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The Role of the Internal Capacitance in Organic Memristive Device for Neuromorphic and Sensing Applications

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Abstract

Organic electronics has recently emerged as a promising candidate for the emulation of brain-like functionalities, especially at the device level. Among the proposed technologies, memristive devices have gained an increasing attention due to their non-volatile behavior which makes them suitable for the implementation of artificial neuronal networks. However, most of them have an energy-costly switching mechanism which limits the approach of brain like energy efficiency. Different from them, organic memristive devices (OMDs) have a narrow switching window and implement neuromorphic characteristics at voltages ≤ 1 V. Despite OMDs potentialities in bioinspired electronics, guidelines for the design of devices and materials are still missing. Here it is shown that the device capacitance represents a significant degree of freedom for targeting devices applications. It is also shown that a single OMD emulates activity dependent synaptic functions and neuronal temporal and spatial summation, taking advantage of its three-terminals configuration. Interestingly, despite the neuromorphic applications, OMDs can also sense and amplify incoming signals on the basis of their capacitive and/or resistive values. This spectrum of applications, ranging from volatile to non-volatile characteristics and from neuromorphic computing to bio signals sensing, sets the stage for the realization of integrated circuits for adaptive sensing.

1 Introduction

Neuromorphic systems are widely considered as powerful alternatives for information storage and handling with respect to traditional computing systems which at the moment are unable to be equal to the brain capabilities in real world information processing.^[1]

The possibility of building integrated and complex neuromorphic systems has to deal with the integration between different brain functions. In brain, neurons are responsible for the temporal and spatial integration of incoming signals and for the signal propagation, while synapses are tasked with the variation of the input signal transmission according to learning paradigms such as the activity dependent plasticity (long term and short term plasticity) or the spike-timing dependent plasticity (STDP) algorithm.^[2] This structural and functional organization enables the energy efficient and the massively parallel information processing that characterize neuronal networks.

Artificial analogs of neurons and synapses can be implemented using traditional electronic elements fabricated with well-established CMOS technology.^[3, 4] However, these implementations require the use of a rather large number of elements,^[5] limiting the effective realization of brain-like systems, especially considering the 3D organization and the possibility of rather long-distance connections. This is the reason why main efforts in the field of artificial neuron networks (one class of neuromorphic systems) were carried out mainly at the software level, limiting the mimicking of several features of brain, for instance, parallel information processing.

Recently, a renovated interest in the hardware realization of neuromorphic systems and, in particular, artificial neuron networks^[6, 7] is due to the progress achieved in the implementation of resistance switching elements,^[8-10] the so called memristive devices,^[11] mimicking synapse properties at the level of single elements, and allowing the realization of neuron analogs. Different groups reported synaptic-

like devices using nanoscale magnetic materials developing spintronic devices,^[12, 13] metal oxides,^[14-16] or organic materials based on redox reactions^[17-19] and ion permeation.^[20-22] The increasing interest in organic materials demonstrating basic forms of neuroplasticity has recently driven the development of different approaches for reducing the operation voltage ranges^[23, 24] and for increasing the networks density.^[25] Short term memory and adaptation functions have been reported in different organic devices^[26-29] who demonstrated the capability of performing paired pulse facilitation or depression (PPF or PPD, respectively), while spatio-temporal neuronal integration has been demonstrated in devices with a multigate configuration^[27] or in NbO_x volatile memristors.^[30]

It has been recently proposed that a neuromorphic system integrated with a sensing part will be able to locally process data and to activate subsequent events.^[1] In this interesting scenario, the lack of a technology able to integrate devices with different specific functions (sensing and neuromorphic computing) seem the major bottleneck.

The implementation of organic based synaptic elements based on polyaniline (PANI) is supported by its theoretical fast resistive switching,^[31] the marked difference between high and low resistance of partially oxidized and reduced states,^[32] the light weight and its electrochromic behavior. Indeed, PANI based organic memristive devices (OMDs) have demonstrated several advantages, including the flexibility, a high and finely controllable ON/OFF ratio and the possibility of monitoring the internal conductivity taking advantage of its electrochromism, instead of external electrical set up. Historically designed as synapse-mimicking electronic element, OMDs have been largely used in circuits and systems and recently, it has been shown that the overlay of noise to the input signal can improve the devices characteristics, similarly to what occurs in nervous system.^[33] Despite these advantages and interesting features, the realization of micro-OMDs (in which the channel dimensions are at the microscale) is relatively recent.^[17, 34] Moreover, the impact of the device geometry on the fundamental mechanism behind their operation remains practically unexplored. Here we show that OMDs performances may be understood using as a key parameter the thin film capacitance that shows a linear dependency on volume and resistance of the PANI channel. This result provides guidelines for the design of devices. We also demonstrate that micro-OMDs owned a wide range of neuromorphic functions that embrace the emulation of synaptic long-term and short-term plasticity and the mimicking of neurons-like spatio-temporal integration activity. Furthermore, OMDs share their geometry with poly(3,4-ethylenedioxythiophene) doped with polystyrene sulfonate (PEDOT:PSS) based transistors (organic electrochemical transistors; OECTs) which find large use in bioelectronics as amplifying transducers. We show that, despite the native neuromorphic applications, OMDs may be employed as amplifying transducers for the recognizing of bio-signals. This possible field of application, mediated by the already mentioned capacitive thin film contribution, could possibly pave the way for the realization of sensing systems integrated with neuromorphic networks in which the same PANI based device is declined in different functions.

2 Results and Discussion

In OMDs, the PANI active layer is deposited in contact with two gold electrodes (drain (D) and source (S)) from which the channel current is monitored during the application of an external bias (V_{SD}). For the correct functioning of this type of memristive devices it is necessary to ensure the direct contact between the polymeric thin layer and the liquid electrolyte, in which a silver wire works as gate electrode (**Figure 1a**). The thickness of the PANI layer is controllable up to the nm scale, thanks to the selected deposition technique (the Langmuir Schaefer method), which allows the conformal deposition of single monolayer of polymers and small molecules (Figure 1b) on selected substrates.

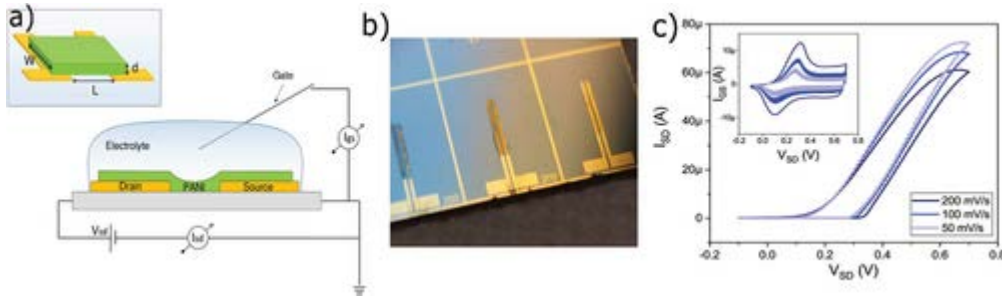


Figure 1

a) OMDs scheme and electrical configuration: gold source and drain electrodes are in contact with a polymeric thin film of polyaniline (PANI). This latter is in direct contact with an electrolytic solution in which a silver wire is inserted as gate electrode. Source and drain electrodes are biased with V_{SD} voltage value, which induces resistivity variations in I_{SD} and I_{GS} currents. In the inset, geometrical details of length (L), thickness (d), and width (W); b) Image of the PANI active layer; c) I_{SD} response to V_{SD} variations as a function of the scan speed. In the inset relative I_{GS} responses.

The channel current is a superimposition of the electronic current flowing in the PANI channel (I_{SD}), which depends on the internal conductivity of the polymer, and the ionic current (I_{GS}) flowing at the interface between PANI and the electrolyte, which depends on the external bias applied to OMD. This latter is to be considered as the expression of the redox activity of the conductive polymer on which the switching mechanism for this type of memristive devices is based on. In other words, the external bias voltage applied to OMDs (V_{SD}) triggers the redox activity of the PANI channel which affects the instantaneous conductivity variations of the entire device (σ). The resulting current follows Equation (1):

$$I_{SD}(t, V_{SD}) = V_{SD}(t) \times \sigma(t, V_{SD}) \frac{dW}{L} \quad (1)$$

where d , W , and L are the thickness, the width and the length of the PANI layer (inset of Figure 1a). Despite the electrical dependence on the PANI conductivity which can vary five orders of magnitude,^[31] this equation implies a reliance of the output current on the geometry of the device. To deepen this aspect, we realized and measured electrical responses of OMDs with PANI channels of different volumes varying the length between 10 and 200 μm , the width from 250 to 6000 μm and the nominal thickness from 10 to 60 monolayers (which correspond to a thickness range between 25 and 150 nm^[35, 36]).

OMDs typical cyclic voltage–current characteristic (Figure 1c) presents a marked hysteresis in the positive range of the voltage and a rectifying behavior in the negative one, that are the reflection of the electrochemical reactions occurring in the PANI channel.^[17] This hysteresis depends on the scan speeds, pH condition,^[37] and on the channel geometry which affects the maximal accessible conductivity of the entire device. Varying the scan speed, the kinetics of PANI electrochemical reactions could be promoted or suppressed^[38, 39] (inset of Figure 1c) resulting in a larger or smaller hysteresis loop in electrical characteristics (Figure 1c).

2.1 Time and Capacitive Response

Beside from electrochemical considerations, I_{GS} versus V_{SD} curves can be used for the estimation of the polymeric thin film capacitance^[38, 39] (Section 4.2.2). Obtained results are in a good agreement with already reported estimation of PANI OMD capacitive values^[35] for pH 1. Reporting calculated results versus the PANI channel volume (**Figure 2a**), a well defined linear trend defines a capacitance per volumetric unit of $C = 2536 \pm 196 \text{ F cm}^{-3}$.

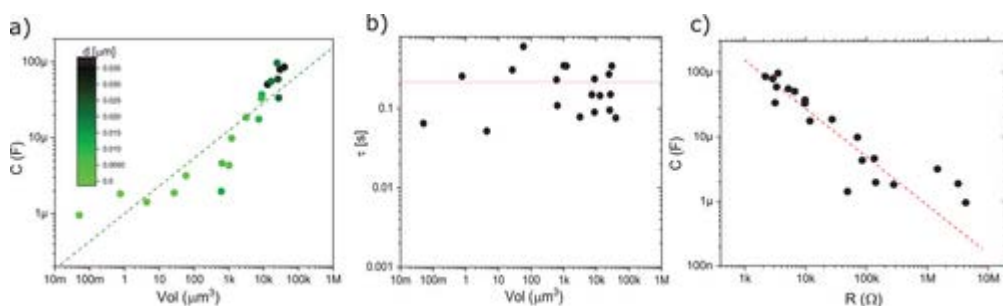


Figure 2

a) Volumetric dependence of the device capacitance. b) Volumetric dependence of the OMDs switching time. Red dotted line is the mean value obtained from the normal distribution of switching times. c) Capacitance dependence on the PANI channel resistance.

This volumetric capacitance is in agreement with the already reported PANI volumetric capacitance^[35, 40, 41] but in any case is an order of magnitude higher with respect to the value obtained for another type of organic electrochemical devices (i.e. OECTs)^[42] widely used in bioelectronics for sensing applications. It has to be noted that despite the linearity with channel volume, PANI OMD capacitance shows a linear trend with the minimum resistance of the channel (Figure 2c). This trend confirms an intrinsic dependence of the capacitance with the amount of deposited polymeric material: wider and thicker devices present in general a large capacitive value and, on the contrary, thinner and narrow sample are characterized by high resistance and low capacitance.

On the contrary, the switching times (τ in Figure 2b), measured following the procedure reported in Section 4.2.2, seems to have not a clear dependence on the volume or the capacitance of organic memristive devices and to be distributed around ≈ 0.2 s with an obtained minimum value of 65 ms (Figure 2b). These values, well below the already reported τ for analogous solid macrodevices^[43] and solid microdevices^[34] are in contrast with the predicted linearity between the switching time and the area of the OMD active channel reported in 2011^[35] and the theoretical switching time of PANI which is expected to be in the range of hundreds of μs .^[31] It has to be noted that the linear trend proposed by Pincella et al., was obtained employing macrodevices with switching times of the order of seconds, well above the here reported results. Moreover, in Lacroix et al.^[31] this reduced switching time was obtained using another experimental configuration, in which the switching event occurred along the PANI thickness plane. In our case instead, it has been reported that PANI resistance switching is a dynamic process involving the entire volume of the polymeric channel which is exposed to a voltage distribution rather than a constant equipotential bias. To this geometrical consideration, we can compound the reported non-homogeneity of the film thicknesses for less than 10–15 transferred layers.^[36] Therefore, we can infer that the combination of these effects deviates the obtained OMD switching time from the predicted PANI value.

2.2 Endurance and Number of Resistive States

To evaluate the stability of OMDs and the stability of their switching processes, we have carried out endurance tests on devices to determine the minimum number of cycles that memristive devices can endure (Figure 3a).

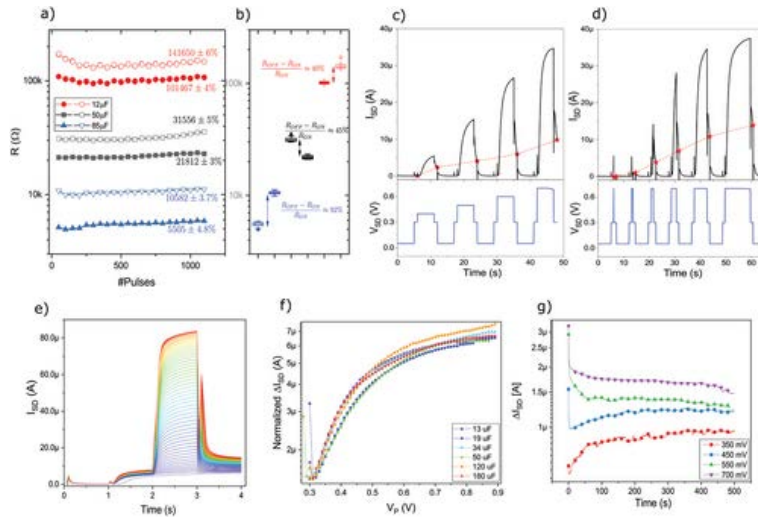


Figure 3

a) Endurance test: evolution of the high and low resistance as a function of the number of switch cycles for devices with different capacitive values. b) Means and standard deviations of panel (a); c,d) Increment of the conductivity as a function of the voltage pulses amplitude (c) or of the pulse dwell time (d). e) Number of resistance states: typical I_{SD} versus time for voltage pulses with amplitude $0.3 \text{ V} \leq V_p \leq 0.89 \text{ V}$ with steps of 10 mV . f) Evolution of the resistance states versus V_p for different devices' capacitances. g) Temporal evolution of selected resistance states.

OMDs with different volumes (and thus with different calculated capacitance values) show different $R_{OFF} - R_{ON}/R_{ON}$ as expected (Figure 3b), devices with higher C values have a larger relative variation between low and high resistance which progressively decreases with the reducing of the C values. In any case, this kind of organic memristive devices with liquid electrolyte have a stability of more than 10^3 cycles with standard deviations within 6% (Figure 3a). This result is in line with already reported endurance tests performed on OMDs based on solid electrolytes,^[34] in which the device presented a rather stable switching between high and low conductivity level up to the 1000th cycle and then started to present larger oscillations.

However, for the integration of OMDs with electronic bio-circuits, where their memorization capabilities must be effectively employed, it is necessary to assess the number of resistance states of organic memristive devices. In OMDs this can be accomplished by applying voltage pulses of fixed dwell time (Δt) and increasing amplitude (V_p) (Figure 3c) or by applying voltage pulses with a fixed amplitude and varying the dwell time (Figure 3d). Both these stimulation schemes efficiently increase the OMD internal conductivity (as indicated in relative figures with red stars), inducing current variations proportional to the voltage amplitude in the first case and to the dwell time in the second.

To estimate the number of resistive states, we decided to follow the procedure with increasing amplitude voltage pulses and we applied to OMD a train of stimuli with $0.3 \text{ V} < V_p < 0.89 \text{ V}$ with steps of 10 mV . As shown in Figure 3e, OMDs discriminate pulses of voltage separated by 10 mV and they can access to 52 different internal resistance states (calculated as $\Delta I_{SD} = I_{SD}^f - I_{SD}^0$ where I_{SD}^f and I_{SD}^0 are the final and the initial current levels after and before the V_p application- Figure 3f), which correspond to a memory with more than 5.5 bits. It is worth noticing that all the tested samples show a minimum of 39 states (5 bits) and this result is of particular relevance if considering the actual record of 6.5 obtained by Stathopoulos et al., with metal-oxide memristive devices.^[44] This behavior is independent from

device's capacitive values (Figure 3f) and shows an initial linear evolution of the internal states with respect to V_p followed by a saturation regime. We further assessed the stability of these resistivity states by monitoring their temporal evolution up to 5×10^2 s (Figure 3g).

2.3 Neuromorphic Properties

OMDs are well known neuromorphic devices thanks to their ability of adjusting the internal resistivity with the amount of charge that passed through them. More in detail, macrodevices have demonstrated to be able to implement activity dependent functions^[45] while solid microdevices successfully demonstrated the implementation of STDP.^[46] Liquid microdevices with the already mentioned faster switching, are predicted to exhibit the same neuromorphic functions of previously reported devices, closing the gap between devices and synapses temporal scales. To evaluate OMDs neuromorphic capabilities, we tested them following already adopted protocols^[45] for the synaptic activity dependent functions (i.e., long term and short term potentiation and depression- LTP, LTD, and STD, STP, respectively) and we explored new neuronal functions of spatial and temporal integration. In line with the results reported on macrodevices, a train of voltage pulses ($V_p = 700$ mV, $\Delta t = 100$ ms) delivered to OMDs following the scheme reported in the inset of **Figure 4d**, promotes the increasing of conductivity and results in the enhancement of the synaptic weight ($\Delta w = I_{SD}^f - (I_{SD}^0 / I_{SD}^0)$) as a function of the number of delivered stimuli (Figure 4a). Differently from what it was reported in ref. ^[45], this stimulation configuration does not result in a short term behavior (in which Δw must be close to 0). This is attributable to the faster switching process of this type of memristive device whose internal conductivity state is sensible to 100 ms stimulation. However, this effect can be modulated by reducing the V_p and the Δt to values allowing this kind of slower transition between resistive states. As a further demonstration, the number of pulses necessary for the reaching of the saturation is markedly reduced respect to the already mentioned work. The administration of negative voltage pulses ($V_p = -200$ mV, $\Delta t = 100$ ms) results instead in a marked reduction of the synaptic weight. These two trends, in which the synaptic weight depends on the train of stimuli and on the number of delivered pulses, can be considered as the voltage based expressions of LTP and LTD of OMDs. However, a form of short term plasticity, namely paired-pulse facilitation (PPF), could be evoked in OMDs when delivering to the device two voltage spikes of 700 mV with different time intervals (from $\Delta t = 50$ ms to $\Delta t = 5000$ ms at 50 mV). As already mentioned, 300 mV voltage is the reading voltage for the correct estimation of the PPF%, whose definition is identical to the Δw one. OMD current response (Figure 4d) is the analogous of the biological paired-pulse facilitation in which the device temporally correlates two subsequent spikes on the basis of the Δt . Shorter is the interval between pulses and higher is the PPF%. Devices with different capacitive values show very similar neuromorphic behaviors which are, however, shifted to higher values in agreement with variations of $(R_{OFF} - R_{ON})/R_{ON}$ reported in Figure 3b.

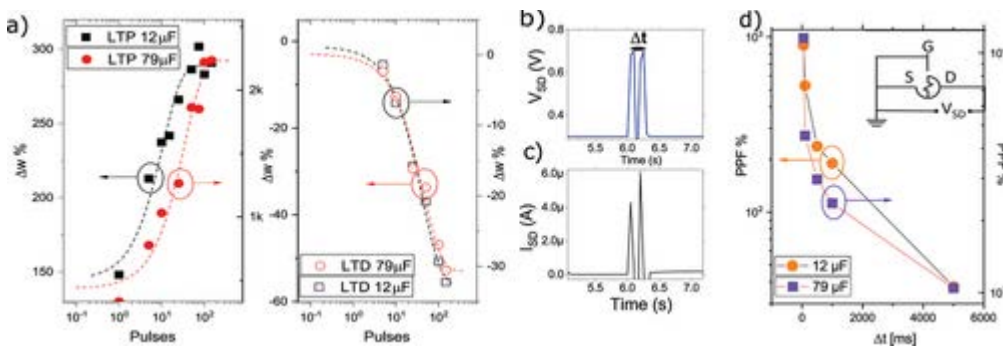


Figure 4

Synaptic properties of OMDs: a) LTP and LTD test: OMDs emulate long term plasticity as a function of the number of delivered voltage spikes. b) Voltage pulses and c) current output used for the induction of the short term plasticity in devices. d) PPF% as a function of the interval time Δt . In inset: circuit wiring diagram for operating the OMD for the emulation of synaptic functions.

For the realization of integrated circuits mimicking different functions of biological neuronal networks, the possibility of implementing neuronal features in addition to synaptic functions, is a crucial aspect. Neurons in a biological network are responsible for the so called temporal or spatial integration which are mechanisms of eliciting postsynaptic potentials in the case of high frequency of unsynchronized presynaptic action potentials or in case of multiple spatial isolated synaptic inputs, respectively. We tested the integration abilities of OMDs following two distinct stimuli protocols, represented in **Figure 5a,d** respectively. To test the temporal summation, we applied to OMDs the voltage profile reported in Figure 5b in which an increasing number of voltage spikes of 700 mV amplitude are delivered with 100 ms time intervals. OMD current response (top panel of Figure 5b) and Figure 5c show clearly that an increasing number of inputs elicits proportionally the final current of the device, which thus, is able to integrate subsequent incoming spikes. This trend mimics well the temporal integration of biological neurons.

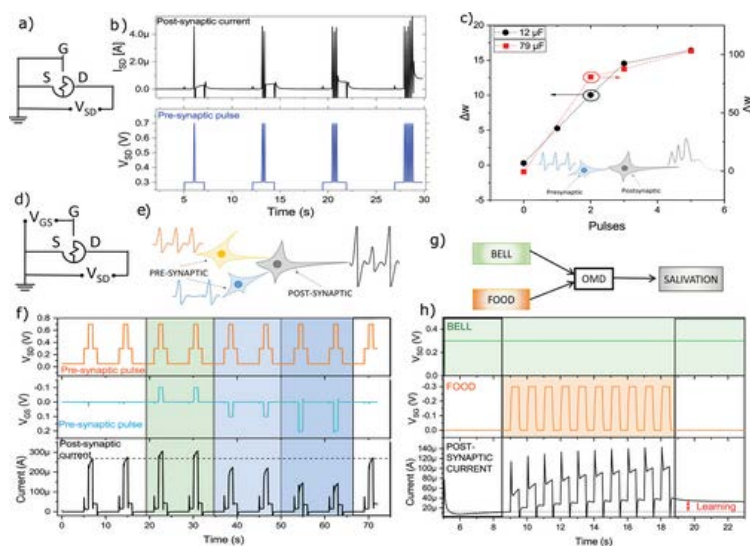


Figure 5

Spatio-temporal integration capabilities of OMDs: a) Circuit wiring diagram for operating the OMD for the temporal integration function. b) Current output (black curve) and voltage profile (blue curve) used for the temporal integration. c) Results of the temporal integration as a function of the number of received stimuli. d) Circuit wiring diagram for operating the OMD for the spatial integration function. e) Schematic and f) results of the spatial integration test. OMDs can integrate (bottom panel) two different “presynaptic” inputs (top and middle panels). g) Schematic and h) results of the Pavlovian conditioning and permanent association test.

To assess the possibility of spatial integration, we took advantage of the three terminals configuration that organic memristive devices naturally present. Presynaptic inputs are represented by the two bias applied to source and drain (V_{DS}) and gate and source (V_{GS}) electrodes (Figure 5e). Results of this test are shown in Figure 5f in which we considered three different scenarios of stimulations: i) Presynaptic 1 delivers signals to postsynaptic cells, while presynaptic 2 is silent; ii) Presynaptic 1 and presynaptic 2 deliver excitatory signals to postsynaptic cells; iii) Presynaptic 1 delivers excitatory signals to postsynaptic cells and presynaptic 2 inhibitory spikes. The protocol (i) (white panels in Figure 5f) produces in the device a stable response that represents the neuronal behavior to the stimulation from a single afferent cell. In contrast, protocols (ii) and (iii) induce in OMDs a variation in the current response which results enhanced in the first case (green panels in Figure 5e) and depressed in the second (light blue panels in Figure 5e). The decrease is proportional to the intensity of the inhibitory input which is able to modulate the output current.

The direct consequence of the capability of OMDs to spatially and temporally integrate signals is the possibility of emulating the Pavlov's dog experiment (Figure 5g) with a single device (Figure 5h). In this experiment, a single OMD is exposed to a neutral signal (green panel-the bell sound) which initially cannot induce variations in the output current (bottom panel). The contemporary administration of a neutral plus an unconditional stimulus (orange panel- food) conditions the device which starts associating the bell sound with the presence of food. After this conditioning phase, the neutral bell sound induces a conditioned response demonstrated by the variation in the final current level.

2.4 Bio-Signal Amplification

Considering the linear trend reported in Figure 2a,c, OMDs can modulate their sensing capabilities on the basis of the internal resistive state and channel volume. Furthermore, variations of the conductivity should affect the amplification capability of the device. To test this feature, we applied to device's gate electrode a simulated electrocardiogram (ECG) signal, while monitoring the PANI channel current with the reading voltage of 300 mV (Figure 6c). This is repeated after having modified the OMD conductivity with depressing and potentiating pulses. OMDs, depending on their internal resistance and on their geometrical aspect ratios (which affect the capacitance) can sense and amplify an ECG biosignal (Figure 6a,b). The role of the capacitance in the capability of detecting an incoming mV signal is confirmed in Figure 6a,b in which two OMDs with different capacitance values show a marked difference in their responses to ECG inputs, as expected from the linearity in Figure 2c.

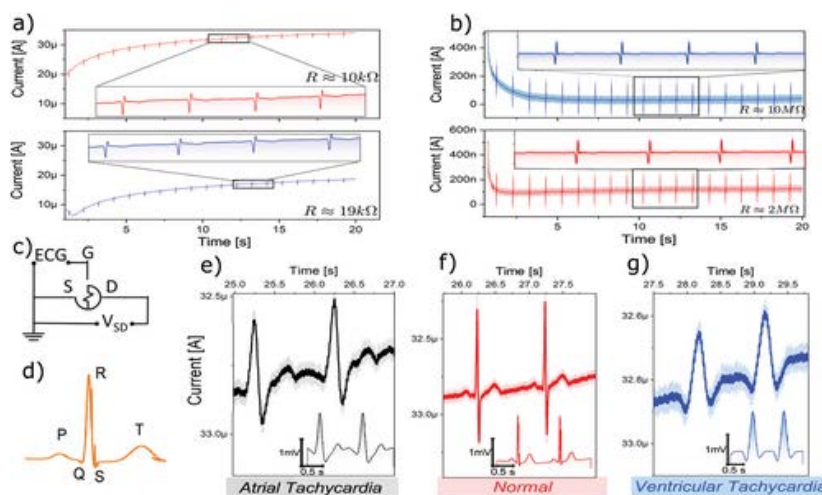


Figure 6

Panel a) Response of a high capacitance OMDs to ECG; panel b) Response of a low capacitance OMDs to ECG; panel c) circuit wiring diagram for operating the OMD for bio-sensing; panel d) ECG main components: the P wave (the atria depolarization); the QRS complex (the depolarization of the ventricles); and the T wave, which represents the repolarization of the ventricles; Response of a high capacitance OMDs to pathological (atrial and ventricular tachycardia: panels e and g) and normal ECG (panel f).

Devices with higher C have a higher signal to noise ratio ($S/N \approx 30$ dB). On the contrary, a low capacitance value results in a device output with lower S/N ($S/N \approx 10$ dB) and the need of a post-acquisition signal treatment to extract ECG classical features. The variation of device conductivity results in an increase or decrease of the S/N , which is mostly due to the gentle amplification of the signal peak-to-peak amplitude, more than a noise reduction.

It is worth emphasizing that devices with higher capacitance values are able to resolve all main components of ECG (Figure 6d). Interestingly, high capacitance OMDs can easily distinguish a normal ECG from a pathological one, as clearly visible in Figure 6e–g where a normal ECG and two pathological signals are sensed with the device.

3 Conclusion

In summary, we have reported new evidences for the importance of the capacitance as parameter for the designing of different applications for OMDs. We also have shown, with a new class of OMDs (liquid based) that these devices can endure for more than 1000 cycles and can easily access to more than 50 different resistive states, equivalent to a 5.5 memory bits. In these devices, the relative ratio between low and high resistance depends on the capacitive values. In the perspective of building integrated systems for the contemporary processing of data coming from sensors, we revealed the potentialities of OMDs both as sensing elements and as neuromorphic analogue. Indeed, we demonstrated that a single PANI based OMD can mimic both synaptic functions, including voltage dependant LTP/LTD and short term PPF. Moreover, a single device is able to implement neuronal spatio-temporal integration functions taking advantage of the three-terminals configuration. In this light, we have also demonstrated that OMD emulates the Pavlovian learning demonstrating associative memory. Furthermore, on the basis of their capacitive values, organic memristive devices can amplify and detect simulated ECG signals being able to recognize pathological features from normal cardiac signals.

4 Experimental Section

Device Realization: Gold electrodes were deposited by e-beam evaporation (ULVAC EBX-14D) of Ti/Au film (thickness 10nm /100nm) on Si wafer (100) finished with 1 μm of thermal oxide, patterned by standard photolithography and wet etching as reported elsewhere.^[47] PANI films were prepared spreading a PANI solution (0.1 mg mL⁻¹) of emeraldine base (Sigma Aldrich, $M_w \approx 100.000$) in 1-methyl-2-pyrrolidinone (Sigma-Aldrich ACS reagent $\geq 99.0\%$) with the addition of 10% of toluene (AnalaR NORMAPUR ACS) on the air–water interface. The so obtained film was then deposited by means of the Langmuir–Schaefer technique onto a masked substrate.^[43, 45] Devices with different ratios $L/W \times d$ were prepared varying the number of transfer processes during the deposition (from nominal 10 layers to 60). As liquid electrolyte, 100–200 μL of HCl 1 M was used.

Preliminary Characterizations: Prepared samples were electrically characterized using two source measure units (NI PXIe-4138/9) controlled by a customized ad hoc LABVIEW code and analyzed and graphed by means of OriginLab software.

All OMDs had been initially characterized sweeping the V_{SD} between -0.1 and 0.7 V, with steps of 0.01 V varying the scan rate of the measurement between 200 and 50 mV s⁻¹.

Capacitance and Temporal Response Characterizations: I_{GS} versus V_{SD} curves, obtained as described in the previous section, had been used for extracting the polymeric thin film capacitance using the following equation^[38, 39]:

$$C = \frac{\int_V I_{GS} dV}{(V_2 - V_1) \times v} \quad (2)$$

where $V_2 - V_1$ is the voltage range used for the measurement and v is the scan speed. Different scan speeds were tested for every sample and the averaged obtained values were reported. For the calculation of the τ , OMDs were stimulated with a voltage pulse of 0.7 V, while monitoring the current.

The so obtained I_{SD} is fitted using the formula $I_{SD}(t) = \gamma_0 + A_1 e^{\frac{t-t_0}{\tau_1}} + A_2 e^{\frac{t-t_0}{\tau_2}}$.

The value considered for the authors' estimations was τ_1 which typically corresponds to the minimum values. Thickness nominal values must be corrected considering the not complete transfer of single monolayers during the deposition. To estimate the correct values, the theoretic conductivity of the PANI

thin film was considered^[48] ($\rho_t = \frac{1}{\sigma_t}$ where $\sigma_t \approx 55 \text{ cm}^{-1}$)

and we extracted the thickness using the formula:

$$d = \frac{\rho_t \times L \times I_{SD}}{W \times V_{SD}} \quad (3)$$

Endurance and Resistive States: In endurance tests, a sequence of voltage pulses (250 ms at 300 mV; 250 ms at 700 mV; 250 ms at 300 mV, and 250 ms at -200 mV) was applied to OMDs. Intervals in which $V_{SD} = 300 \text{ mV}$ corresponded to "reading" phases whose only purpose was the reading of the instantaneous resistivity of the device. 700 and -200 mV correspond instead to "writing" voltages that modify internal conductivity of OMDs.

For the estimation of the total number of resistive states, the device current was monitored while applying to V_{SD} the profiles reported in the bottom panels of Figure 3c,d. For both, the reading phase consisted 1 s at 300 mV while 5 s at 50 mV was used as reset between one stimulation and the following one. In the first case, a 5 s pulses at 400, 500, 600, and 700 mV were tested while in the second stimulation scheme, 100, 500, 1000, 2000, 5000, and 10000 ms pulses at 700 mV were used as inputs.

Then, a more dense stimulation routine was applied to OMDs in which a 1 s voltage pulses of amplitude $V_{pi} = 0.3 \text{ V} + i \cdot 0.01 \text{ V}$ were followed and preceded by 1 s of reading phase (300 mV). This test was limited to a maximum value of $V_p = 0.9 \text{ V}$ for preventing electrodes damaging and undesired reactions. For the estimation of the maximal number of states, as a discrimination tool the accuracy reported in the specifications of the electrical set up (National Instruments) was used. Finally the temporal stability of selected resistive states was assessed by applying to the device a routine similar to the one used for determining of the number of internal resistive states but in which the last reading phase was extended to 500 s.

Neuromorphic Characterizations: For the realization of LTP-LTD experiments, a sequence of 100 ms pulses (700 mV for LTP and -200 mV for LTD) separated by 100 ms interval at 300 mV was applied. Reading phases prior and after this train of stimuli were performed by applying 1 s pulses at 300 mV.

For the PPF test, two 100 ms pulses at 700 mV were progressively separated by 50, 100, 500, 1000, and 5000 ms intervals at 50 mV. Conductivity variations were estimated in the reading phases at 300 mV before and after the two voltage spikes.

In the temporal integration test, the evolution of the conductivity before and after the delivering to OMD of short 700 mV pulses (100 ms) was monitored as a function of an increasing number of spikes. Between every acquisition, device conductivity had been reset to initial value with 50 mV bias. In the spatial integration and in the Pavlov's dog experiments, the OMD current was monitored while applying different voltage pulses to V_{GS} and V_{DS} . In the first one, nine cycles of the following voltage sequence (5 s at 50 mV, 1 s at 300 mV, 1 s at 700 mV, and 1 s at 300 mV) were applied as V_{DS} while pairs of 1 s pulses

at -100 , 100 , and 200 mV were used as V_{GS} . In the Pavlov's dog experiment instead a constant bias of 300 mV was used as V_{DS} , while a sequence of 10 500 ms pulses at -300 mV was used as food stimulus.

Bio-Signal Stimulus: The authors' delivered to OMD as V_{GS} simulated normal ECG signals (NI LabVIEW Biomedical Toolkit) with heart beat of 60 bpm and a maximal allowed amplitude of 3 mV. To sense the effect of the internal resistance state on the amplification and sensing capabilities, sensing phases (in which $V_{DS} = 300$ mV) were alternated to potentiating ($V_{DS} = 700$ mV) and depressing phases ($V_{DS} = -300$ mV). To test the capability of OMDs to sense and amplify normal and pathological ECG signals, ECG signals (NI LabVIEW Biomedical Toolkit) with heart beat of 60 bpm and a maximal allowed amplitude of 2 mV were employed. Collected data were then smoothed with the adjacent-averaging method for graphical purposes.

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Conflict of Interest

The authors declare no conflict of interest.

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