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On-Tip Photodetection: A Simple and Universal Platform for Optoelectronic Screening†

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A novel platform for transient photodetector component screening has been developed whereby an optical fiber tip serves as the counter electrode when placed in a variety of dielectric media, connected to a photoresponsive working electrode. The soft processing conditions allows for ubiquitous photodetection for organic and biological systems.

Research into organic electronic and optoelectronic materials and devices has received sustained interest over the past 40 years, with several applications making the transition from laboratory demonstrations to commercially viable products.[1] While the performance of organic materials still lags behind inorganics, especially in terms of speed and stability, the secondary benefits of organics, such as flexibility and tunability, as well as the possibility for low-cost, large-area fabrication has supported their continued study. Indeed, these secondary benefits are likely to see the emergence of novel devices and applications that would otherwise be impossible to achieve with inorganic materials.[2]

We have previously reported on the transient photocurrent response induced by a Metal/Semiconductor/Insulator/Metal (MISM) architecture, where the semiconductor is a blend or single component organic film, and the insulator can take the form of an organic polymer dielectric or an ionic liquid (IL) (*c.f.* Fig. 1 & Fig. S1 in the ESI†).[3] The operation mechanism of such devices differs from conventional Metal/Semiconductor/Metal (MSM) devices,

where the photogenerated charges are selectively extracted at the opposed electrodes, and recombine via the external circuit to generate a DC response under the stimulus of constant light. The presence of the insulator layer induces accumulation of photogenerated charges at the S/I interface (Fig. S1 in the ESI†). This, in turn, draws a compensating current from the external circuit, with characteristic time dependence, to balance the new potential across the dielectric layer. Such an architecture benefits from soft processing conditions compatible with sensitive active layers, and the photoresponse, while being a transient, can exceed the steady-state response of conventional Metal/Semiconductor/Metal (MSM) devices. Furthermore, it is inherently less sensitive to the common shortcomings of organic materials, namely low mobility and pin-hole defects, which can decrease device speed and lifetime, respectively.
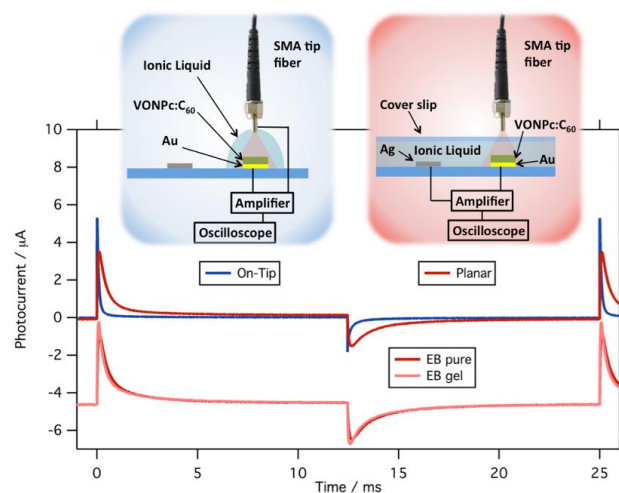
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† Electronic Supplementary Information (ESI) available: [Full experimental details, including device fabrication and testing conditions; raw data used for Fig. 2; and further experimental data relevant to this study]. See DOI: 10.1039/x0xx00000x
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Fig. 1 Photocurrent waveforms for IL-MISM devices of VONPc:C_{60} in an on-tip and planar arrangement (top traces) and a comparison of waveforms of pure ionic liquid (1-ethyl-3-methylimidazolium tetrafluoroborate, EB) and ionic gel of EB dispersed in a polymer matrix (poly(vinylidene fluoride-hexafluoropropylene, PVDF-HFP) in a planar device architecture. In all cases, the fiber carried a square wave modulated light signal from an LED ($\lambda_{MAX} = 850$ nm, $P_{incident} = 700$ µW, $r = 1$ mm, $f = 40$ Hz) and was positioned 1 mm from the substrate; (inset) schematic depictions of the experimental setups for on-tip and planar device testing.

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In this communication we have sought to explore the limits of the MISM architecture in terms of ease of fabrication, versatility of component layers and compatibility with sensitive materials. Beyond simple curiosity, the developed architecture, where an optical fiber tip acts simultaneously as light source and reusable counter electrode, has allowed us to rapidly assess and compare various active layers in the search for enhanced performance organic photodetectors. This platform is not limited to transient photocurrent response, but could be extended to dye-sensitized solar cells, showing steady-state response, by the inclusion of a suitable redox mediator in the dielectric media.[4] Furthermore, the fiber tip can be freely modified, by *e.g.* electroplating, to tune its workfunction and/or surface area.[5]

As a representative photoactive layer, we employed a blend film of vanadyl-2,3-naphthalocyanine (VONPc):C_{60} (d = 50 nm, 40% VONPc, λ_{MAX} = 844 nm). The film was characterized as previously reported, and planar devices, optimized in terms of stability and performance, have shown good photoresponse (>10 mA/W) in passive mode using an ionic liquid as the insulator layer.[6] From this previous study, optimized devices showed minimal degradation over several days constant testing under ambient conditions, and a deviation of <5% between devices. The ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate (EB) was identified as the best choice for achieving stability for this active layer system, and thus served as the starting point of this study.

To test the comparability of response from the on-tip architecture to that previously reported, a drop of EB was placed on the working electrode of a device comprising a parallel electrode arrangement of Au/active layer working electrode and Ag counter electrode, separated by a 4 mm gap, with the working electrode connected to a transimpedance amplifier (Fig. 1). The ferrule of an optical fiber, carrying the light signal, was inserted into the droplet, and grounded to the amplifier, thereby serving the dual role of light source and reusable counter electrode, and the resultant signal visualized on an oscilloscope ("on-tip" response). The waveform was compared to a discrete device by placing a glass cover slip over the drop, thereby spreading it over the whole electrode array, and the silver electrode was then grounded to the amplifier, and the measurement repeated ("planar" response). Both architectures yield the same characteristic transient waveform, with positive (light on) and negative (light off) components, generated through photoinduced charging/discharging of the ionic liquid dielectric by the active layer, with a peak-to-peak amplitude of the same order of magnitude. However, the waveform of the on-tip device showed significantly faster rise and decay times on account of the smaller resistive drop through the bulk of the IL, due to the reduced electrode separation distance.

For the purposes of this study, the devices were fabricated on glass substrates. However, as a means to develop flexible devices, the substrate could be exchanged for more flexible materials, such as polyethylene terephthalate (PET). The use of a liquid dielectric in such devices, even if non-volatile, could decrease the lifetime under mechanical stress due to its
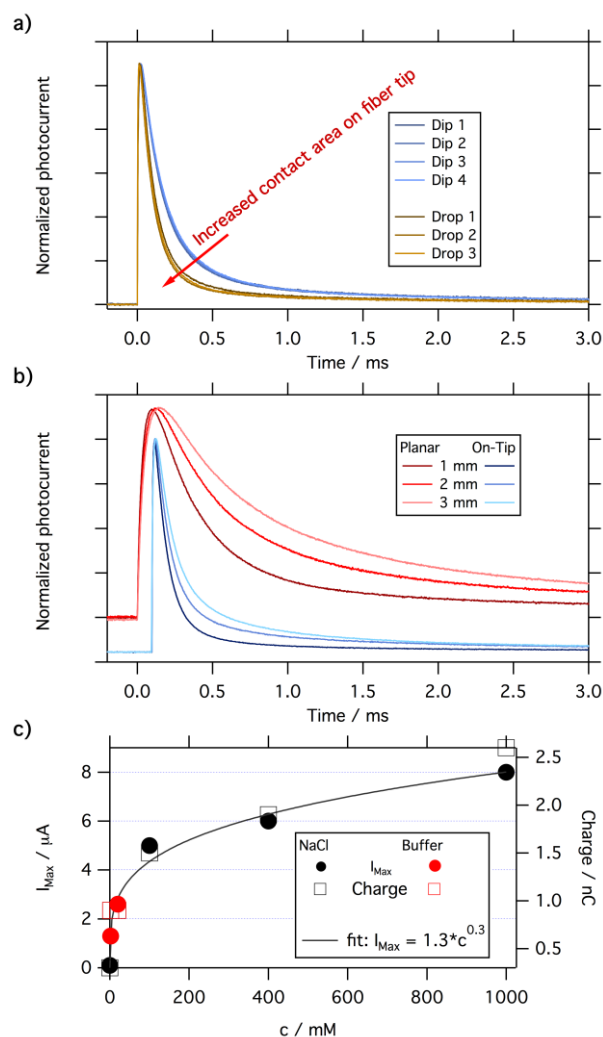

Fig. 2 Effect of device variables on the waveforms of VONPc:C_{60} devices: (a) Normalized waveforms for on-tip measurement of VONPc:C_{60} films upon repeated dipping into a drop of EB, and between drops of EB; (b) Effect of fiber tip height on the normalized waveforms for on-tip (blue, offset) and planar (red) arrangements; (c) Effect of ionic concentration of aqueous electrolytes on the waveform of on-tip devices.

tendency to flow. Recently, gel electrolytes, comprising an ionic liquid dispersed in an organic polymer matrix, have been reported, and have shown good performance and stability in other electronic devices, such as field-effect transistors (FETs). Interestingly, the operation speeds of these gels, while macroscopically more viscous, are similar to that of the pure ionic liquid, suggesting that the ions remain highly mobile in the polymer matrix. A gel was made based on a dispersion of EB in poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) by drop casting, with a thickness of about 0.5 mm. The gel was free-standing, and maintained sufficient structural integrity to be cut and manipulated using tweezers. Compared to the pure IL, the IL-gel device showed an almost identical waveform in terms of peak-to-peak amplitude and response speed in both the planar and on-tip configurations (Fig. 1, Fig. S2 in the ESI†).

The success of the "on-tip" measurement meant that the fiber tip could adequately serve as a reusable counter electrode, and thus substrate fabrication could be reduced to just the working electrode/active layer steps. Therefore,

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subsequent tests were performed on macroscopic single electrode Au/active layer substrates. In order that this simple architecture can serve as a screening platform, the deviation in response (both within and between devices) should be sufficiently small compared to the dependence on the active layer or dielectric under study.

Repeated dipping into the same drop, as well as sequential dipping into different drops was shown to have negligible effect on the shape of the waveform (Fig. 2a), though a saturable increase in amplitude (and thus extracted charge) was observed with time (Fig. S3 in the ESI†). Increasing the area of the IL/tip contact showed a decrease in the decay time of the response, but had minimal effect on the rise time, suggesting that the increased electrode area reduces the response time of the dielectric to the generated photovoltage. Due to the good wetting of the tip by EB, this effect could be maintained for subsequent dips. The effect of tip height, and thus light power density (Fig S4 in the ESI†), on the waveform was measured as the fiber was raised from the substrate in increments, with the drop following the tip by surface tension. As the tip was raised, the waveform showed a significant slowing of the rise and decay components of the waveform, corresponding to the reduced light intensity of a more diffuse light spot. In order to exclude the effect of a change in IL/tip contact area, the same experiment was performed for the planar device, which showed the same trend, albeit with a slower overall waveform. It can therefore be seen that the on-tip waveform is largely reproducible if the tip height and contact area are controlled, and that this configuration is sufficiently stable to assess the relative photoresponse of different active layer and dielectric systems.

The soft processing conditions, facilitated by this architecture, were thought suitable for biological samples that are inherently more sensitive to heat and other physical or chemical stresses. For such materials, it would be desirable to use a dielectric media more sympathetic to the biomaterial's needs, *i.e.* aqueous solutions of physiological buffers. Again, using VONPc:C_{60} as a testing platform, the photoresponse from different aqueous media was examined. Here, the macroscopic size of the working electrode allowed multiple tests to be performed on the same substrate, reducing the number of substrates required, and providing a direct comparison between dielectric media. As representative media, saline solutions, and a phosphate buffer (pH 7.0) of different concentrations were tested, and their waveforms compared to Millipore water. With the exception of the pure water device, the peak amplitude and extracted charge of the photoresponse for all the solutions was within the same order of magnitude (Fig. 2c), and the shape and magnitude of the response converged as the ionic content increased (Fig. S5 in the ESI†).[8] Such a trend is reasonable since even mM ionic content would be sufficient to decrease the solution resistance, and hence the uncompensated resistance drop, between the electrodes, and would reduce the power dissipation within the device.[9]
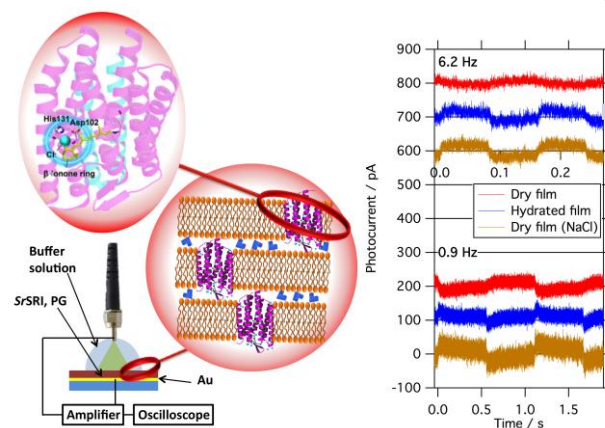

Fig. 3 (left) Pictorial representation of the device setup and protein film structure for an on-tip biological photodetector (blue circle indicates ion binding site). (right) Photocurrent response to a square-wave light chain from an LED (λ_{MAX} = 530 nm, $P_{incident}$ = 1.16 mW, $\varnothing$ = 3 mm, f = 6.2, 0.9 Hz) for pristine dry film and under the effect of rehydration and added NaCl.

These results were encouraging, and suggested a large degree of freedom in the electrolyte media was possible and, due to the relative insensitivity of the response to the nature of the ions in solution, such a method could be used for basic screening of the photoelectric activity of biological samples depending on the pH or composition of the buffer solution. Furthermore, due to the flexibility of the testing platform, the influence of other external parameters, such as temperature or the combination with other *in situ* measurements are possible.

To demonstrate the applicability to biomaterials, a representative photoactive membrane protein, *Sr*SRI, was chosen due to its high stability, even in the presence of light, and the confirmed uptake/release of a proton during the photocycle in the absence of chloride ions.[10] While the movement of protons can generally be expected to result in a slow response compared to that of electrons, its ease of film formation, high stability and absorption in the visible region (λ_{MAX} = 540 or 560 nm in the absence and presence of NaCl, see Fig. S6 in the ESI†), made *Sr*SRI an ideal system for study.

Robust and continuous films of *Sr*SRI in phospholipid (PG) bilayers (*Sr*SRI:PG 1:50, d = 0.2–5 μm depending on concentration) were fabricated on macroscopic gold electrodes by drop casting, and were dried under reduced pressure. A drop of phosphate buffer served as the electrolyte medium for the on-tip measurement (Fig. 3). Although the responsivity of the devices was about 50 pA/mW, and was thus significantly weaker than for the organic blends, the resultant waveform showed a clear photoresponse. Furthermore, compared to other proteins from the rhodopsin family, such as BR, the photoelectric activity of *Sr*SRI is weak, but the responsivity of these devices exceed that of a previous study using BR by an order of magnitude, without optimization.[11] The initial magnitude of this response was largely insensitive to film thickness, despite the huge thicknesses of the active layer and its strongly insulating nature, with values within the measurement error of the devices. Interestingly, for films tested immediately after drying, the polarity of the response was inverted compared to

hydrated samples, and the addition of NaCl to the solution, resulted in an inversion of the signal response, after initial loss of signal. This inversion process (upon addition of salt or hydration) was faster for thinner films. While the exact reason for this change is unclear, and is the subject of further study, one possibility is that the photoelectric activity of the proteins is confined to the surface layers in dry films, inducing a potential response only at the counter electrode, due to the largely insulating nature of the thick films. The addition of NaCl to the solution inhibits the uptake/release of the proton and, with increased film hydration, the photoresponse can take place at the working electrode surface with a potential response to compensate the proton uptake.
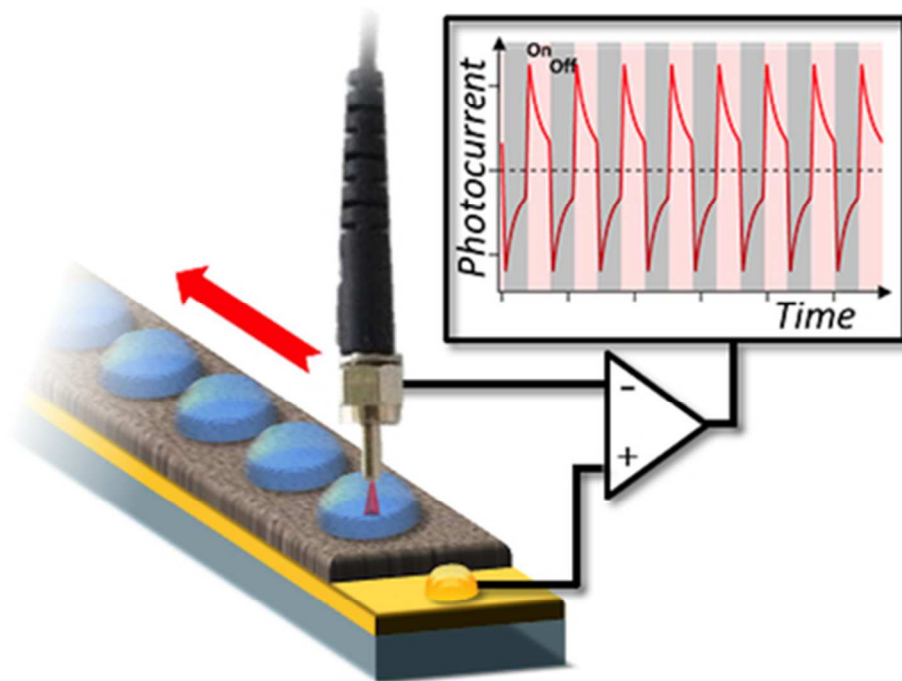
In summary, a simple and versatile platform has been developed for the rapid screening of different photoactive layers in photodetector devices, whereby an optical fiber tip can serve simultaneously as reusable counter electrode and light source with inherently low reflective/refractive loss. The reproducibility of device performance is sufficient to assess the relative performance of different active layer systems, even when very thick or poorly conducting. Furthermore, the device processing is exceptionally soft so as to allow the testing of sensitive active layers, such as biological films, and is flexible enough to allow *in situ* studies of ionic interactions within such films, either directly or in combination with other techniques such as ATR-FTIR. Our ongoing efforts to provide a physical description of the photoresponse in MISM devices would allow this simple platform to yield information on the various physical phenomena occurring in the active layer and dielectric that give rise to the transient waveform.

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Using an optical fiber tip as a sampling probe allows for efficient photoresponse screening of any photoactive film.

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