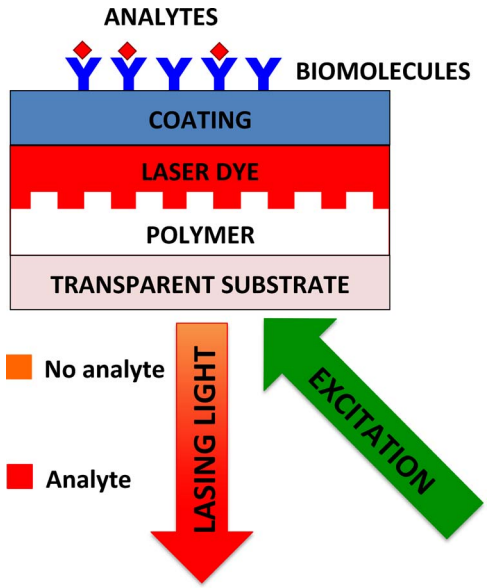
IEEE Photonics Journal
An IEEE Photonics Society Publication

Open Access
Invited Paper

Breakthroughs in Photonics 2012: Breakthroughs in Organic Photonic Sensors

Volume 5, Number 2, April 2013

F. Scotognella
G. Lanzani
M. R. Antognazza



DOI: 10.1109/JPHOT.2013.2252331
1943-0655/$31.00 ©2013 IEEE

IEEE photonics SOCIETY

IEEE

Breakthroughs in Photonics 2012: Breakthroughs in Organic Photonic Sensors

F. Scotognella,[1] **G. Lanzani,**[1,2] **and M. R. Antognazza**[2]

(Invited Paper)

[1]Politecnico di Milano, Dipartimento di Fisica, Piazza L. da Vinci 32, 20133 Milano, Italy
[2]Center for Nanoscience and Technology@PoliMi, Istituto Italiano di Tecnologia, 20133 Milano, Italy

DOI: 10.1109/JPHOT.2013.2252331
1943-0655/$31.00 ©2013 IEEE

Manuscript received February 8, 2013; revised March 3, 2013; accepted March 5, 2013. Date of publication March 12, 2013; date of current version May 2, 2013. Corresponding author: F. Scotognella (e-mail: francesco.scotognella@polimi.it).

Abstract: This review highlights results obtained in 2012 in the field of organic photonic sensors for chemical detection and organic photodetectors for bio-inspired and biological applications.

Index Terms: Sensors, organic materials, analyte detection, organic photodetectors, organic bioelectronics, artificial photoreceptor.

1. Introduction

We report here on the progress made in 2012 in the broad field of organic photonic sensors (OPSs). This paper does not intend to be exhaustive of the whole subject but aims at giving an overview of very recent trends in use of organic functional materials for optical sensing. More specifically, we focus our attention on the exploitation of OPSs in two emerging and attractive fields: chemical sensing and coupling to living tissues for biological applications. Section 1 highlights results reported on photonic crystals (PCs), distributed-feedback (DFB) lasers, optical fibers, and molecule-functionalized nanoobjects. Section 2 sheds light on the emerging field of organic bioelectronics, focusing in particular on the realization of photodetectors able to work in a bio-like environment.

2. OPSs for Analyte Detection

2.1. PCs

PCs are the optical analogs of electronic semiconductor crystals since, in these systems, a periodicity in refractive index along one, two, or three spatial dimensions comparable with optical wavelengths generates photonic band gaps, while point, line, bend, and planar defects give rise to intragap states that enable localization, guiding, and trapping of light.

2.1.1. One Dimension

One-dimensional porous PCs are very interesting materials, due to their easy fabrication and their exploitation for many applications, as lasers and switches [1], [2]. For sensing application, the fabrication of 1-D PCs, based on microporous metal–organic framework (MOF) material layers and

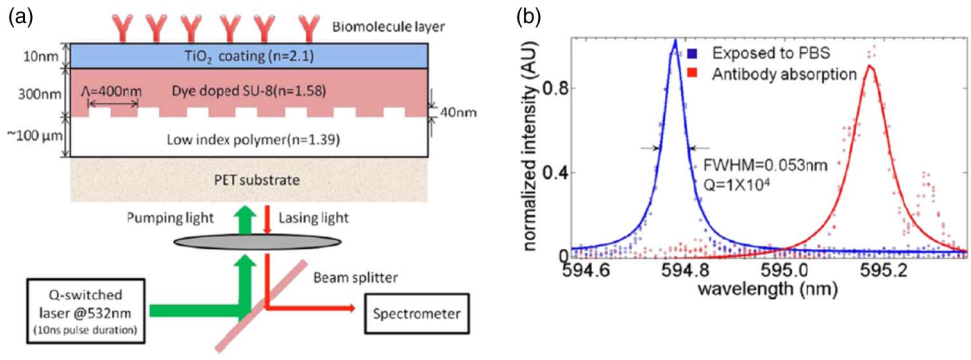


Fig. 1. Schematic of a DFBLB structure (a) and Lorentz fitted spectrum of DFB laser emission. The blue curve was measured when the sensor surface was exposed to PBS, while the red curve shows the laser spectrum after application of the anti-TNF-a capture molecules (reprinted with permission from [7]).

mesoporous titanium dioxide layer, has been shown. The peculiarity of Zeolitic imidazolate framework ZIF-8 is molecular selectivity, while mesoporous TiO_2 has been employed to ensure high refractive index contrast and to guarantee molecular diffusion within the whole PC. Sorption behavior of the photonic material was studied as a function of partial pressure of organic vapors, resulting in a good sensitivity and selectivity toward a series of chemically similar solvent vapors. For methanol vapor, with this sensor, a steep increase in the photonic band-gap shift is already observed at a partial pressure of 0.1 [3].

2.1.2. Two Dimension

Li and Lotsch, in April 2012, showed a stimuli-responsive 2-D PC based on a monolayer inverse opal of polyelectrolyte gel. A remarkable feature of this monolayer inverse opal is that it holds tunable photonic properties despite a submicron thickness. For this reason, the photonic sensing for solutes does not suffer from slow diffusion and the response can be greatly sped up. As P2VP is well known as a weak cationic polyelectrolyte that exhibits fast and substantial swelling under acidic conditions due to protonation of the pyridine group, a pH sensor based on this 2-D photonic structure is demonstrated, showing a band-gap shift of 6, 15, and 29 nm to pH 5, 4, and 3, respectively [4].

2.1.3. Three Dimension

3-D ordered inverse-opal films bearing a reactive trifluoroacetyl group have been successfully constructed. Through the specific reaction between cyanide and trifluoroacetyl, these photonic films can selectively detect, at a submicromolar level, cyanide by a shift of the photonic band gap [5]. Pan *et al.* [6] synthesized a polyacrylamide inverse-opal hydrogel (IOHPAM) film by *in situ* polymerization in a polystyrene colloidal crystal template. The IOHPAM shows periodically ordered interconnecting porosity, giving rise to a photonic band gap (with reflectivity up to 80%). The IOHPAM film exhibits a rapid reversible change, in volume and in refractive index, in response to alcohol. For this reason, the structural color of the IOHPAM film quickly changes with these changes. The reflection peak of the IOHPAM film shows blue or red shifts that depend on the structure of the alcohols. The extent of the shift depends on the number of -OH groups and on chain length, structure, and concentration of the alcohols. Photonic band-gap shifts of several nanometers are observable at 10% methanol solutions. The IOHPAM film is also sensitive to polyethylene glycol (PEG), displaying different blue-shift responses to PEGs with different molecular weights.

2.2. DFB Lasers

DFB lasers are a type of laser where the feedback mechanism is provided by a photonic structure in which the active material is embedded or in close contact.

A process that combines polymer nanoreplica molding with horizontal dipping has been proposed to fabricate large-area (approx. 3×5 in^2) DFB laser biosensors (DFBLBs) on flexible plastic

substrates, which have been subsequently incorporated into standard format 96-well microplates (see [7, Fig. 1]). A room-temperature nanoreplica molding process has been employed to fabricate subwavelength periodic grating structures, while a horizontal dipping process was used to apply a dye-doped polymer film of about 300 nm. The DFBLB emission wavelength, used to characterize the device uniformity, demonstrated a coefficient of variation (CV) of 0.41%. The fabricated sensors have been also characterized for sensitivity uniformity by measuring the bulk refractive index of the media exposed to the sensor surface and by measuring adsorption of biomolecular layers. An assay for detection of the cytokine Tumor Necrosis Factor-alpha (TNF-α) has been used to demonstrate the operation of the sensor in the context of label-free detection of a disease biomarker. The lowest TNF-α concentration measured with this system has been 0.625 μg/mL, comparable with previously measured values obtained by dual color fluorescence cross-correlation spectroscopy [8]. The demonstrated capability represents an important step toward roll-to-roll manufacturability for very sensitive biosensing [7].

Organic PC and DFB laser sensors are very interesting since they are easy to fabricate and versatile for a wide range of analyte detection. Organic DFB lasers have been demonstrated to inherently be very sensitive taking advantage of the criticality of stimulated emission phenomenon. However, these kind of lasers need to be optically pumped.

2.3. Optical Fibers

Miniaturized optical relative-humidity (RH) sensor based on a polymer-infiltrated PC fiber interferometer has been demonstrated [9]. The sensor shows a high sensitivity to RH variations with a change in its reflected power of about 12 dB for a humidity change of 84% RH. The sensor has the advantages of a very compact length of 1 mm, and an end-type probe configuration makes it suitable for monitoring humidity in microenvironments (for example, with respect to fiber bends [10] and long period gratings [11]). The response time of the sensor is found to be 400 ms for a change in RH of $\sim$30%. The fast response time suggests that the sensor can potentially be used as a human breath rate monitor in a clinical situation (e.g., during magnetic resonance imaging scan because of its immunity to magnetic-field interference).

Yuan *et al.* [12] have shown stable wavelength tunable inscription of polymer optical fiber Bragg gratings (FBGs). By straining the fiber during FBG inscription, the center wavelength over 7 nm can be linearly tuned with less than 1% strain. Above 1% strain, the tuning curve saturates, resulting in a maximum tuning of 12 nm with 2.25% strain.

2.4. Functionalized Nanoobjects

Porphyrin-functionalized ZnO nanorod photoconductivity (under visible-light illumination) change has been reported [13], modulated by exposure to two volatile organic compounds, ethanol and triethylamine (chosen as model analytes). The sensitivity to triethylamine exceeds that to ethanol by more than two orders of magnitude, showing a selectivity that is not found in other porphyrin-based gas sensors, higher with respect to other types of porphyrin-based gas sensors [14].

The synthesis of luminescence-quenched shell cross-linked nanoparticles as photonic nanoprobes for protease sensing has been recently shown. Proteases are overexpressed in most cancers and proteolytic activity has been shown to be a viable marker for cancer imaging *in vivo*. Protease sensing scheme is based on a "turn-on" mechanism where the protease cleaves peptide cross-linkers of the fluorescence-quenched shell cross-linked NP (OFF-state) leading to a highly emissive noncross linked NP (ON-state). The cross-linked particles can be strained by exposure to a good solvent and proteolysis allows for particle expansion (swelling) and a recovery of the luminescence [15].

2.5. Genomics and Proteomics

In 2012, diverse organic optical sensors, in the area of genomics and proteomics, have been described. Nyberg *et al.* [16] demonstrated a single-step method to obtain a DNA barcode, visualized using nanofluidic devices and fluorescence microscopy. Using a mixture of YOYO-1, a

bright DNA dye, and netropsin, a natural antibiotic with very high AT specificity, DNA map with a fluorescence intensity profile along the DNA that reflects the underlying sequence has been obtained. Compared with other existing barcoding techniques, such method is single step, the barcode is formed already in the test tube, and only commercially available molecules have been employed.

Seefeld *et al.* [17] have shown on-chip protein synthesis/capture methodology to create a protein microarray from a double-stranded DNA microarray in a microfluidic format that can be used immediately for surface plasmon resonance imaging biosensing measurements. Such microarray needs only 10^{-14}–10^{-15} moles of DNA for its operation.

The coordination complex terpyridine-$CuCl_2$ has been demonstrated to be an efficient fluorescent sensor for histidine, an essential amino acid for human growth, in aqueous solution [18]. The system is very sensitive since, in presence of 10^{-4} M of L-hystidine, the complex emission increased 700 times with respect to the initial value.

3. OPSs for Bio-Inspired and Biological Applications

The most advanced OPS has been realized by the thousand-year work of the natural evolution, and this is the eye. Historically, there have been many attempts to reverse engineering the human visual system in order to reproduce its amazing characteristics for various applications, such as light sensing, robotic systems, imaging, biomedical research, and development of artificial visual implants. Scientists have developed many bio-inspired systems, based on different materials, mainly inorganic semiconductors. Only very recently, organic semiconductors have started attracting attention for the realization of artificial photonic sensors, due to their specific advantages: intrinsic bioaffinity with natural systems, excellent mechanical and biocompatibility properties, ability to conduct both electrons and ions, low-cost and simple processing technologies, and intrinsic sensitivity to visible light allowing for a trichromatic system [19]–[21]. For all these reasons, semiconducting polymers are optimal candidates for the realization of biologically inspired artificial visual systems and even retinal prosthetic implants.

In the field of visual imaging applications, the organic technology represents a much more cost-effective approach, as compared with existing device fabrication techniques. Highly sensitive polymer photodetectors and image sensors have been extensively demonstrated in different configurations, able to work both in the visible and in the near IR, covering wide sensing areas also on flexible substrates. Last year, a novel hybrid organic/inorganic imager device has been reported, in which semiconducting polymers, deposited by low-cost spray coating techniques, replace the silicon photodiodes and cover a conventional CMOS-pixel array as a continuous film, without further structuring [22]. In this case, the imager works on a grayscale. Color sensitivity is usually obtained by adopting two possible approaches, either by using three detectors sensitive to different spectral regions, or, more commonly, by coupling a monochromatic detector to an array of color filters. An original work by Narayan and coworkers [23] reported the fabrication of a single-polymer pixel array yet capable of multicolor sensing. The smart design does not require any color filtering and works without external bias; instead, it is based on an appropriate thickness of the active polymer layer that results in a characteristic polarity and temporal profile of the photovoltage signal in response to various incident colors. Interestingly, the authors highlight nice similarities between the device characteristics and certain biological systems, such as purple membrane proteins, photosynthetic membranes with chlorophyll and, even more strikingly, mammalian retinas. The device structure comprises here an anodic contact made by indium–tin oxide, covered by a bulk heterojunction photovoltaic blend, in direct contact with a saline electrolyte, thus closely resembling a bio-like environment. Indeed, many other conjugated polymers (including regioregular poly(3-hexylthiophene-2,5-diyl), rr-P3HT, poly-[N-90-heptadecanyl-2,7-carbazole-alt-5,5-(40,70-di-2-thienyl-20,10,30-benzothiadiazole), PCDTBT, poly(3-octylthiophene), P3OT, poly(9,9-dioctylfluorene-co-benzothiadiazole, F8BT, poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene-vinylene], MEH-PPV, poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylene vinylene], MDMO-PPV, poly [2,6-(4,4-bis-(2-ethylhexyl)-4Hcyclopenta[2,1-b;3,4-b′]-dithiophene)-alt-4,7-(2,1,3

benzothiadiazole)], PCPDTBT) have been demonstrated to work as active layers in direct contact with saline aqueous solutions and biological media, such as saline buffers and culturing media [24], [25]. Based on this same configuration, the realization of a polymer-based electrochemical cell for water splitting applications has been recently proposed [26]. A photocatalytic semiwater splitting reaction, leading to hydrogen evolution, occurs at the polymer surface, directly contacted to the saline solution, as a consequence of visible-light generated photocurrent. The device absolves thus a twofold function, acting both as a photocatalytic and a photovoltaic system.

The most appealing application of the hybrid polymer/liquid light-sensitive interface is perhaps in the neuroscientific and biomedical fields. It has been demonstrated that an organic photovoltaic blend [namely P3HT doped with (6,6)-phenyl-C61-butyric acid methyl ester], with PCBM, deposited on a transparent ITO conducting layer is able to elicit upon photostimulation electrical activity in primary neurons grown on top of it [27]. The high spatial and temporal resolutions of the photoexcitation, together with the good biocompatibility properties demonstrated for the organic semiconductors, open the way to potential applications in the field of retinal prosthetics. The goal here is to restore photosensitivity in retinas whose natural photoreceptors are damaged or lost. Very recently, Ghezzi *et al.* [28] reported that such bioorganic interface, working in photovoltaic conditions and minimally invasive, is capable of restoring light sensitivity in *ex vivo* blind retinas, at levels indistinguishable from those of healthy control retinas. Interestingly, dose-response measurements revealed a threshold intensity for the photostimulation of about 0.3 μW/mm^2, closely matching the range of retinal irradiance during outdoor activity (0.1–10 μW/mm^2). The reported results demonstrate that organic semiconductor represent a valuable and reliable alternative to the more traditional devices used for retinal implants, thus opening the way to a fully unexplored application of OPSs.

References

[1] F. Scotognella, D. P. Puzzo, M. Zavelani-Rossi, J. Clark, M. Sebastian, G. A. Ozin, and G. Lanzani, "Two-photon poly(phenylenevinylene) DFB Laser," *Chem. Mater.*, vol. 23, no. 3, pp. 805–809, Jan. 2011.

[2] L. Criante and F. Scotognella, "Low-voltage tuning in a nanoparticle/liquid crystal photonic structure," *J. Phys. Chem. C*, vol. 116, no. 40, pp. 21 572–21 576, Sep. 2012.

[3] F. M. Hinterholzinger, A. Ranft, J. M. Feckl, B. Ruehle, T. Bein, and B. V. Lotsch, "One-dimensional metal–organic framework photonic crystals used as platforms for vapor sorption," *J. Mater. Chem.*, vol. 22, pp. 10 356–10 362, Mar. 2012.

[4] C. Li and B. V. Lotsch, "Stimuli-responsive 2D polyelectrolyte photonic crystals for optically encoded pH sensing," *Chem. Commun.*, vol. 48, no. 49, pp. 6169–6171, Apr. 2012.

[5] X. S. Li, L. H. Peng, J. C. Cui, W. N. Li, C. X. Lin, D. Xu, T. Tian, G. X. Zhang, D. Q. Zhang, and G. T. Li, "Reactive photonic film for label-free and selective sensing of cyanide," *Small*, vol. 8, no. 4, pp. 612–618, Feb. 2012.

[6] Z. Pan, J. Ma, J. Yan, M. Zhou, and J. Gao, "Response of inverse-opal hydrogels to alcohols," *J. Mater. Chem.*, vol. 22, pp. 2018–2025, Jan. 2012.

[7] Y. Tan, C. Ge, A. Chu, M. Lu, W. Goldshlag, C. S. Huang, A. Pokhriyal, S. George, and B. T. Cunningham, "Plastic-based distributed feedback laser biosensors in microplate format," *IEEE Sensors J.*, vol. 12, no. 5, pp. 1174–1180, May 2012.

[8] L. Borras, T. Gunde, J. Tietz, U. Bauer, V. Hulmann-Cottier, J. P. Grimshaw, and D. M. Urech, "Generic approach for the generation of stable humanized single-chain Fv fragments from rabbit monoclonal antibodies," *J. Biol. Chem.*, vol. 285, no. 12, pp. 9054–9066, Mar. 2010.

[9] J. Mathew, Y. Semenova, and G. Farrell, "Relative humidity sensor based on an agarose-infiltrated photonic crystal fiber interferometer," *IEEE J. Sel. Topics Quantum Electron.*, vol. 18, no. 5, pp. 1553–1559, Sep./Oct. 2012.

[10] J. Mathew, Y. Semenova, G. Rajan, P. Wang, and G. Farrell, "Improving the sensitivity of a humidity sensor based on fiber bend coated with a hygroscopic coating," *Opt. Laser Technol.*, vol. 43, no. 7, pp. 1301–1305, Oct. 2011.

[11] Y. Liu, L. W. Wang, M. Zhang, D. S. Tu, X. H. Mao, and Y. B. Liao, "Long-period grating relative humidity sensor with hydrogel coating," *IEEE Photon. Technol. Lett.*, vol. 19, no. 12, pp. 880–882, Jun. 2007.

[12] W. Yuan, A. Stefani, and O. Bang, "Tunable polymer fiber Bragg grating (FBG) inscription: Fabrication of dual-FBG temperature compensated polymer optical fiber strain sensors," *IEEE Photon. Technol. Lett.*, vol. 24, no. 5, pp. 401–403, Mar. 2012.

[13] Y. Sivalingam, E. Martinelli, A. Catini, G. Magna, G. Pomarico, F. Basoli, R. Paolesse, and C. Di Natale, "Gas-sensitive photoconductivity of porphyrin-functionalized ZnO nanorods," *J. Phys. Chem. C*, vol. 116, no. 16, pp. 9151–9157, Apr. 2012.

[14] C. Di Natale, K. Buchholt, E. Martinelli, R. Paolesse, G. Pomarico, A. D'Amico, I. Lundstroem, and A. Lloyd-Spetz, "Investigation of quartz microbalance and ChemFET transduction of molecular recognition events in a metalloporphyrin film," *Sens. Actuators B, Chem.*, vol. 135, no. 2, pp. 560–567, Jan. 2009.

[15] C. Cordovilla and T. M. Swager, "Strain release in organic photonic nanoparticles for protease sensing," *J. Amer. Chem. Soc.*, vol. 134, no. 16, pp. 6932–6935, Apr. 2012.

[16] L. K. Nyberg, F. Persson, J. Berg, J. Bergstroem, E. Fransson, L. Olsson, M. Persson, A. Stalnacke, J. Wigenius, J. O. Tegenfeldt, and F. Westerlund, "A single-step competitive binding assay for mapping of single DNA molecules," *Biochem. Biophys. Res. Commun.*, vol. 417, no. 1, pp. 404–408, Jan. 2012.
[17] T. H. Seefeld, A. R. Halpern, and R. M. Corn, "On-chip synthesis of protein microarrays from DNA microarrays via coupled in vitro transcription and translation for surface plasmon resonance imaging biosensor applications," *J. Amer. Chem. Soc.*, vol. 134, no. 30, pp. 12 358–12 361, Aug. 2012.
[18] Z. Huang, J. Du, J. Zhang, X.-Q. Yu, and L. Pu, "A simple and efficient fluorescent sensor for histidine," *Chem. Commun.*, vol. 48, no. 28, pp. 3412–3414, Apr. 2012.
[19] M. R. Antognazza, D. Musitelli, S. Perissinotto, and G. Lanzani, "Spectrally selected photodiodes for colorimetric application," *Org. Electron.*, vol. 11, no. 3, pp. 357–362, Mar. 2010.
[20] S. E. Moulton, M. J. Higgins, R. M. I. Kapsa, and G. G. Wallace, "Organic bionics: A new dimension in neural communications," *Adv. Funct. Mater.*, vol. 22, no. 10, pp. 2003–2014, May 2012.
[21] M. Muskovich and C. J. Bettinger, "Biomaterials-based electronics: Polymers and interfaces for biology and medicine," *Adv. Healthcare Mater.*, vol. 1, no. 3, pp. 248–266, May 2012.
[22] D. Baierl, L. Pancheri, M. Schmidt, D. Stoppa, G. Dalla Betta, G. Scarpa, and P. Lugli, "A hybrid CMOS-imager with a solution processable polymer as photoactive layer," *Nat. Commun.*, vol. 3, no. 10, p. 1175, Nov. 2012.
[23] V. Gautam, M. Bag, and K. S. Narayan, "Single-pixel, single-layer polymer device as a tri-color sensor with signals mimicking the retinal cone cells," *J. Amer. Chem. Soc.*, vol. 133, no. 44, pp. 17 942–17 949, Nov. 2011.
[24] M. R. Antognazza, D. Ghezzi, D. Musitelli, M. Garbugli, and G. Lanzani, "A hybrid solid-liquid polymer photodiode for the bioenvironment," *Appl. Phys. Lett.*, vol. 94, no. 24, pp. 243501-1–243501-3, Jun. 2009.
[25] V. Gautam, M. Bag, and K. S. Narayan, "Dynamics of bulk polymer heterostructure/electrolyte devices," *J. Phys. Chem. Lett.*, vol. 1, no. 22, pp. 3277–3282, Nov. 2010.
[26] E. Lanzarini, M. R. Antognazza, M. Biso, A. Ansaldo, L. Laudato, P. Bruno, P. Metrangolo, G. Resnati, D. Ricci, and G. Lanzani, "Polymer-based photocatalytic hydrogen generation," *J. Phys. Chem. C*, vol. 116, pp. 10 944–10 949, May 2012.
[27] D. Ghezzi, M. R. Antognazza, M. Dal Maschio, E. Lanzarini, F. Benfenati, and G. Lanzani, "A hybrid bioorganic interface for neuronal photoactivation," *Nat. Commun.*, vol. 2, no. 1, p. 166, Jan. 2011.
[28] D. Ghezzi, M. R. Antognazza, R. Maccarone, S. Bellani, E. Lanzarini, N. Martino, M. Mete, G. Pertile, S. Bisti, G. Lanzani, and F. Benfenati, "A polymer-based interface restores light sensitivity in rat blind retinas," *Nat. Photon.,* Mar. 2013, doi:10.1038/nphoton.2013.34.