Directed Growth of Dendritic Polymer Networks for Organic Electrochemical Transistors and Artificial Synapses

Matteo Cucchi,* Hans Kleemann, Hsin Tseng, Giuseppe Ciccone, Alexander Lee, Darius Pohl, and Karl Leo

Organic electrochemical transistors (OECTs) are an emerging class of devices which operate in electrolytic solution and show controllable memory effects. For these reasons, OECT hold great potential for applications in bioelectronics and neuromorphic computing. Among the methods proposed to fabricate OECT channels, electropolymerization stands out because it allows to produce electrical connections on the substrates on-demand and further modify them to adjust their electrical properties to meet circuit requirements. However, the practical application of this method is hampered by the difficulty in controlling the growth direction as well as the morphology of the film, resulting in a large device-to-device variability and limiting the down-scaling of the devices. In this study, AC-electropolymerization is proposed to produce directionally controlled channels. The method allows to adjust physical properties such as resistance and capacitance by varying the polymerization parameters, such as voltage, frequency, and salt concentration. The growth mechanism, material morphology, and network topology is investigated, and the advantages of this approach by showing tunable neuromorphic features and the possibility to scale down the channels to the micrometer scale is demonstrated.

1. Introduction

Organic semiconductors have been intensively researched due to a multitude of promising applications for flexible, carbon-based electronics. Organic transistors as key devices for circuits have made significant progress in terms of performance and applications in bioelectronics.[1–3] Recently, organic transistors and organic electrochemical transistors (OECTs) have found much interest. In these devices, the gate dielectric of a traditional field-effect transistor is absent; instead, the channel is in electrical contact with the gate through an ion-containing solution.[4] The channel consists of an organic mixed ionic-electronic conductor (OMIEC) sensitive to the local concentration of mobile ions. By using the gate electrode to deplete or augment the channel with charged species, the doping state of the semiconductor polymer is altered and its conductance modulated. The operation in a liquid environment, the interplay between ionic and electronic conduction, and the soft nature of the organic materials open several fascinating applications for these devices, for example, in bioelectronics,[5,6] where they can operate in and interact with biological tissues and body fluids, and hardware-based artificial neural networks,[7,8] where they may be used as artificial synapses (i.e., an electronic device with reversible and controllable resistance). The neuromorphic features of OECTs have been thoroughly investigated and their dependency on the intrinsic properties of the channel was elucidated, generally dominated by the $R_sC$ time-constant (where $R_s$ is the resistance of the solution and $C$ is the capacitance of the channel).[9]

Three main approaches are used to produce OECT channels: photolithographic patterning,[4,10] inkjet printing,[11,12] and oxidative electropolymerization.[7,13] Printing and photolithography are most frequently employed, as they ensure low device-to-device variability and the higher quality of the channel associated with superior transfer characteristics. In contrast, electropolymerized devices often suffer from poor control over the deposition area, very limited scalability, and severe restrictions in the freedom of design of OECT circuits. Moreover, electropolymerization might result in larger variation of device parameters (transconductance and capacitance) compared to printing or lithography due to inhomogeneities in the electric field, monomer and salt concentration, or impurities in the solution.[7] On the other hand, electropolymerization also bears interesting advantages: the fabrication method is simpler and cheaper; the simplicity of the method allows for low-cost fabrication; furthermore, the possibility to have pre-patterned metal lines whereby the channel is subsequently produced on-demand allows the realization of dynamic circuitry and possible rewiring of the connections. In

M. Cucchi, H. Kleemann, H. Tseng, G. Ciccone, A. Lee, K. Leo
Dresden Integrated Center for Applied Physics and Photonic Materials
Technische Universität Dresden
Helmholtzstr. 10, 01069 Dresden, Germany
E-mail: matteo.cucchi@tu-dresden.de
D. Pohl
Dresden Center for Nanoanalysis
Technische Universität Dresden
Helmholtzstraße 18, 01069 Dresden, Germany

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this regard, Gerasimov et al. demonstrated an evolvable circuit in which the resistance of OECT channels could be varied by forming or over-oxidizing a channel.\textsuperscript{[13]} Unfortunately, carrying out electropolymerization with a DC electrical signal causes the coverage of the full metal electrode exposed to the solution, resulting in inhomogeneous channels with no directionality and random morphology, hampering performance and scalability (Figure S1, Supporting Information). DC electropolymerization is, in fact, often employed to cover metal surfaces with thin films. Considering these arguments, it would be interesting to exploit the benefits of electropolymerization and at the same time control the growth.

In a different context, much work has been carried out on the growth of metallic filaments and dendritic networks.\textsuperscript{[14,15]} There, it has been proven that an AC driven growth provides further parameters to control the growth of the dendritic structures. Notable examples of AC-grown organic structures have been employed in the field of microfluidics\textsuperscript{[16]} and have been shown to produce OECTs with long-term stability.\textsuperscript{[17]} However, the exploitation of the dendritic structure originating by the AC growth was never demonstrated as an additional degree of freedom for neuromorphic devices and artificial synapses. Here, we employ this technique to realize organic semiconductive devices with adjustable properties and controllable direction of the growth.

We demonstrate controlled growth of OECT channels through AC stimulated electropolymerization. We use this technique to connect two (or multiple) metal pads on the substrate with selective directionality and desired channel morphology. By varying the polymerization parameters, dendritic networks are obtained with width and branching depending on the frequency. We study the growth mechanism and determine the relevant dependencies and scaling properties. Since the resistance of the networks can be controlled by increasing the number of bridging fibers, we can realize electronic devices with neuron-like properties (e.g., that reinforce when stimulated). Moreover, changing the frequency of polymerization leads to networks with different response time, a feature that can be exploited to produce devices having short-term plasticity with tunable time-constants. In this regard, the organic dendritic networks not only encompass the benefits of traditional lithographically-made OECTs\textsuperscript{[18,19]} but introduce a new degree of freedom in growing fibers with controllable material properties. We demonstrate other neuromorphic features, such as controllable long-term plasticity (LTP), spike-timing-dependent plasticity (STDP), and Pavlovian conditioning. Finally, we tackle a typical problem of electropolymerized devices: the coverage of the full metal surface exposed to the solution, leading to device-to-device variability, parasitic capacitance, and hampering the down-scaling.

We show that the AC electropolymerization can be used to miniaturize the devices down to the micrometer scale by growing thin fibers at high frequency and appropriate concentrations, without covering the full electrode exposed to the solution.

2. Results and Discussion

2.1. Growth Mechanism and Material Characterization

For the formation of organic dendritic networks, an electrolytic solution containing the precursor monomer must immerse the area between the two electrodes that will be bridged (Figure 1a and Video S1, Supporting Information). The monomer we employ is 3,4-ethylenedioxythiophene (EDOT) and the salt is tetrabutylammonium hexafluorophosphate (TBAPF6). TBAPF6 is not only a suitable salt with a large electrochemical window, but it is also an oxidizing agent for the monomer and an efficient dopant for the resulting polymer poly(3,4-ethylenedioxythiophene)-tetrabutylammonium hexafluorophosphate (PEDOT:PF6).\textsuperscript{[20,21]} The polymerization proceeds in three steps:

1. The application of a positive voltage larger than the oxidation potential of EDOT triggers the radicalization of the

Figure 1. Set-up and growth of the dendritic networks. a) Setup and materials used to grow the organic dendritic networks (for details, see the Section 6). b) Sketch of the polymerization process: during the positive polarity of the applied electrical signal, the anions oxidize the monomers at the interface and trigger the reaction; during the negative polarity, the monomer surrounded by cations is inert (see Section 2). c) Networks grown at 4 V with varying frequency: higher frequencies promote thinner fibers and a higher degree of bifurcation.
monomers present at the electrode/electrolyte interface. Simultaneously, (PF$_6^-$) anions drift to the electrode and accumulate, forming an electrical double layer (EDL).

2. The radical cation EDOT$\cdot^+$ is neutralized by a PF$_6^-$ anion.

3. The complex EDOT:PF$_6$ is now neutral and reactive with other EDOT$\cdot^+$ (Figure 1b). These are provided by the bulk solution or by the already-formed polymer on the electrode. This way, the polymer PEDOT:PF$_6$ grows from the metal pad following the electric field lines because more PF$_6^-$ anions accumulate where the field is stronger (Figure 1c). The reaction is a nucleation-and-precipitation process: Figure 2a shows a microscopic image of a fiber with visible nucleation clusters. A DC voltage would cause an almost isotropic growth, resulting in a closed film covering the whole surface of the positively biased electrode, and extending in every direction which is undesirable for transistor channels, as shown in Figure S1, Supporting Information. In contrast, using an AC stimulus (square wave, duty cycle 50%) causes the polymerization of a small amount of monomer per cycle: the limited time given by the duration of semi-cycle allows the reaction only where the kinetics is fast. Since the reaction rate depends on the concentration of anion, the fibers grow preferably where the local field is higher. In turn, the newly grown fibers cause the field to be stronger during the next cycle (tip effect), accelerating the reaction at the extremity of the fiber rather than at the base (Faraday cage) as simulated in Figure 2b.

To support these observations, we measure the fiber thickness and find that it is proportional to the period $T$ of the AC signal (see Figure 2c). We find that in a first approximation, the reaction kinetics can be described by a rate equation in the form

$$\frac{dP}{dt}(t) \propto k[M][A^-](t)$$

where $dP/dt$ is the rate of polymer formation, $k$ is the equilibrium constant, $[M]$ is the monomer concentration, and $[A^-]$ is the concentration of the anion at the electrode/electrolyte that accumulate during one half-cycle. As a result, we find the following relation for the fiber width $w$

$$w \propto \int_0^{T/2} k[M][A^-](t) dt$$

Figure 2. a) Scanning electron microscopy picture of a PEDOT:PF6 fiber. Nucleation sites are visible as spherical structures. Scale bar is 2 µm. b) Simulation of the electric field during the growth. The colorbar represents the field strength (a.u.). The fibers only grow where the field is high because of the large ion (dopant) accumulation during the positive half-cycle. Meanwhile, where the field is low, the kinetics rate is slow. c) Dependence of the fiber thickness on the polymerization frequency at different electrolyte/dopant concentrations. d) Elemental analysis performed by energy-dispersive X-ray spectroscopy on a PEDOT:PF6 conducting polymer fiber. Carbon, phosphorus, and sulfur have been mapped. The elemental analysis shows that PEDOT and PF6 homogeneously blend within the polymeric matrix (scanned area = 180 nm × 300 nm).
This result rules out a diffusion-limited aggregation mechanism. Following Equation (1), we have performed Monte-Carlo simulations to simulate the growth. We report an exemplary result in Figure 2b. Here, by setting a reaction probability proportional to the local field and to the cross product between the field and the reaction growth, a good agreement with the experiment is found. With these simulations, we observe that the local field is the trigger for the reaction due to heterogeneous dopant accumulation. Each incremental growth of the electrode changes the field and thus modifies the ionic distribution in the next semi-cycle.

Occasionally, and with higher likelihood at high frequency, bifurcation occurs, resulting in higher bifurcation degree of the network. Conversely, during the negative polarity of the signal, cations accumulate at the interface, keeping the monomer in its inert state \( \frac{dP}{dt} = 0 \), while the reaction occurs at the other electrode.

The final product, PEDOT:PF₆, contains a large amount of anions, as recognizable by its high conductivity and elemental analysis (Figure 2d) carried out by energy-dispersive X-ray spectroscopy with a transmission electron microscope. We observe a homogeneous distribution of the elements within a fiber, judging from the distribution of sulfur (coming from the PEDOT) and phosphorus (featured in the dopant). Carbon, belonging to both molecules, is evenly distributed. Furthermore, by gating a dendritic network with an electrolyte, we can compare its material properties with existing channel materials for OECTs. By analyzing its transfer characteristics, the figure of merit \( \mu C^* \) typically used to benchmark OECTs\(^{[22]} \) is extracted for OECTs. By analyzing its transfer characteristics, the figure of merit \( \mu C^* \) typically used to benchmark OECTs\(^{[22]} \) is extracted for OECTs. By analyzing its transfer characteristics, the figure of merit \( \mu C^* \) typically used to benchmark OECTs\(^{[22]} \) is extracted for OECTs. By analyzing its transfer characteristics, the figure of merit \( \mu C^* \) typically used to benchmark OECTs\(^{[22]} \) is extracted for OECTs.

\[ g_n = \frac{dI_n}{dV_{CS}} = \frac{WdL}{\mu C^*} (V_{th} - V_{CS}) \]  

(3)

where \( W, d, L \) are the geometrical width, thickness, and length, \( \mu \) is the mobility, \( C^* \) is the volumetric capacitance, \( V_{CS} \) is the gate voltage and \( V_{th} \) is the threshold voltage. As the networks are composed of many fibers, the channel width \( W \) can be replaced by the fiber width \( w \) multiplied by the number of fibers \( n \). Moreover, by assuming the reaction at the extremity to be isotropic (i.e., growing in every direction in a sphere-shaped manner as in Figure 2a), we can set \( w = d \). Equation (3) becomes:

\[ g_n = \frac{w^2}{4L} \mu C^* (V_{th} - V_{CS}) \]  

(4)

At the peak of the transconductance, \( \mu C^* = 0.4 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1} \), in agreement with bench-marked OMIECs\(^{[22]} \) (see Figure S2, Supporting Information). For this analysis, \( L \) has been approximated to the electrode distance and \( w \) was measured as in Figure 2c. This parameter of merit does not depend on the growth parameters in the investigated range, as both capacitance and conductance scale similarly with \( w \) and the number of fibers \( n \). Hence, we assume that the morphology and elemental distribution within the fibers are not influenced by the growth which is an additional benefit of this method for circuit integration. Although the transfer characteristics (e.g., mobility and transconductance) are lower than traditional PEDOT:PSS-based OECTs, our focus is to show the modulation of the physical properties of the channel, rather than absolute performance parameters.

For the dendritic growth, the choice of the waveform is crucial: to obtain dendritic shapes, the waveform must contain both positive and negative polarity, to sequentially attract and repel the ions. Here, we use square and sinusoidal excitations, but pulses and any other arbitrary waveform work as well, affecting differently the network topology. For instance, a spike similar to the nerve action potential was used to grow (see Figure S3, Supporting Information). In contrast, pulses of only one polarity make the fibers grow radially from the electrode because during the off-time, monomers diffuse away rather than drift along the field. The thickness of the fibers is controlled by modulating the frequency: this is understandable by considering that the time available for the reaction during each cycle is proportional to the waveform period, as the rate is given by how many monomers can diffuse at the interface and how much charge (dopants) drift. This results in increasing thickness for increasing AC period (Figures 1c and 2c). Finally, it is worth noting that electrical properties are quite homogeneous and reproducible, although the same parameters for growth do not translate into identical networks.

### 2.2. Plasticity of the Organic Dendritic Networks

During the growth, multiple fibers branch out from the electrodes and grow along the field lines until they bridge the electrodes. Koizumi et al. used this technique in the framework of bipolar electrochemistry, and reported an abrupt termination of the growth upon the first contact\(^{[23]} \). In contrast, probably due to the much smaller gap used here, we observe continued growth and branch formation. We utilize this effect to further increase the network’s conductance. This effect is reminiscent of the reinforcement of neurons, which show increased formation of synapses when stimulated (a process known as learning-induced synaptogenesis). This mechanism is emulated with OECTs based on dendritic channels as shown in Figure 3a: the idea is to strengthen the connection between two electrodes when those are stimulated repeatedly over time. During the growth, we recognize three stages: one in which the fibers are growing but none of them bridged yet (characterized by high resistance); a second one in which, after the first contact, more fibers add up to the network contributing to the whole conductance (reinforcement); finally, a phase in which the ionic transport in the solution is negligible and no other fibers can grow (saturation). In this way, we show that the learning curve, and thus the behavior of the long-term plasticity, can be controlled by modulating the frequency used during the training as well as the training time. In Figure 3b and Figure S2, Supporting Information, we characterize the transfer characteristics of the networks during the three different stages (3s, 6s, and 9s) of the growth. By adding more bridging fibers to the network, the total conductance of the channel is increased, strengthening the synaptic weight. Moreover, Figure 3c shows that the reinforcement rate can be controlled by changing the polymerization frequency. In particular, faster reinforcement...
is obtained for decreasing frequencies. The conductance of the network is non-volatile, hence assuring a LTP mechanism needed in neuromorphic systems, without the need of using a third electrode (i.e., gate electrode).[13,24]

For neuromorphic applications, implementing a forgetting mechanism is as important as learning. Hence, it is mandatory to successfully implement a controlled forgetting/depression mechanism in brain-inspired hardware. A major figure 3. a) Learning curve during the formation of the dendritic networks, that is, training, using an AC signal of 50 Hz and amplitude 5V. Blue area: prior to connection; red area: sharp increase of current indicating gap bridging; yellow area: more synapses/branches are formed. Inset figures taken from Video S1, Supporting Information. b) I–V characteristics of a single device measured at different training times, (corresponding to the three colored areas in a). Transfer characteristics in Figure S3, Supporting Information. c) Conductance of a dendritic networks as a function of the number of pulses used to grow. The lower the frequency, the faster the learning process. d) Conductance decay of dendritic networks grown at a different stage of reinforcement. Reinforced network are very stable over time, while weak connections see their resistance increasing steadily. During the 8th day, the networks are reinforced, showing the possibility to update their strength at any time. e) The STDP behavior and f) STD of the synapses depend on the frequency used to grow the network, leading to a control of the short-term memory based on the fabrication process. In the inset in (e), the voltage applied a Ag/AgCl gate, used as pre-synaptic neuron is shown and the inset in (f) shows how ΔT is defined. It is the time interval between two pulses: these cause the conductance depression reported (normalized) on the y-axis.
process underlying the gradual erasure of long-term memories is synaptic decay. Here, we tune the decay time of a synapse by controlling the degree of synaptic reinforcement. The networks decay can be controlled by the strength of the connections: In Figure 3d, we grow and characterize the decay of two synapses with different degrees of synaptic reinforcement. A highly reinforced synapse (close to saturation) with a dense fiber network formed with longer polymerization time ensures fault tolerance, improved conductance, and longer retention. In contrast, a weak connection (slightly reinforced after the first fiber bridged) witnesses a conductivity drop of 50% in 48 h. We assign the decay to the solubilization of the dopant in the solution, which reduces the doping level in the semiconductor and thus its conductivity.

On the millisecond to second timescale, short-term plasticity assists the brain in computational tasks and ensures rapid adaptation. Conventional demonstrations of short-term plasticity of OECTs are carried out by using a gate electrode as presynaptic neuron. We show that we can modulate the device response time based on the polymerization frequency, and we use it to tune the retention time for the short-term plasticity. In Figure 3e, we report an important learning mechanism referred as to spike-timing-dependent plasticity (STDP): STDP dictates the potentiation or depression of the synapse based on the temporal order of spikes. The degree of potentiation or depression depends on the frequency used to grow the network: specifically, the difference in synaptic depression or potentiation for different growth frequencies is as large as 50%. Controlling the time-constants of electronic and ionic conduction is key to adjust the degree of plasticity in synaptic networks. This property is useful in neuromorphic applications. Hence, depending on the requirements for the network, the growth frequency might be used to foster or weaken the networks ability to be trained by spike-timing-dependent plasticity. To achieve this result, it is key to minimize the PEDOT coverage of the gold electrodes, a typical unwanted effect of DC oxidative polymerization (Figure S1, Supporting Information). This is because the capacitance of the device must be dominated by the capacitance of the fibers forming the networks.

The same concept applies for short-term depression (STD) mechanisms, as shown in Figure 3f. Here, pulses of fixed pulse-width and varying duty cycle are applied to networks grown at different frequency. A faster depression is observed for synapses grown with higher frequency because the dedoping cations can quickly penetrate through the thinner fibers. Further details about the STDP and STD measurements are given in Figure S4, Supporting Information. Hence, growth parameters directly affect the material properties, which in turn translate into a learning rule with tunable time-constants: we can thus control the time-constants that ultimately rule the neuromorphic time-dependent learning/forgetting mechanism. This control over the material properties is new in electropolymerized devices and can be effectively used to produce evolvable circuitry in electrolytic solutions.

More complex neuromorphic features are attained with multiple electrodes. Here, interconnectivity is implemented and the electric field in the solution is shaped to achieve directed growth: First, complex electrode configurations can be used and controlled channels are grown where and when desired (Figure 4a–e). Moreover, the use of multiple electrodes at a potential lower than the oxidation potential is a powerful tool to stimulate or prevent the growth of selected connections. This is achieved by applying a low potential to neighboring electrodes (Figure S5, Supporting Information). The need of such a threshold potential assures the presence of an activation function to begin the reaction; similarly to biological nerves, where the weighted sum of the inputs is passed through an activation function, the combined effect of multiple electrodes can trigger or inhibit the learning/growth process at an electrode. Furthermore, we emulate acquisition in the framework of Pavlovian conditioning by producing a connection that links an initially uncoupled stimulus (see Figure S6, Supporting Information).

3. Toward High-Density Integration

For real applications, the technique we propose should allow for miniaturization in order to realize high density integration of analog, digital, or neuromorphic circuits. In terms of fiber width, Figure 2c shows how the diameter of each fiber can be reduced simply by increasing the AC frequency and reducing the salt concentration. In fact, growing at 200 Hz in a solution concentrated 0.5 mM, fibers down to 1 µm are formed, opening up the possibility to build micrometric devices. In addition, the properties of the fibers scale with the electrode distance because the R, C time-constant is reduced by a lower electrolyte resistance. Hence, higher frequencies are required for smaller distances. One aspect that is still limiting the miniaturization of electropolymerized devices is that often the whole area of the metal exposed to the solution is covered in polymer, with poor or no directional selectivity. We successfully prevent this effect by patterning sharp electrodes, hence enhancing the field: the growth can be achieved at lower voltage and it is confined to the area between the two tips (Figure 4f) because the dopants quickly accumulate where the field is the highest.

Based on this idea, we construct a crossbar array on a flexible polyimide substrate (Figure S7, Supporting Information) in which we grow connections only where required without affecting the surrounding electrodes (Figure 4g). Finally, further improvements could be achieved by using monomers that can initiate polymerization at very low potential (for example self-doped monomers as in refs. [28,29]) to polymerize at lower voltages and enable the use of this technique in water, pointing toward in-vivo applications. Overall, knowing the scaling rules, networks of organic dendritic networks based on electropolymerization might be miniaturized below the µm-scale. In particular, directed growth of thin polymer fibers should be possible by increasing the frequency, reducing the salt concentration, and sharp electrodes for large potential gradients. The passive matrix in Figure 4g is a proof-of-concept device to demonstrate that the integration of multiple fibers in a crossbar with a micrometric size is possible. For real-world application (e.g., computation), an active matrix is needed, realizable adding blocking and access devices. A notable example of an active matrix of OECTs was reported by Fuller et al. (102)
4. Conclusions

In this work, we investigate the growth of organic dendritic networks composed of the semiconductor PEDOT:PF$_6$, and we vary the growth parameters to show various neuromorphic properties. By using AC stimulation for the polymerization, we achieve deposition directionality and scalability, traditionally challenging objectives for electropolymerized devices: The method allows control over the channel formation by varying the voltage, frequency, and duration of the electrical stimulus. Moreover, it allows the growth with spatially selectable directionality in order to bridge two or more electrodes on the substrate, whereby the channels can be updated multiple times. By changing the frequency, we are able to modify the resistance of the channel, as well as its response time, important for brain-inspired learning rules. We investigate the factors that control the fibers morphology, and we find dependence on the AC frequency used to grow and monomer concentration, ruling out a diffusion limited process (Equation (1)). The resulting polymer has a figure of merit $\mu C_\nu$ in agreement with other OMIECs, and similar transfer properties when employed in an OECT configuration. The growth method is very advantageous for neuromorphic applications because it allows the making of devices that follow learning rules with desired time-constants. In this regard, we show typical neuromorphic features often demonstrated for traditional OECTs (short and long-term memory, STDP, and Pavlovian conditioning). Finally, we tackle the problem of miniaturization, and show devices on the sub-micrometer scale, integrated in a dense crossbar array on a flexible substrate.

5. Experimental Section

Fibers of the conductive poly-3,4-ethylenedioxythiophene doped with hexafluorophosphate (PEDOT:PF$_6$) were prepared by AC electropolymerization in an electrolyte solution under AC signals (square wave 10–200 Hz) with a HP 8114A pulse generator between two gold electrodes. All the substrates were patterned starting with a 50 nm gold covering 3 nm Cr on glass. Standard photolithographic steps were used to pattern the gold. The photoresist used was nLof 2000. The electrolyte solution of acetonitrile contained 1 mm TBAPF$_6$, and 50 mm EDOT. Note that the solvent dissolves the salt and the monomer, but poorly dissolves the resulting polymer (PEDOT). The highly doped PEDOT:PF$_6$ was formed and featured a dark blue color. After the deposition it was rinsed in isopropanol, and annealed at 110 °C for 10 min. A better and more reproducible growth was obtained by preventing parasitic currents, using an insulating layer (SU8, microchem) patterned on top of the gold leads prior to the deposition, leaving the channel area open. Moreover, the substrate underwent 10 min of plasma cleaning to have a cleaner gold surface. When the precursor solution was dropped for the growth, its evaporation inevitably raised the concentration of salt. Therefore, frequent rinsing in ethanol leads to more reproducible results. The transfer and output characteristics were measured with a pair of Keithley SMUs (models 2600 and 2400) using the software SweepMe! (sweep-me.net) with the device immersed in an aqueous solution containing 1 mm NaCl and gated with a Ag/AgCl electrode immersed in the same solution. Vg was swept at 0.1 V s$^{-1}$. An equivalent configuration was used to carry out the STDP and STD experiments, where the gate was biased using an arbitrary function generator rather than an SMU. Likewise, the action potential-like waveform was programmed using an arbitrary function generator with dual output channel. The gate electrode used was an Ag/AgCl pellet immersed in the solution. For the decay characterization, the devices were stored in an aqueous electrolytic solution of 1 mm NaCl over the whole time of the experiment (1 week).

Figure 4. a–d) Neuron-shaped electrodes can be used, in combination with the field-directed growth, to produce multiple connections (grown at different times) with specific resistances. e) I–V characteristics of the networks in panel (a). f) By changing the geometry of the electrode, the field is influenced and so is the growth of the fibers. Using sharp tips allow minimal to absent PEDOT coverage of the gold electrode, minimizing parasitic capacitance and leakage resistance. The figure shows a fiber of length 20 µm grown at 1 kHz and 2.5 V. g) A crossbar array realized with sharp electrodes allows the selective and controlled growth of fiber of submicrometric size. The sites of the crossbar can be addressed subsequently and independently: the PEDOT:PF$_6$ only grows between the two tips.
Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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