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A Bacterial Photosynthetic Enzymatic Unit Modulating Organic Transistors with Light

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The photochemical core of every photosynthetic apparatus is the reaction center, a transmembrane enzyme that converts photons into charge-separated states across the biological membrane with an almost unitary quantum yield. A light-responsive organic transistor architecture, which converts light into electrical current by exploiting the efficiency of this biological machinery, is presented. Proper surface tailoring enables the integration of the bacterial reaction center as photoactive element in organic transistors, allowing the transduction of its photogenerated voltage into photomodulation of the output current up to two orders of magnitude. This device architecture, termed light-responsive electrolyte-gated organic transistor, is the prototype of a new generation of low-power hybrid bio-optoelectronic organic devices.

Evolution has engineered multi-protein complexes to efficiently convert solar radiation into chemical energy,[1] sustaining the energy needs of life on planet Earth via the photosynthetic process. These photoenzymes catalyze the uphill conversion of oxidized molecules to their reduced forms, using light as the energy source. Photosynthetic organisms, such as plants, algae, and some bacteria are the sole kind of organisms on the planet able to harvest and store energy.[2] The photosynthetic anoxygenic bacteria possess a photosynthetic apparatus based on a single functional unit, the reaction center (RC), which converts photons into charge-separated states across the membrane with unmatched quantum yield.

Rhodobacter sphaeroides (R. sphaeroides) is a purple non-sulfur bacterium, whose RC is a three-subunit transmembrane protein sitting within the photosynthetic membrane.[3] Light impinges a cascade of electron transfer reactions that forms the hole–electron couple with a unitary quantum yield.[4] In the absence of exogenous electron donors and acceptors, this state does not evolve further and has a lifetime ranging from 100 ms to 3 s[5] (Figure S1, Supporting Information).

This highly efficient photoconverting architecture has spurred numerous mimicking attempts such as photoactive molecules called triads,[6] carefully designed molecular architectures,[7]

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The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/aelm.201900888.

DOI: 10.1002/aelm.201900888

or the very sophisticated artificial leaf.[8] Recently, bio-hybrid systems encompassing an RC coupled with organic moieties were shown to be efficient transducers of solar radiation.[9–11] RC-based bio-hybrids have been demonstrated in bio-optoelectronics,[12,13] functionally integrated onto devices,[14,15] and exploited as active elements in bio-photonic power cells.[16] Here we report the integration of bacterial RC as photoactive element in electrolyte-gated organic transistors (EGOTs), obtaining photoresponsive bio-hybrid EGOT devices.

EGOTs (**Figure 1**A), featuring a semiconductive channel exposed to an electrolyte whose potential is fixed by a gate electrode, have been demonstrated as sensors for the quantification of bio-markers,[17,18] ionic and molecular analytes,[19,20] and as transducers of bioelectrical signals.[21,22]

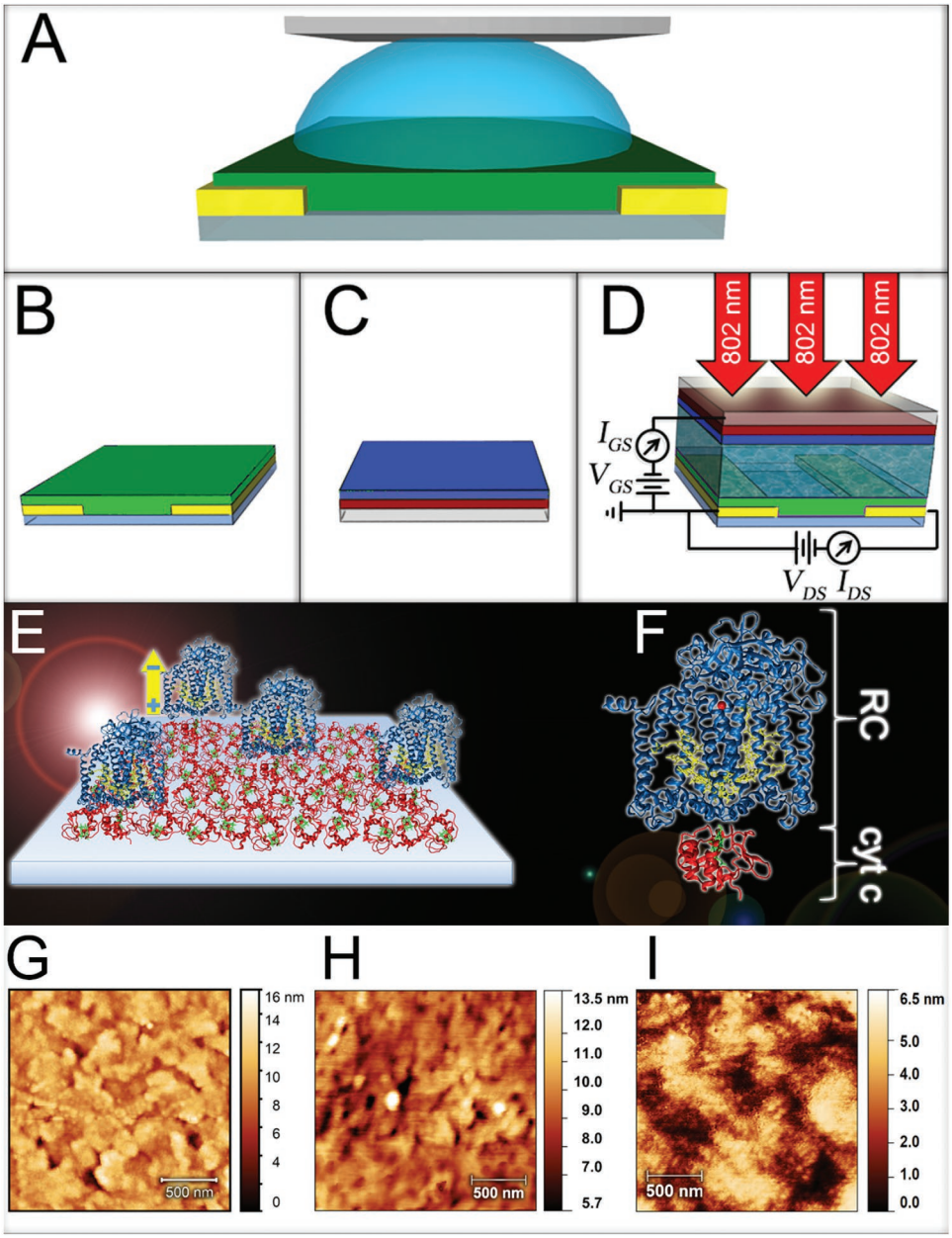

Figure 1. A) Conceptual scheme of a generic top-gate bottom-contact EGOT device, showing gold source and drain electrodes (yellow) patterned on a substrate (grey), and bridged by a semiconductor thin-film (green). The channel is exposed to an electrolyte solution, whose potential is fixed by a metallic plate (light grey). Schematic representation of the functional units of LEGOT: B) transduction element, featuring the channel of an EGOT with source and drain contacts; C) light-sensitive element, made of a transparent ITO gate electrode (grey) coated with cyt (red) and RC (blue); D) final LEGOT layout with transducing and light-sensitive elements coupled by the electrolyte solution, with sketched illumination path and electrical connections. E) Oxidized form of cyt is deposited by drop-casting on the ITO surface; RC is successively deposited by drop-casting on top of the cyt layer; the orientation of the photoinduced dipole is highlighted (yellow arrow). F) Crystallographic structure (PDB 1L9B) of the complex cytochrome c-RC.[34] 2 μm × 2 μm atomic force microscopy topographies of G) bare ITO, H) ITO with cyt , and I) ITO with cyt and RC.

A prototypical bio-organic EGOT, light-gated by means of the photosynthetic RC from *R. sphaeroides*, is presented and termed light-responsive electrolyte-gated organic transistor (LEGOT).

In the most studied EGOT architectures, namely the electrolyte-gated organic field-effect transistor (EGOFET) and the organic electro-chemical transistor (OECT), the application of a gate bias with respect to the grounded source electrode, V_{GS}, drives ions from the electrolyte toward the organic active materials. This ionic redistribution causes accumulation or depletion of charge carriers in the semiconductive channel, thus modulating the transistor current, I_{DS}, driven by the drain–source bias, V_{DS}. The gating capacitance in EGOTs is large,[23,24] hence small variations of the charge distribution at the gate/electrolyte interface result in large I_{DS} variations, therefore EGOT sensors usually rely on gate functionalization.[25–27]

LEGOT, accordingly, exploits photogenerated charge redistribution to modulate I_{DS}.

In LEGOT, RC is adsorbed on an indium tin oxide (ITO) gate electrode and the channel is either a solution processed 6,13-bis(triisopropylsilylethynyl) pentacene (TIPS-P5) layer or a printed poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) film, for EGOFET and OECT architectures, respectively. The device is depicted in Figure 1B–D.

The RC photoconversion ability is driven by the efficient absorption of photons in the range 250–950 nm,[28,29] in particular in the near-IR (NIR) range. Since both active materials are NIR transparent,[30,31] NIR excitation allows to unambiguously ascribe photoinduced effects to the sole RC.

The major issue in the deposition of RC on ITO gate is the random orientation of light-generated dipoles,[32,33] which would result in null net potential variation. Control of RC orientation, a compulsory requirement to provide an additional gating effect, can be obtained by casting a layer of oxidized horse heart cytochrome *c* (cyt) on the ITO surface. Cyt is a redox protein that, in its reduced form, acts as physiological electron donor to the photogenerated hole within the RC. This transfer requires binding of the cyt to the specific docking site on the RC periplasmic face,[34] arising from purely electrostatic interactions and independent of the redox state of the cyt.[35] In its oxidized form, cyt can be used to preferentially orient the RC on the surface of the ITO gate, albeit avoiding faradaic currents associated with electron transfer reactions.

This approach has been exploited in LEGOT light-sensitive unit, by casting a layer of oxidized cyt onto the ITO gate, prior to RC deposition, to induce an orientation of the photoenzyme, as shown in Figure 1E.

The process was monitored via atomic force microscopy, Figure 1G–I, showing the formation of a compact layer of cyt (Figure 1H) and the presence of RC aggregates onto the cyt matrix after the two consecutive deposition steps (Figure 1I).

Light-sensitive unit was characterized by surface photovoltage spectroscopy, monitoring the surface potential at different wavelengths. The normalized photovoltage spectrum, shown in **Figure 2**, exhibits close similarity to the absorption spectrum of the RC. Surface potential has been further investigated by means of chronopotentiometry, in light–dark cycles (λ = 802 nm), as shown in **Figure 3**A. Upon illumination, the light sensitive unit potential negatively shifts ($\Delta V = 55 \pm 9$ mV) on a relatively slow timescale ($\tau = 18 \pm 5$ s), longer than the normal lifetime of the hole–electron couple (between 100 ms and 3 s). This is due to the accumulation, induced by continuous illumination, of usually negligible transient species in the RC having much longer lifetime. The relative weight of these slower phenomena is artificially increased when the experimental setups have a lower collection rate than the fast component of the recombination time.[36]

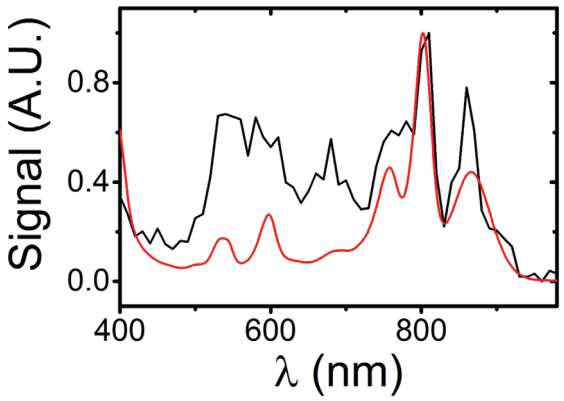

Figure 2. Absorption spectrum of RC in solution (red) and normalized photovoltage spectrum of the light-sensitive unit of the EGOT (black).

For LEGOT characterization, transfer characteristics have been acquired continuously. During acquisition, the light excitation source has been switched ON and OFF every 200 s. The time evolution of transfer characteristics is reported in Figure 3B,C for TIPS-P5 and PEDOT:PSS devices, respectively.

In both cases, the light-induced negative gate potential shift results in higher current upon illumination, although the rationale is different. In accumulation EGOFET, a more negative gate potential causes larger (negative) currents, inducing more holes in the semiconductive channel. In depletion OECT, the current increase is ascribed to the decreased positive gate voltage, which injects a smaller amount of cations in the semiconductive channel. In EGOFETs, the negative chronopotentiometric shift results in a positive shift of the threshold voltage, V_{th} ($\Delta V_{th} = 52 \pm 3$ mV, Figure 3D). These trends are confirmed by the output characteristics of both architectures (Figure S3, Supporting Information).

This phenomenon allows to modulate the device response by the sole use of light. In the dark, a V_{GS} of –0.5 V, less negative than V_{th}, does not turn the device ON. Upon illumination, V_{th} is crossed and the device responds with a 20-fold current increase, Figure 3E. The analogous experiment in OECTs, Figure 3F, shows a current increase as high as 25 µA upon illumination. Noticeably, the current responses in EGOFET and OECT (Figure 3E,F) show different temporal evolutions. This may be ascribed to the different gating mechanisms of the two architectures, as discussed above: for the accumulation EGOFET, which rely mainly on interfacial processes, a faster doping/de-doping kinetic is observed with respect to the depletion OECT, in which cations have to physically leave/penetrate the PEDOT:PSS bulk. This trend is mirrored by the time evolution of leakage currents (Figure S3, Supporting Information).

At 802 nm only RC exhibits significant absorption,[3,29–31,37,38] hence the observed phenomena are due to the additional gating effect of photogenerated oriented dipoles at the gate/electrolyte

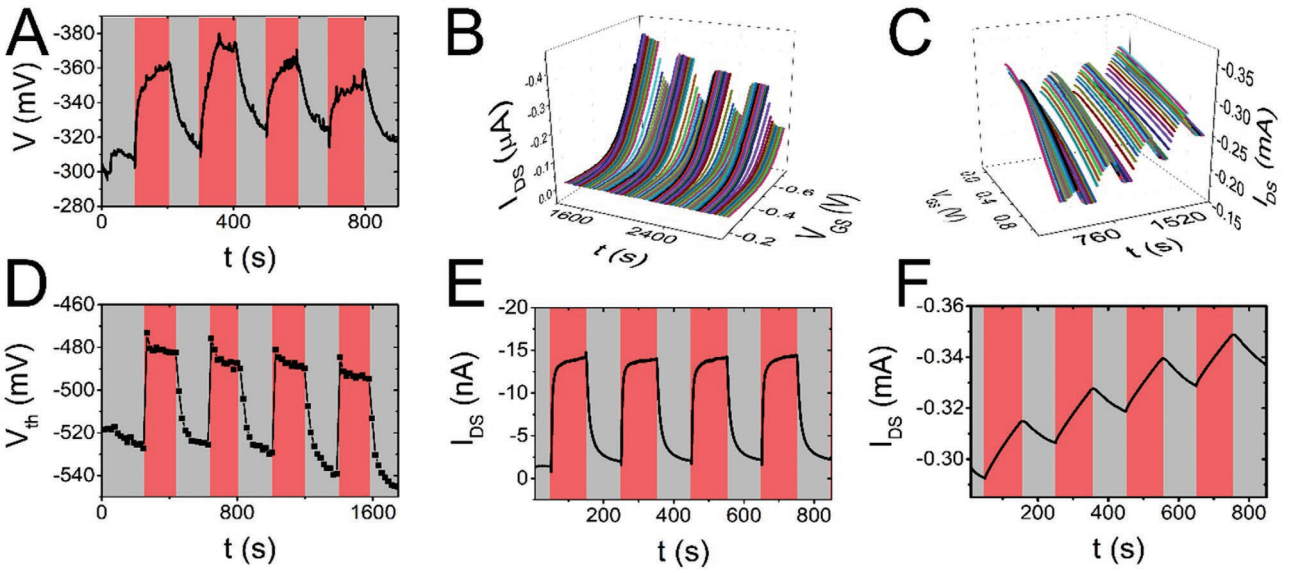

Figure 3. A) Chronopotentiometry of the light-sensitive element. Illumination with an NIR (λ = 802 nm) LED negatively shifts the electrode potential. I_{DS} versus V_{GS} versus time plots showing evolution of transfer characteristics of B) TIPS-P5 and C) PEDOT:PSS devices upon dark–light cycles. D) Threshold voltage of TIPS-P5 EGOT. E) I_{DS} versus t plot of TIPS-P5 EGOT (V_{DS} = –0.5 V, V_{GS} = –0.5 V). F) I_{DS} versus t plot of PEDOT:PSS EGOT (V_{DS} = –0.5 V, V_{GS} = 0.3 V).

interface. This additional unscreened negative charge distribution at the gate shifts its electrochemical potential and modulates the charge carrier density in the semiconductive channel.

In conclusion, building on the EGOT's nature of interfacial charge/voltage amplifiers, RC functionalized EGOTs technologically exploit the transduction capability of the photoenzyme in the NIR, leading to a novel bio-based low-power device, here termed LEGOT, that enables light-powered amplification of current in an aqueous environment.

Experimental Section

TIPS-P5 EGOT Fabrication: Au source and drain interdigitated electrodes were deposited onto quartz substrates by photolithography and lift-off (FBK, Trento, Italy), obtaining a 15 µm long and 7.5 mm wide channel. TIPS-P5 was deposited onto these piraña-etched substrates via spin coating of a 1% w/w solution in a 8:2 mixture of toluene and *n*-hexane and was thermally cured.

PEDOT:PSS EGOT Fabrication: Devices were manufactured by screen printing on PET foils (Polyfoil Bias), thermally treated prior to use (140 °C, 45 min). Silver tracks and carbon contact pads were printed using Ag5000 silver ink (DuPont, UK) and a commercial carbon ink (C2130307D1, Gwent, UK), respectively. Clevios SV3 PEDOT:PSS ink (Heraeus Group, Germany) was used to print the transistor channel.

Reaction Center Production/Extraction: The RC was isolated and purified from cultured *R. sphaeroides* and its integrity and activity were checked by UV–vis–NIR spectroscopy and by flash-induced absorbance change measurements performed on an instrument of local design.[9,39,40]

Light-Sensitive Gate Fabrication: 4 nmol of horse heart cytochrome *c* (Sigma-Aldrich, CAS: 9007-43-6) in phosphate 20 mM, Triton X-100 0.03%, EDTA 1 mM buffer (pH = 8) were drop-cast onto ITO. After drying, 0.73 nmol of RC in the same buffer were casted, to a final ratio of 5.5 cyt:RC.

Photovoltage Spectroscopy: Photovoltage spectra were acquired in a home-built setup (Figure S2, Supporting Information).

Chronopotentiometry: V versus t curves were acquired using a CHI760C potentiostat in a two-electrode configuration, using the light-sensitive unit as working electrode.

LEGOT Characterization: Electrical measurements were performed using a Source-Measure Unit (Agilent-B2912A) and a custom designed software, in common ground configuration, in a 20 mM phosphate buffer (pH = 8). NIR excitation has been provided using an Osram LED (802 nm, 2.1 W).

Control Experiments: See Figure S4, Supporting Information.

Supporting Information

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

Acknowledgements

M.D.L. and S.I.G. contributed equally to this work. The authors would like to acknowledge Ms. Marie Nilsson and Mr. Lorenz Theuer for design and fabrication of the PEDOT:PSS channel. The authors would also like to acknowledge EuroNanoMed-III AMI project, Life Science Department of UNIMORE through "FAR 2015," Marie Curie ETN project iSwitch (GA No. 642196), Swedish Foundation for Strategic Research (Smart Intra-Body Network; grant RIT15-0119), and EU project 800926 (HyPhOE) for funding.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

biophotonics, electrolyte-gated organic field-effect transistors, near-infrared light conversion, organic electro-chemical transistors, photosynthetic reaction centers

Received: August 16, 2019
Revised: October 16, 2019
Published online: November 29, 2019

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