figure 4c). In this way the cantilever can break the surface tension of the liquid while starting to bend and touch needle 2 just above the liquid and closes the external circuit. This will result in the switching-on of the LED in the external circuit (Figure 4d). Upon simultaneous electrochemical polarization and illumination with light, the actuator tends to move downwards away from the needle 2. This opens the electronic circuit and the LED switches off as illustrated in Figure 4c and 4e. However, when the light is switched off again and the polarity of the feeder electrodes is inverted, the actuator moves back in the upward direction due to its δ^+ polarization, thus restoring the connection with needle 2. The closing of the external circuit not only allows the LED to glow (Figure 4d and 4f), but also induces water splitting at the tips of needle 1 and 2, visualized by the formation of small gas bubbles (Supporting information Video S3).

3. Conclusion

In conclusion, we have successfully demonstrated a dual stimuli effect, based on the synergy of an electric field and light, for the wireless actuation of a hybrid polypyrrole-TiO₂ actuator, mimicking the operation of a logic AND gate. The actuation efficiency can be optimized by adding a dye sensitizer, as well as by adjusting the light intensity and the electric field. The amplitude of actuation is directly correlated with the light intensity, and reversibility can be achieved by controlling the electric field polarity. The stimulated deformation can be used to design a wireless switch, illustrated by the on/off operation of an electronic circuit comprising a LED. The concept might enable the development of multifunctional actuators e.g. in the frame of soft robotics or biomimetic devices.

4. Experimental Section

4.1 Materials: Pyrrole, methylene blue and sodium dodecylbenzenesulfonate were purchased from Sigma-Aldrich. Na₂SO₄ was purchased from Agar scientific. TiO₂ paste was purchased from Solaronix Ltd. All solvents used for the experiments are of analytical grade.

4.2 Synthesis of the hybrid actuator: For the synthesis of the hybrid actuator, gold plated glass (gold thickness 300 nm) slides were modified with TiO₂ paste (50 % diluted in ethanol) in a specific area (2.5 x 0.5 cm) by using the doctor blade approach. The resulting thin film was annealed at 450 °C for 1 hr and subsequently dipped in a methylene blue solution (0.05 wt. % in isopropanol) for 1 hr. After soaking the TiO₂ with the dye, the gold coated glass substrate was washed to remove extra dye and dried. In the next step, polypyrrole was electrogenerated on the so-obtained surface. A solution of pyrrole monomer (0.2 M) and dodecylbenzene sulfonate (0.25 M) was prepared in ultrapure water (Milli-Q station, resistivity 18.2 M Ω .cm at 25 °C). After complete dissolution of the two chemicals, the substrate was dipped in a beaker containing 12 mL of precursor solution and used as working electrode. Another gold coated glass of the same size was positioned parallel to the working electrode at a distance of 1.5 cm and used as a counter electrode with Ag/AgCl as reference electrode. A current of 4.0 mA (Potential of the working electrode around 0.7-0.75 V) was applied for 1.5 h to carry out the pyrrole polymerization with the help of a potentiostat/galvanostat (AUTOLAB PGSTAT 204 from Metrohm using the NOVA 2.1.4 Software). After completion, the polymer coated substrate was kept in a KI + I₂ solution overnight for the dissolution of gold, thus enabling the removal of the hybrid film. The recovered freestanding hybrid film was then washed with water and dried. SEM experiments were performed using a Hitachi TM-1000 tabletop microscope. Photo-

electrochemical measurements of the TiO₂ and TiO₂-methylene blue films immobilized on an ITO coated glass slide were carried out by chronoamperometry in 0.5 M Na₂SO₄ at a voltage bias of 0.25 V and under light irradiation with a LED (pE-300white) equipped with shamrock filters.

4.3 Dual stimuli based bipolar actuation: For light induced bipolar electrochemical actuation, the different types of actuator films i.e. PPy, TiO₂-PPy and TiO₂-MB-PPy (1.1 cm length) were fixed in the center of the bipolar cell on an inert support. Here the cantilever size is 5 mm. Two graphite feeder electrodes were positioned at the extremities of the cell (5 cm apart) to apply the electric field (HP 6438B DC Power Supply from Hewlett-Packard). 0.5 M Na₂SO₄ was used as supporting electrolyte to provide a sufficient number of ions for charge compensation in the conducting polymer during bipolar actuation. UV-Vis light (LEICA CLS 150 LED) was used for the actuation. The bending of the polymer strip was recorded with a macroscope (LEICA Z16 APO) in video mode.

4.4 Actuator as an electric switch: An electric switch is designed by using the bipolar electrode as a connector between two needles 1 and 2. The two needles act as terminals of an electric circuit comprising a light emitting diode (LED). The connection between needle 1 and the bipolar electrode is fixed. However, the mobile part of the bipolar electrode is designed with a folded arm, obtained by mechanically bending the extremity of the polymer. During actuation, this helps establishing a connection with needle 2, which is positioned just above the air/electrolyte interface. It is important that needle 2 is outside of the electrolyte; otherwise the electrolyte solution will act as a conductor and close the external electric circuit, resulting in a switching-on of the LED. An electric field is applied and its polarity is switched every 10 s. When the bipolar electrode in the electrolyte moves downwards due to the dual stimulus by light and the electric field, connection with needle 2 is lost and the LED switches off. Upward movement of the bipolar electrode extremity towards needle 2 is achieved by inverting the orientation of the electric field. Once the bipolar electrode establishes again the contact with needle 2 it closes the circuit and the LED switches on again.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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A hybrid film, based on the combination of polypyrrole and dye-sensitized TiO₂, is proposed as an actuator, stimuable by the simultaneous interaction with light and an electric field. This synergy allows wireless electromechanical actuation, which can be used as a switching mechanism in an electric circuit, and mimics a logic AND gate.

A. A. Melvin#, B. Gupta#, K. Tieriekhov, W. Nogala, P. Garrigue, S. Reculosa, A. Kuhn*

Wireless dual stimuli actuation of dye sensitized conducting polymer hybrids

