Supporting Information

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Polymer-Based Composites for Engineering Organic Memristive Devices

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S1.- Profilometry Characterization

Each sample consists of sixteen different devices that can be studied independently. That is, the finished sample possesses sixteen spots, or cross-sectional areas, where the three layers (bottom electrode, active material, top electrode) coexist. These areas are present in eight rows that can be numbered (Figure S1.1).

![Figure S1.1: Schematic of a finished sample with eight rows of two devices each. The spin-coated active material (yellow) is sandwiched between the bottom electrode (ITO layer, darker region) and the top electrode (Ag layer, grey) in sixteen areas (devices).](image)

In order to extract sufficient statistical data, profilometry was performed once for each row of devices, totaling eight measurements per sample. This was done between the Ag segments, so that the scratched area only took the active material layer away. This means that the measurements performed only correspond to the thickness of the active material layer.

The results for a batch of twelve samples, which were spin-coated with the standard setting of 2000rpm (1 minute), are shown in Table S1.1. The equipment utilized was the Ambios XP-1 profilometer.

|            | Samples |
|------------|---------|
| Rows       | 1  2  3  4  5  6  7  8  9  10  11  12 |
| 1          | 212 216 205 209 211 246 198 183 197 194 208 214 |
| 2          | 205 218 202 207 215 225 193 193 203 204 205 204 |
| 3          | 223 216 221 208 224 220 203 203 195 205 216 203 |
| 4          | 231 218 213 208 216 220 196 212 205 213 207 199 |
| 5          | 220 217 210 213 209 212 206 216 193 206 214 221 |
| 6          | 238 216 208 211 218 221 198 206 199 197 212 204 |
| 7          | 204 219 208 214 207 212 198 203 203 207 200 210 |
| 8          | 225 217 207 207 206 201 205 189 197 196 201 221 |
| Average    | 209 ± 10.2 nm |

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S2.- AFM Imaging

The topography of the spin-coated substrate was imaged using a Bruker Dimension Icon Atomic Force Microscope set in tapping mode. The tip used was of silicon with a resonant frequency of 300 kHz and a force constant of 40 N/m, while the scan rate was of 0.6 Hz. Six 5x5µm images were taken for a sample spin-coated at 2000rpm for 1 minute (Figures S2.1-S2.5). These images were extracted employing the *Gwyddion* v2.58 software.

AFM images of the sample showed the absence of huge aggregates. However, small features are observable, corresponding to bubble-like formations or holes that may form during the annealing process. Additional experiments are suggested in order to study the effects that different annealing times and temperatures, spin-coating speeds, or ratios of components present in the active layer, can exert on the topography characteristics of the finished samples.

*Figure S2.1: AFM, 2000rpm (1).*
Figure S2.1: AFM, 2000rpm (2).

Figure S2.2: AFM, 2000rpm (3).
Figure S2.3: AFM, 2000rpm (4).

Figure S2.4: AFM, 2000rpm (5).
S3.- Exponential Fitting of the STM and LTM decays

In Figure 3d (main document), the evolution of the conductance ($\Delta G$) versus $t_{\text{wait}}$ is represented. In the experiment, we observed that, for $t_{\text{wait}}$ values longer than 500ms (2s for 3V excitation), the expected exponential relaxation of the conduction was present. These decays were fitted to a modified Kohlrausch equation (S3.1) using a minimum squares method as implemented in the program IGOR PRO 8. (Figure S3.1):

$$\frac{G_f}{G_0} = y_0 + Ae^{t/\tau}$$

(S3.1)

Figure S3.1: Fitting of the relaxation rates for short time (red, blue) and long time (black) memory states as functions of waiting time (dashed line: fitting; dots: experimental data).

The parameters resulting from the empirical fitting are summarized in Table S3.1. In all the cases, the $y_0$ parameter value must be $\sim 1$ as it represents the minimum value for the $G_f/G_0$ ratio. Besides, the parameter $A$ can be ascribed to the inertia felt by the ions due to the potential bias gradient. Finally, regarding the characteristic times, which shapes the curves and gives an insight of the relaxation procedure, we obtained $\tau_S = 2.5 \sim 3 s$ for STM and $\tau_L = 4.7 s$ for LTM.

Table S3.1: Summary of fitting parameters obtained from the STM / LTM experimental tests.

| Experimental Test       | $y_0$  | $A$   | $\tau$ (s) |
|------------------------|--------|-------|-------------|
| 10 pulses / 1V (*)     | 1.01   | 0.374 | 2.57        |
| 50 pulses / 1V (*)     | 1.01   | 0.91  | 3.01        |
| 10 pulses / 3V (*)     | 1.05   | 3.30  | 4.73        |
S4.- Degradation vs. time in air and in a N\textsubscript{2}-filled glovebox

Figure 2a (main document) shows the most common electrical characterization technique that was performed in this study in order to discern between functioning and broken devices, and to get a rough estimate of their conductivity. This type of measurement was performed with the Keithley 2450 SourceMeter, along with self-made programming code written in the Keithley Test Script Builder.

The hysteresis curves themselves consisted of ten voltage sweeps between 0 and either 1.2 or 3V for ‘low’ or ‘high’ voltage studies, respectively. For the case of studying degradation vs. time, a ‘high’ voltage setting was used, since it represents the most demanding test for the devices, and it involves internal processes happening within the active material (i.e., movement of Li\textsuperscript{+} cations). The rate of sweeps was kept at 0.62 V/s, with a 10s delay between each cycle.

A non-encapsulated sample containing sixteen independent devices was left outside of the N\textsubscript{2}-filled glovebox in order to test its robustness against room conditions. Two devices were measured once every other day until Day 14 after fabrication, in the following way: at Day 0 (just after evaporating the Ag electrode on top), a pair of devices was characterized; at Day 1, this pair was also measured, along with a new pair of devices from the same sample, and so on. This was done in order to differentiate between changes caused by excitation, and those caused by time degradation (Figure S4.1). The incidence of light was not controlled for this sample.

| Day 0 | Day 1 | Day 3 | Day 5 | Day 7 | Day 10 | Day 12 | Day 14 |
|-------|-------|-------|-------|-------|--------|--------|--------|
| ![Graph](image1.png) | ![Graph](image2.png) | ![Graph](image3.png) | ![Graph](image4.png) | ![Graph](image5.png) | ![Graph](image6.png) | ![Graph](image7.png) | ![Graph](image8.png) |

**Figure S4.1:** Degradation vs. time study of multiple devices in a single non-encapsulated sample, which remained in air at room temperature. Columns represent days after fabrication. Hysteresis curves demonstrate correct functioning of the devices until Day 14, when all of them simultaneously show an erratic behaviour. Measured devices not shown in the figure present similar or identical curves.
We found that changes caused by excitation are negligible at this days-long time scale, since devices measured for the first time in the following days display similar or identical curves than those that were measured previously. Furthermore, the devices showed nicely-shaped hysteresis curves that increased in conductance levels every successive cycle until Day 14, after which they stopped functioning properly. This suggests that our devices can work in air and under room temperature for around 300 hours.

Additionally, a pair of non-encapsulated samples remained inside a N$_2$-filled glovebox to test its robustness against time, rather than air. Sample 1 was kept in the absence of light, while Sample 2 remained with the light turned on at all times. Both of them exhibited a perfect behaviour even at the 14$^{th}$ day after fabrication (Figure S4.2).
**Figure S4.2:** Hysteresis curves of devices kept inside a N₂-filled glovebox for two weeks after fabrication. Sample 1 was kept in the absence of light, while Sample 2 remained with the light turned on. No discernible, clear differences were found between devices kept within light and those kept in the dark, although further experimentation is suggested in this regard to discover the optimal conditions for storing the devices, as well as their real lifetime. Moreover, given the more aggressive nature of the electrical characterization performed in these experiments, where a changing voltage is applied for 10s per cycle, with just 10s between each one to relax, some devices may deteriorate, showing much higher currents. Thus, the dispersion from the group in this experiment is higher compared to the softer pulsed voltage studies displayed in the main document. Overall, the robustness of our non-encapsulated devices was found to be high, especially compared with standard organic devices. However, further chemical design is being developed to improve this in future iterations.

**S5.- Optical images of the memristive device**

In this section we provide several illustrative optical images of the memristive device. Notice that each substrate is composed of a total of 16 junctions.

**Figure S5.1:** Optical images of a sample with 16x2-T independent devices. The observed yellow color is provided by the SY polymer.

**Figure S5.2:** Optical microscope images of the sample shown in Figure S5.1. The brighter yellow areas correspond to the devices’ top electrodes made of silver. (left) 5x magnification; (right) 100x magnification.