Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Resistive Switching Controlled by the Hydration Level in Thin Films of the Biopigment Eumelanin

*Eduardo Di Mauro, Olivier Carpentier, Sergio Iván Yáñez Sánchez, Ndembi Ignoumba Ignoumba, Myriam Lalancette-Jean, Josianne Lefebvre, Shiming Zhang, Carlos F. O. Graeff, Fabio Cicoira, Clara Santato**

Eduardo Di Mauro, Olivier Carpentier, Myriam Lalancette-Jean, Sergio Iván Yáñez Sánchez, Ndembi Ignoumba Ignoumba, Dr. Josianne Lefebvre, Prof. Clara Santato
Department of Engineering Physics
Polytechnique Montréal
C.P. 6079, Succ. Centre-ville, Montréal, Québec, H3C 3A7 Canada
*Email: clara.santato@polymtl.ca

Prof. Fabio Cicoira, Shiming Zhang
Department of Chemical Engineering
Polytechnique Montréal
C.P. 6079, Succ. Centre-ville, Montréal, Québec, H3C 3A7 Canada

Prof. Carlos F. O. Graeff
DF-FC, Universidade Estadual Paulista
Av. Eng. Luiz Edmundo Carrijo Coube 14-01
17033-360 Bauru, Brazil

Type of eumelanin	Intrinsic Cl^- amount (% wt. over eumelanin)	NaCl added (mg/ml)	Cl^- added (% wt. over eumelanin)	Final Cl^- amount (%wt. over eumelanin)	Referred to as
Sigma	0.83±0.04	0.8	3.2	≈4	Intermediate chloride amount
		1.8	7.3	≈8	High chloride amount
DMSO-melanin	0.10±0.01	0.8	3.2	≈3	Intermediate chloride amount
		1.8	7.3	≈7	High chloride amount

Table S1. Chloride concentrations for different suspensions of eumelanin in dimethyl sulfoxide (DMSO) used in this work.

Resistive switch	ON/OFF ratio			Number of samples
	Minimum	Maximum	Average	
Standard	$9 \cdot 10^2$	$5 \cdot 10^4$	$2 \cdot 10^4$	16
Hybrid	$2 \cdot 10^1$	$7 \cdot 10^2$	$3 \cdot 10^2$	5

Table S2. ON/OFF ratios for the *standard* and *hybrid* resistive switch.

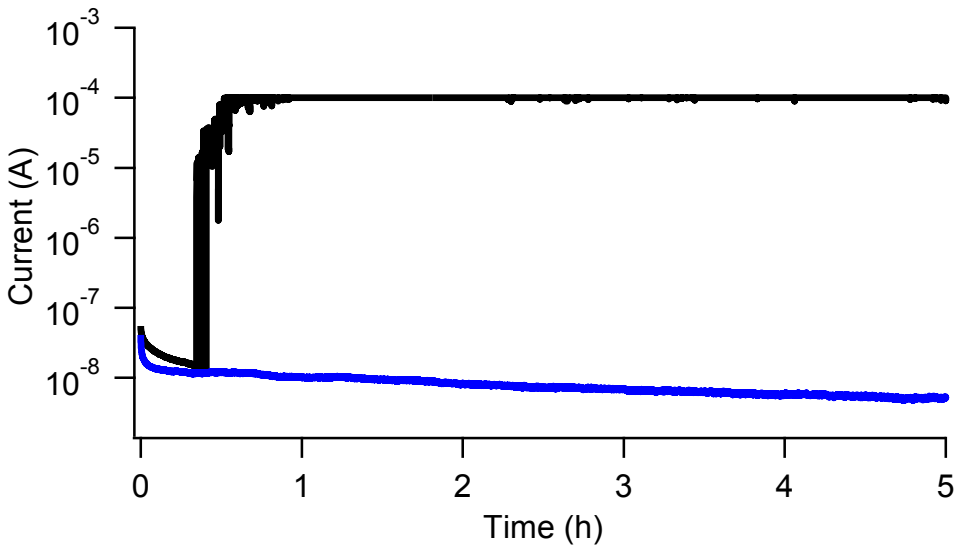

Figure S1. Current vs time plots for the first 5 hours of transient current measurements performed on (i) a thin film of Sigma eumelanin, hydrated for 1 hour at 90% RH and biased for ≈28 hours at 1 V, wherein a resistive switch took place after 23 minutes (current compliance set at 10^{-4} A, black curve) and (ii) a thin film of Sigma eumelanin, hydrated for 1 hour at 90% RH and biased for 15 hours at 1 V, wherein a resistive switch did not take place (blue curve).

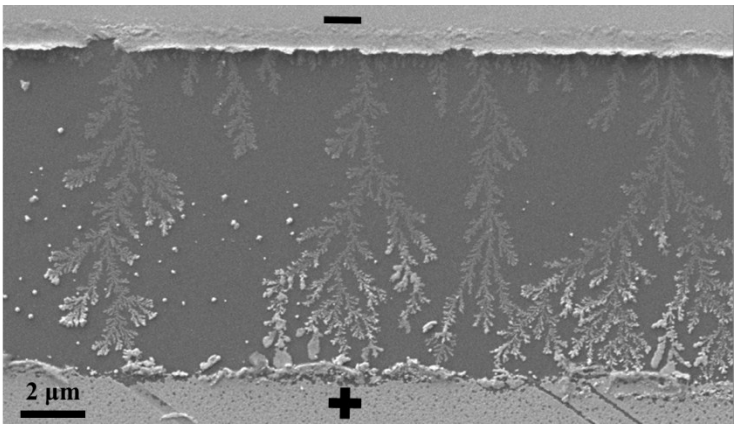

Figure S2. SEM image of dendrites bridging the two electrodes and of nanoclusters migrating, in a thin film of Sigma eumelanin, hydrated for 1 hour at 90% RH and biased at 1 V for 19 hours. The resistive switch took place after 28 minutes. SEM voltage = 5kV.

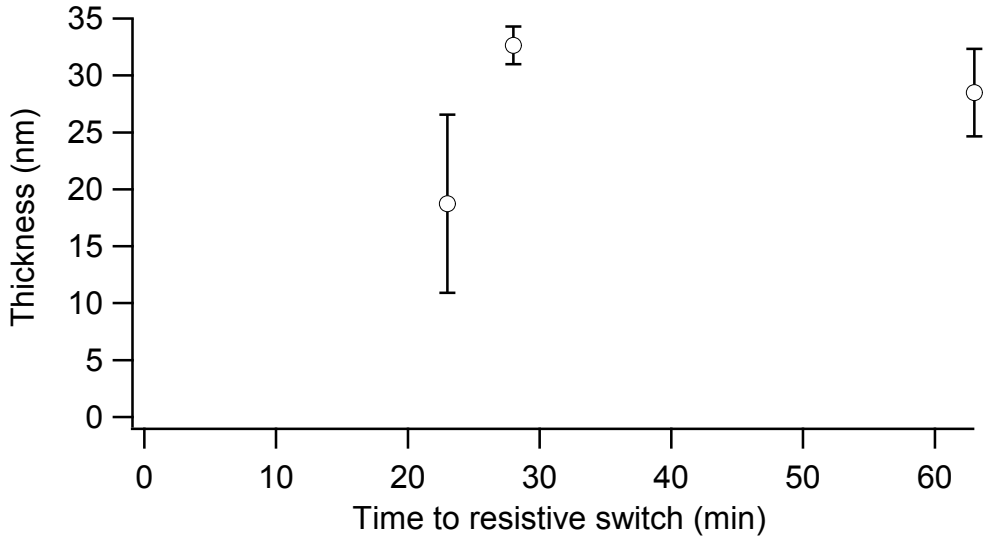

Figure S3. Average thickness versus time to resistive switch for Sigma eumelanin thin films (1 hour-hydration, 1 V electrical bias) that showed a *standard* resistive switch within the first hour of the measurement (each point refers to a sample).

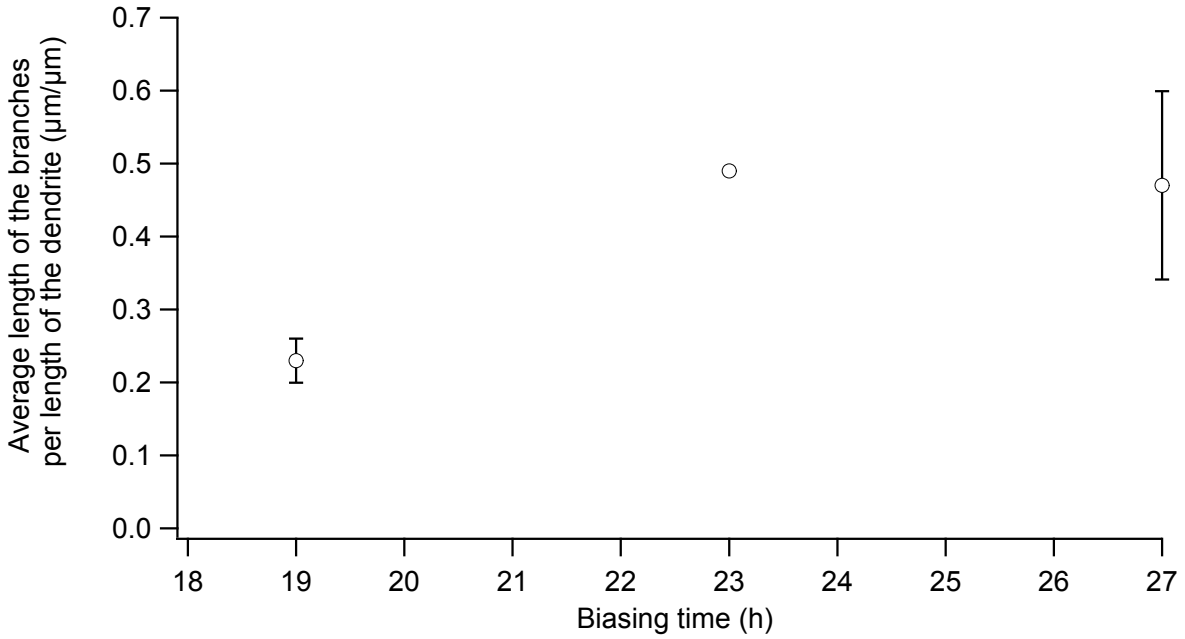

Figure S4. Average length of the branches of the dendrites, normalized by the length of the dendrite from which the branches were developing (*L*), versus biasing time (protruding dendrites shorter than 3 microns were not considered). The farther *L* is from 0, the more the dendrite growth is lateral rather than straight. As the electrical measurements were not stopped when the resistive switch took place, only a correlation with the biasing time, rather than with the time to resistive switch, could be found, as expected, as once the dendrite has produced the bridge, the rest of the biasing time can likely only promote an increase of its lateral extent.

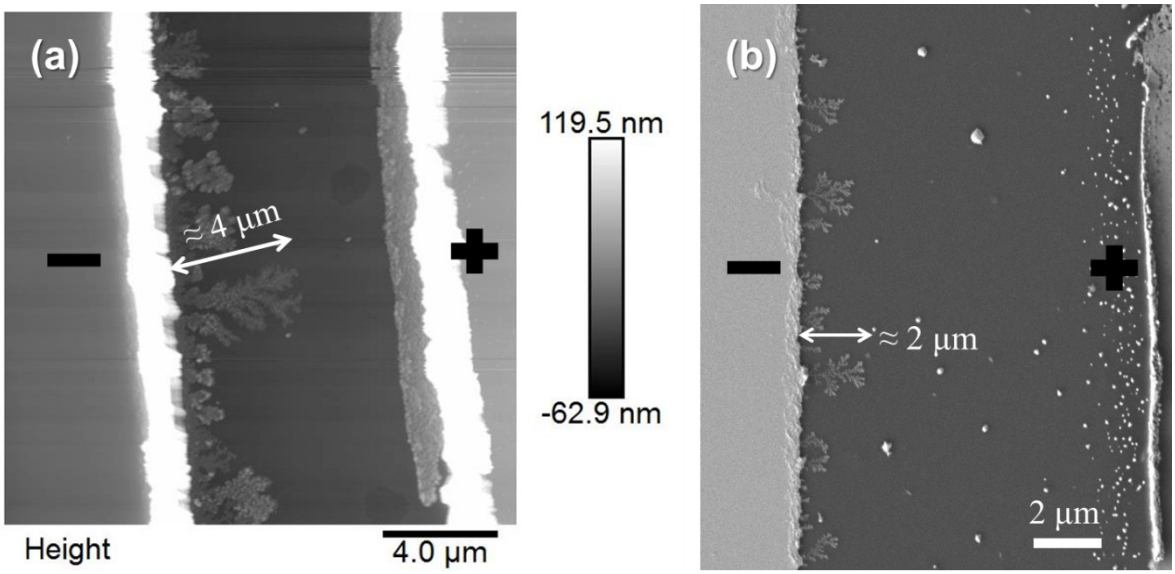

Figure S5. Effects of the hydration time: AFM and SEM images comparing the length of the dendrites in two Sigma eumelanin thin films that differ for the hydration time (spin-coated from the same suspension, hydrated at 90% RH, and biased at 1 V) (a) AFM image, 18 µm × 18 µm, film hydrated for 1 hour (biasing time of approximately 28 hours), (b) SEM image, film hydrated for 4 ½ days (biasing time of 24 hours). SEM voltage=5kV.

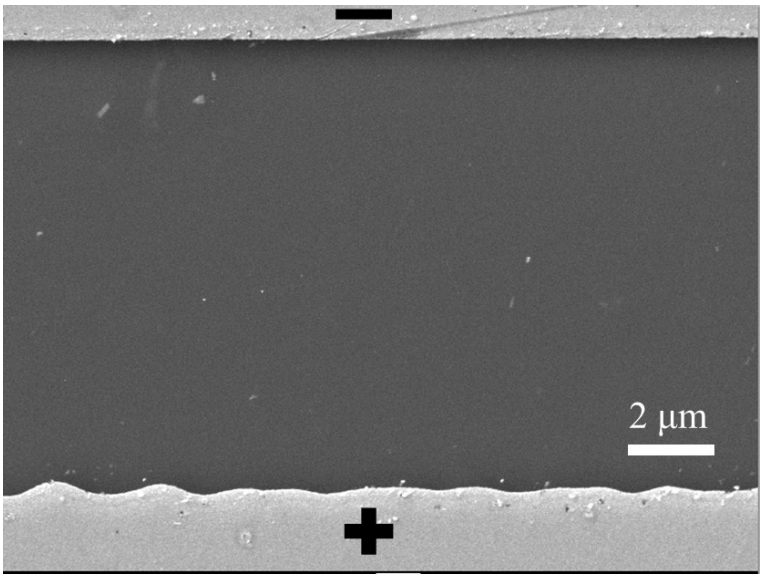

Figure S6. SEM image of a thin film of Sigma eumelanin hydrated for 14 days at 90% RH and biased for 3 hours at 1 V. No dissolution of the positive electrode was observed. SEM voltage=10kV.

Late resistive switch for thin films with high chloride content

For thin films with 8% wt. Cl^- content, hydrated for one hour at 90% RH, in one case the resistive switch took place after 52 minutes of biasing at 1 V: SEM images reveal that several dendrites grew one next to the other in the channel (Figures S7 and S8). Consequently, the late resistive switch may be due to the fact that the preferential pathways for nanoclusters were very close one to the other, and came to competition, causing the opening of several lateral branches, thus promoting a lateral (rather than straight) dendrite growth. The effect was a delay of the whole process. This is confirmed by a study of the shape of the dendrites: the lateral extension of the

dendrites for this sample was 9.7±2.4 μm, more than twice the average for other samples with a resistive switch within 7 minutes (3.5±0.5 μm).

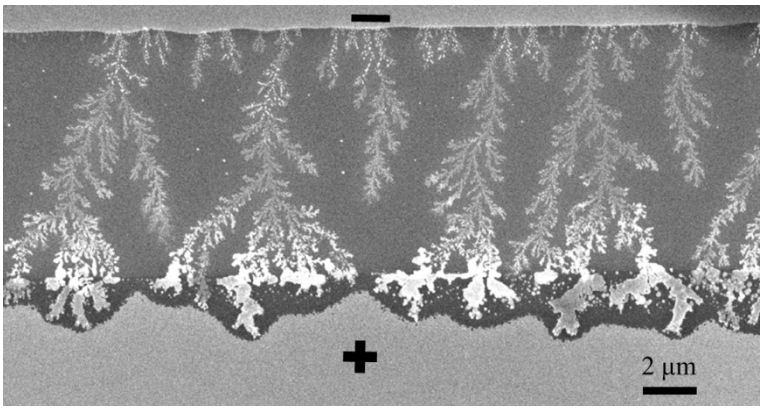

Figure S7. SEM image of dendrites bridging the two electrodes in a Sigma eumelanin thin film (8% wt. Cl^-), hydrated for 1 hour at 90% RH and biased for 12 hours at 1 V, where the resistive switch took place after 52 minutes. SEM voltage=10kV.

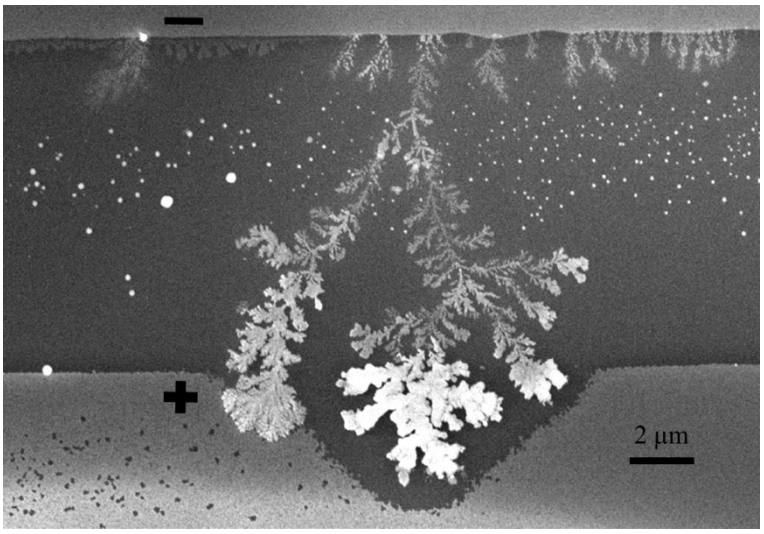

Figure S8. SEM image of dendrites bridging the two electrodes in a eumelanin thin film, same sample of Fig. S7. It is worth noting that, once the dendrite reached the cove that had generated the material for its growth, the dendrite started receiving nanoclusters also from its sides. This is

the reason why the thickness at its end, in the cove, appears higher (corresponding to the brighter region in the image) than that of the body of the dendrite. SEM voltage=10kV.

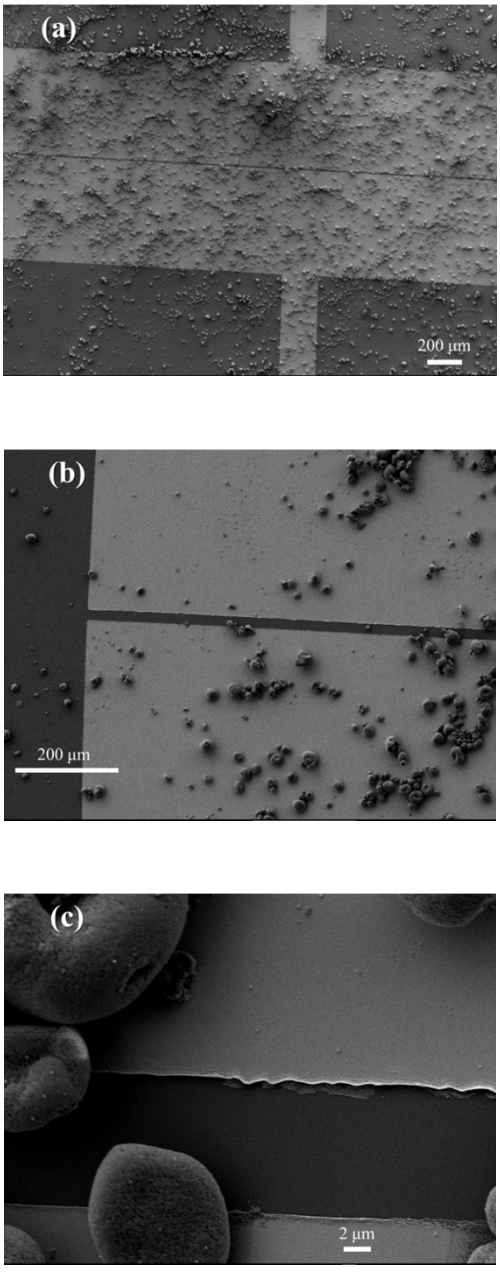

Figure S9. SEM images of gold electrodes after the spin coating of a suspension of Sepia eumelanin in DMSO at different magnifications: (a) 40X, (b) 250X and (c) 3330 X. Several granules can be observed. SEM voltage=5 kV.

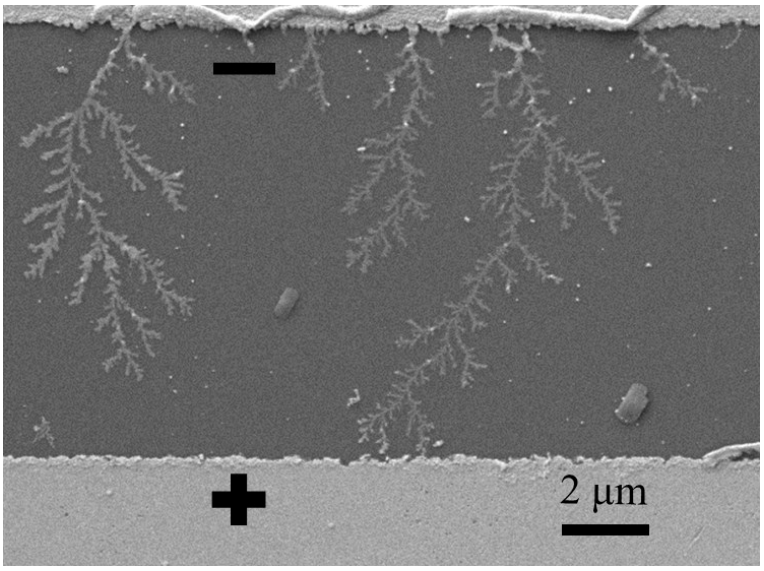

Figure S10. SEM image of dendrites bridging one electrode to the other after 3 hours of electrical bias at 1 V in a thin film of Sepia eumelanin (7% wt. Cl^-), hydrated for 1 hour at 90% RH. The resistive switch took place after 34 minutes. It is worth noting that dendrites grew where there were no granules, revealing the presence of a thin film of Sepia eumelanin. SEM voltage=5kV.

Chloride amount	Number of suspensions tested	Absence of resistive switch within 3 hours (% of samples)	Resistive switches (%) within		
			7 min	30 min	63 min
Low (1% wt., intrinsic in Sigma eumelanin)	4	57	0	29	43
High (7% wt., Sepia eumelanin)	2	25	25	50	75
High (8% wt., Sigma eumelanin)	4	11	78	78	89

Table S3. Summary of the occurrence of the resistive switch within certain time frames for thin films of eumelanin with different chloride contents, hydrated for 1 hour at 90% RH and biased at 1 V.

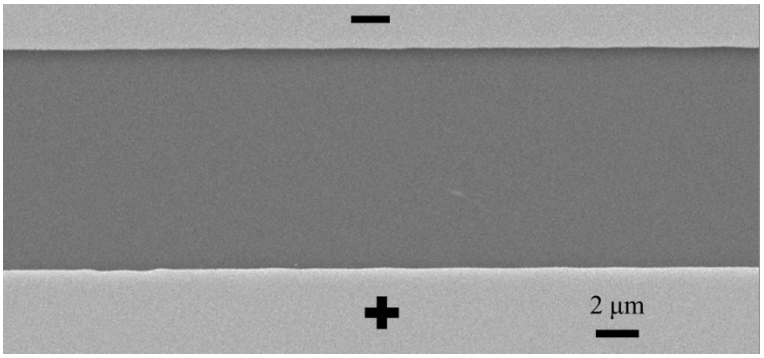

Figure S11. SEM image of Au electrodes in contact with a DMSO-melanin thin film, 7.4% wt. Cl^-, hydrated for 1 hour at 90% RH and biased at 1 V for 3 hours. The positive electrode did not dissolve. The absence of dissolution and material migration in the channel could be observed also for samples biased for 12 hours, with the same hydration treatment and at the same electrical bias. SEM voltage=10kV.

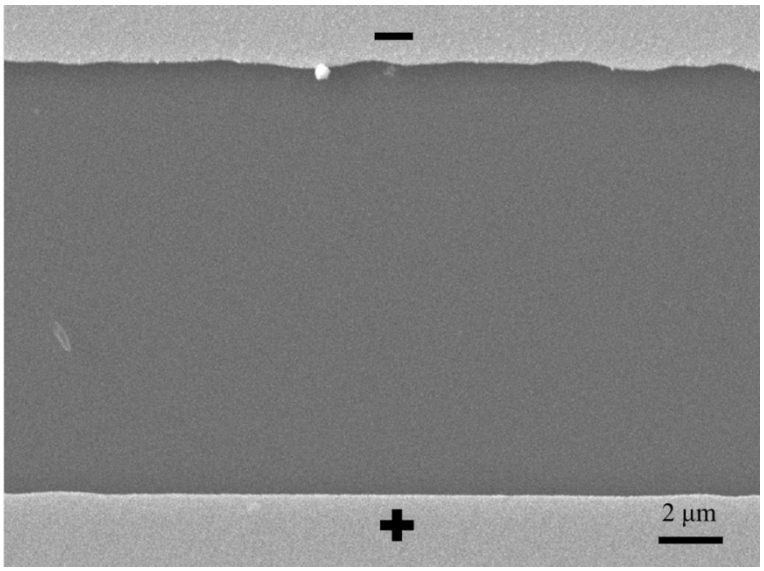

Figure S12. SEM image of the interelectrode area after 19h½ of biasing at 1 V after a DMSO drop had been confined between the electrodes. SEM voltage=10kV

DMSO drops on Au electrodes at different electrical biases and chloride contents

The results observed with the DMSO drop confined in the channel depend on the electrical bias and on the chloride amount:

Biasing voltage (V)	Effect of		
	DMSO drop	**DMSO drop 0.8mg/ml NaCl**	**DMSO drop 1.8mg/ml NaCl**
1	No dissolution of the positive electrode	Growth of nanostructures	Growth of nanostructures
2.1	Fine dendrites	Interelectrode region filled by the material originated by the massive dissolution of the positive electrode	Interelectrode region filled by the material originated by the massive dissolution of the positive electrode

Table S4. Summary of the phenomena occurring when a DMSO drop, with and without NaCl added, is confined between gold electrodes under electrical bias.

At 2.1V, when a drop of pure DMSO is confined in the channel, fine dendrites grow from the negative electrode after 3 hours of electrical bias (Figure S14). At 2.1V in the presence of chlorides, conversely, the positive electrode was severely damaged: it was massively consumed, so that a resistive switch was caused by the interelectrode distance filled with material originating from the dissolution of the positive electrode, after less than 1 minute (approximately 40 seconds).

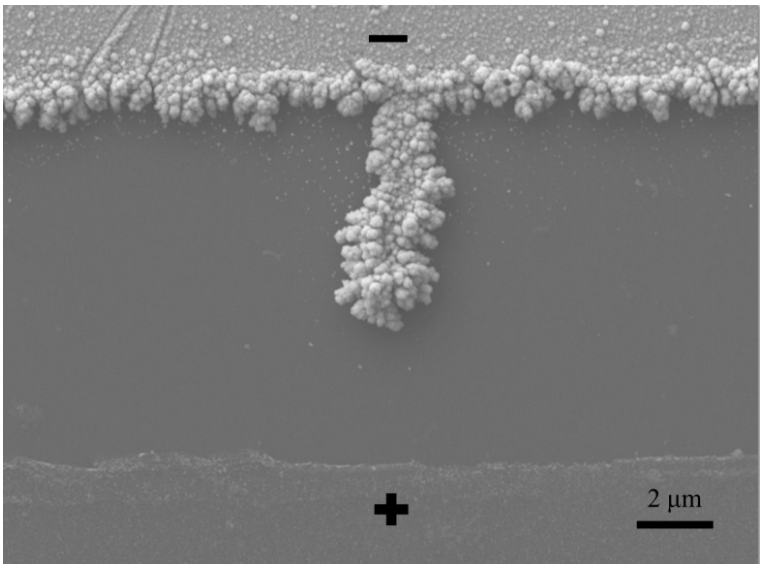

Figure S13. SEM image of gold electrodes after 3 hour-biasing at 1 V while a DMSO drop with 1.8mg/ml of NaCl was confined between the electrodes. SEM voltage=10kV.

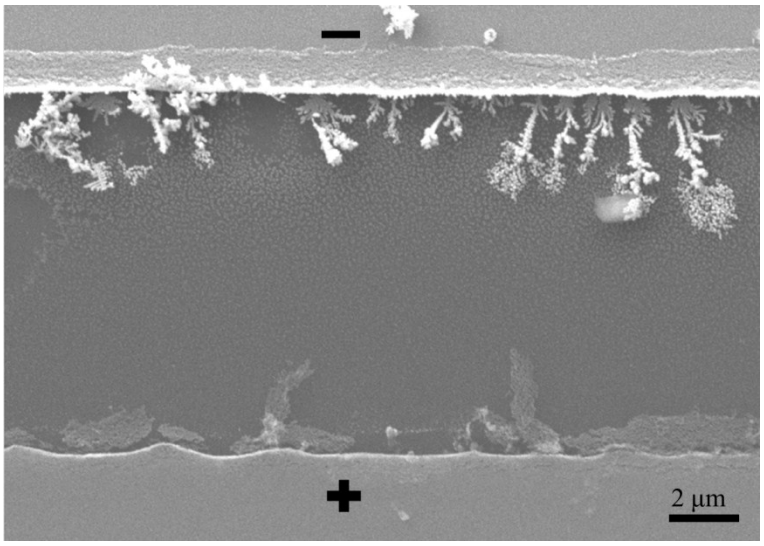

Figure S14. SEM image of gold electrodes after 3 hour-electrical biasing at 2.1 V while a DMSO drop was confined between the electrodes. The positive electrode dissolved and fine dendrites grew from the negative electrode. SEM voltage=10kV.

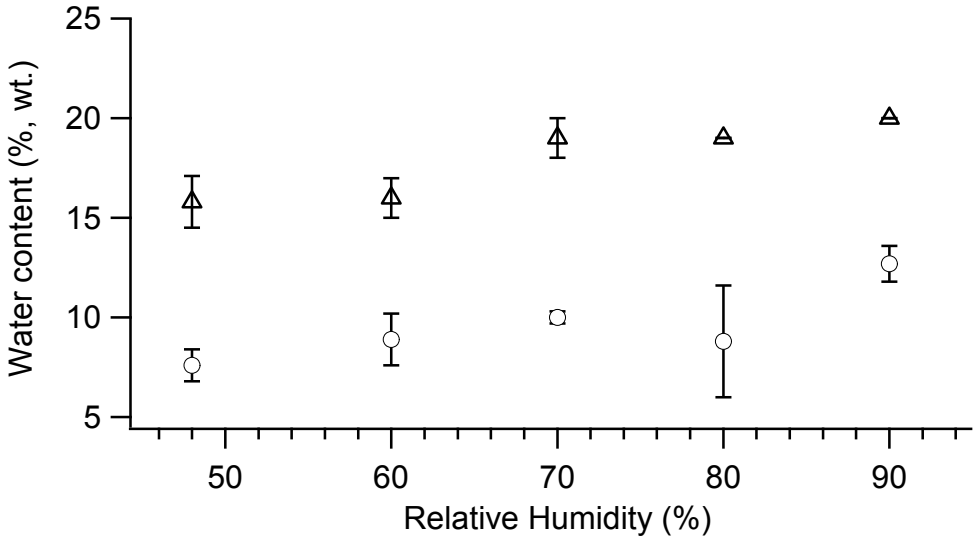

Figure S15. Water content of Sigma (circles) and Sepia (triangles) eumelanin powders hydrated for 1 hour at different relative humidity levels as deduced from Thermogravimetric Analyses.[1]

Hydration at 48% and 60% RH

For synthetic eumelanin 8% wt. Cl^-, at 48% RH (water content of approximately 7.6±0.7% wt.)[1] and 60% RH (water content of approximately 8.9±0.2% wt.),[1] the process of conductive bridge formation proved to be ongoing after 1 hour of electrical bias (respectively, little nanocluster migration in the channel -Figure S16- and dendrites protruding from the negative electrode, Figure S17).

This result indicates that at RH levels up to 60%, that is, when the amount of water in the thin films is lower than approximately 9% wt.,[1] the phenomenon takes place but at a slower pace and the consumption of the positive electrode is very uniform.

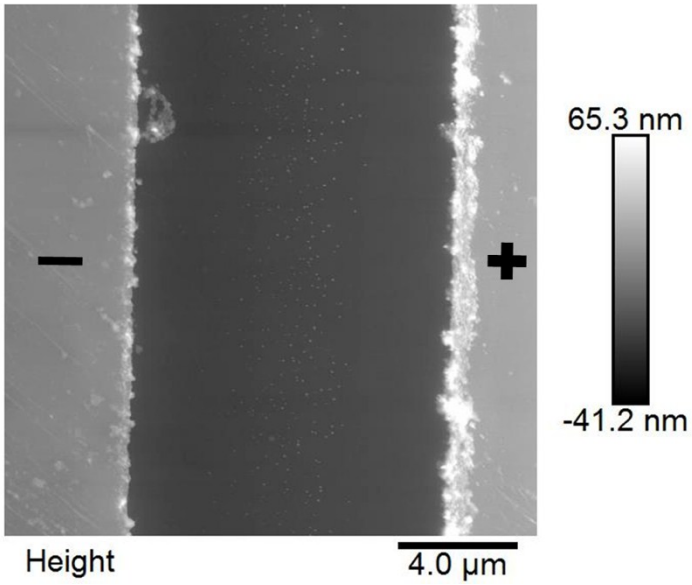

Figure S16. AFM image, 17.5 µm x 17.5 µm of the interelectrode area of a Sigma eumelanin thin film (8% wt. Cl^- content) hydrated for 1 hour at 48% RH and biased for 1 hour at 1 V. The migration of nanoclusters can be observed.

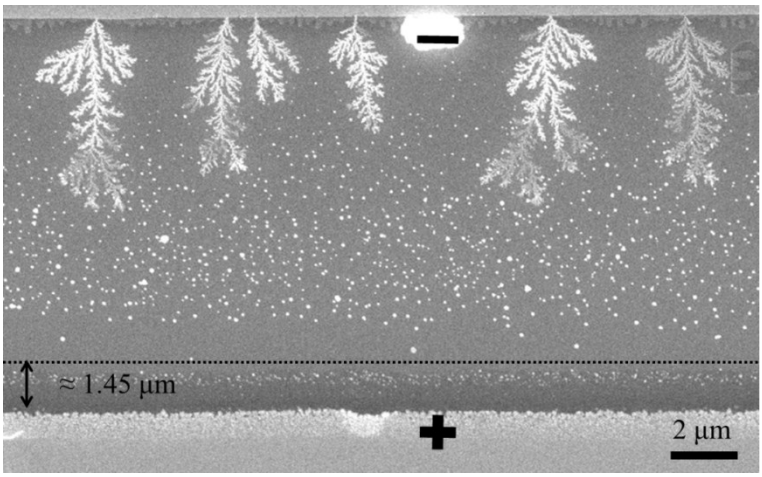

Figure S17. SEM image of a Sigma eumelanin thin film hydrated for 1 hour at 60% RH and biased for 1 hour at 1 V. The dotted line represents the initial position of the positive electrode before biasing: in spite of the high Cl^- content (8% wt.), the positive electrode is uniformly consumed. Image taken at 10 kV.

Relative Humidity (%)	Hydration time (min)	Water content (% wt.)	Standard deviation (%)
70	60	10.3	0.1
80	60	10.8	0.3
90	45	11.2	0.8

Table S5. Water content of Sigma eumelanin powders hydrated for different times and at different Relative Humidity levels as deduced from Thermogravimetric Analyses.[1]

(1) Albano, L. G. S.; Di Mauro, E.; Kumar, P.; Cicoira, F.; Graeff, C. F. O.; Santato, C. Novel Insights on the Physicochemical Properties of Eumelanins and Their DMSO Derivatives. *Polym. Int.* **2016** (in press)

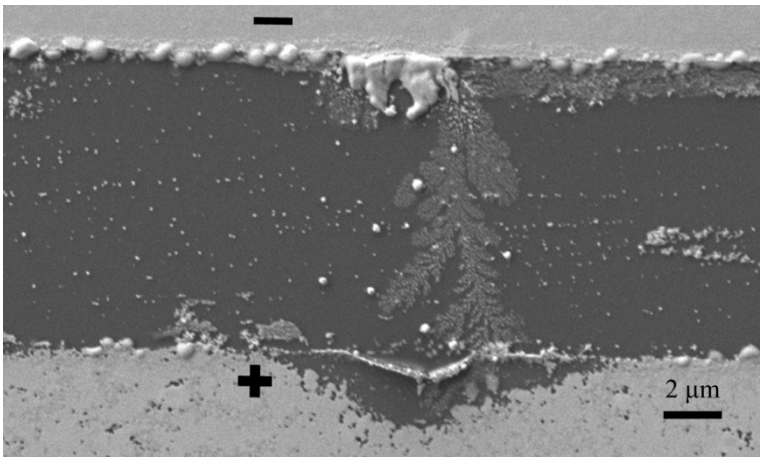

Figure S18. SEM image of a dendrite bridging the two electrodes in a thin film of Sigma eumelanin (8% wt. Cl^-), hydrated for 30 minutes at 90% RH and biased for 3 hours at 1 V. The hybrid resistive switch took place after 11 minutes. SEM voltage=5kV.

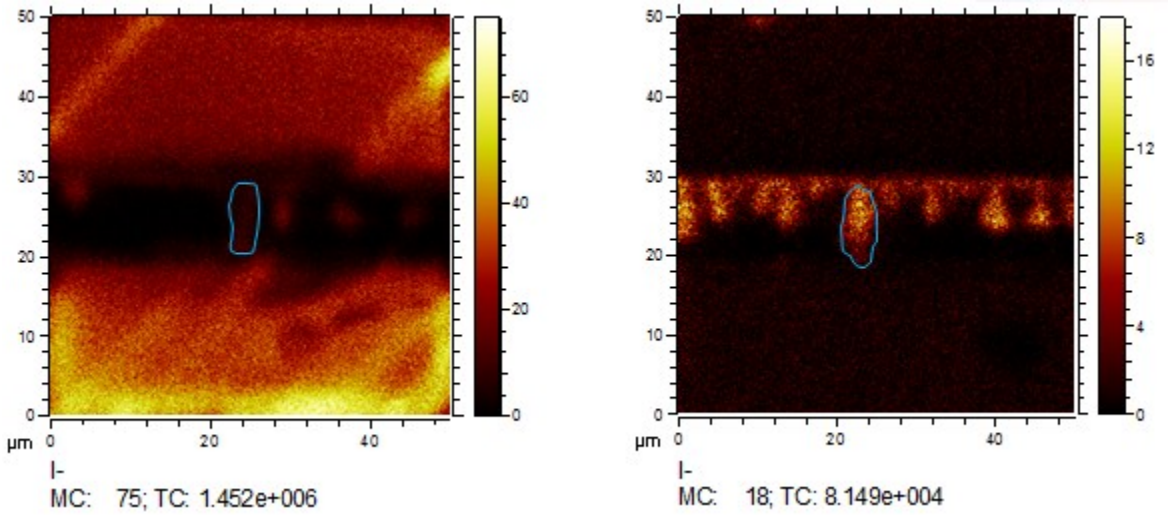

Figure S19. Reconstructed Tof-SIMS images (I^- ion) of dendrites formed between two Au electrodes in (a) Sigma eumelanin thin film, 8% wt. Cl^-, hydrated for 1 hour at 90% RH, biased for 1 hour at 1 V (*standard* resistive switch after ≈5 minutes) (b) Sigma eumelanin thin film, 8% wt.

Cl^-, hydrated for 1 hour at 80% RH, biased for 1 hour at 1 V (hybrid resistive switch after ≈12 minutes). The blue lines enclose the regions from which the spectra were selected to extract the ion intensities of Table S6 and Table S7.

Center Mass (u)	**Assignment**	**Area**		**Normalized to Au^- intensity**	
		Dendrite of the *standard* RS	**Dendrite of the *hybrid* RS**	***Standard* dendrite**	***Hybrid* dendrite**
38.01963	C_2N^-	83	113	9.01E-02	1.69E-01
42.00102	CNO^-	968	745	1.05E+00	1.11E+00
50.02183	C_3N^-	1017	1493	1.10E+00	2.23E+00
51.00242	C_3NH^-	94	92	1.02E-01	1.38E-01
61.97614	*C_4N^-*	*674*	*89*	*7.31E-01*	*1.33E-01*
66.03133	*C_3NO^-*	*357*	*234*	*3.87E-01*	*3.51E-01*
71.95398	C_6^-	114	143	1.24E-01	2.14E-01
74.0123	C_5N^-	503	655	5.46E-01	9.79E-01
83.98354	*C_7^-*	*162*	*68*	*1.76E-01*	*1.02E-01*
86.00078	*C_6N^-*	*108*	*70*	*1.17E-01*	*1.05E-01*
86.98935	*C_6HN^-*	*94*	*46*	*1.02E-01*	*6.88E-02*
96.98573	$C_4H_3NO_2^-$	388	305	4.21E-01	4.56E-01
98.00895	C_7N^-	308	275	3.34E-01	4.11E-01
120.9917	$C_6H_3NO_2^-$	148	155	1.61E-01	2.32E-01
144.9473	$C_8H_3NO_2^-$	133	106	1.45E-01	1.59E-01
196.9794	Au^-	922	669	1.00E+00	1.00E+00

Table S6. Peak intensity of selected TOF-SIMS negative ions normalized to Au^- intensity of the dendrites of Figure S19. In italic the peaks with unit mass resolution. ToF-SIMS data was acquired in burst alignment mode so only unit mass resolution is achieved. For this reason, ions other than the one assigned could contribute to the peak intensities (spectra from the selected regions only).

$CNAu_x$ fragments		
Ion	**Normalized to $CNAu^-$ intensity**	
	Dendrite of the *standard* RS	**Dendrite of the *hybrid* RS**
$CNAu^-$	1	1
$CNAu_2^-$	1.17E+00	1.26E+00
$CNAu_3^-$	4.29E-02	1.37E-01
$CNAu_4^-$	1.47E-01	1.16E-01
$CNAu_6^-$	3.07E-02	6.32E-02
$CNAu_8^-$	3.07E-02	6.32E-02
$CNOAu_x$ fragments		
Ion	**Normalized to $CNOAu^-$ intensity**	
	Dendrite of the *standard* RS	**Dendrite of the *hybrid* RS**
$CNOAu^-$	1	1
$CNOAu_2^-$	4.84E-01	8.53E-01
$CNOAu_4^-$	1.25E-01	4.41E-01
C_3NAu_x fragments		
Ion	**Normalized to C_3NAu^- intensity**	
	Dendrite of the *standard* RS	**Dendrite of the *hybrid* RS**
C_3NAu^-	1	1
$C_3NAu_2^-$	4.33E-01	1.38E+00
$CNAu_xI$ fragments		
Ion	**Normalized to $CNAuI^-$ intensity**	
	Dendrite of the *standard* RS	**Dendrite of the *hybrid* RS**
$CNAuI^-$	1	1
$CNAu_3I^-$	7.83E-02	1.35E-01
$CNAu_5I^-$	3.48E-02	2.03E-02
$C_6NOAu_xI_2$ fragments		
Ion	**Normalized to $C_6NOAuI_2^-$ intensity**	
	Dendrite of the *standard* RS	**Dendrite of the *hybrid* RS**
$C_6NOAuI_2^-$	1	1
$C_6NOAu_3I_2^-$	4.49E-01	3.54E-01
C_6NOAu_xI fragments		
Ion	**Normalized to C_6NOAuI^- intensity**	
	Dendrite of the *standard* RS	**Dendrite of the *hybrid* RS**
$C_6NOAu_2I^-$	1	1
$C_6NOAu_4I^-$	6.27E-01	5.74E-01

Au_xI fragments		
Ion	**Normalized to C_6NOAuI^- intensity**	
	Dendrite of the *standard* RS	**Dendrite of the *hybrid* RS**
AuI^-	1	1
Au_2I^-	2.00E+00	2.90E+00
Au_3I^-	1.33E-01	2.31E-01
Au_4I^-	3.94E-01	3.83E-01
Au_5I^-	3.19E-02	4.62E-02
Au_6I^-	3.72E-02	1.58E-01

Table S7. Normalized peak intensity of selected ToF-SIMS negative ions corresponding to MAu_x ($x \geq 2$)/MAu (where M is a eumelanin-Au complex, that is $CNAu_x$, $CNOAu_x$, C_3NAu_x, with $x \geq 2$) for the two samples of Figure S19. Cells highlighted in red indicate ions for which the peak intensity was less than 10 counts which is roughly the noise level and no peak could be seen (spectra from the selected regions only).

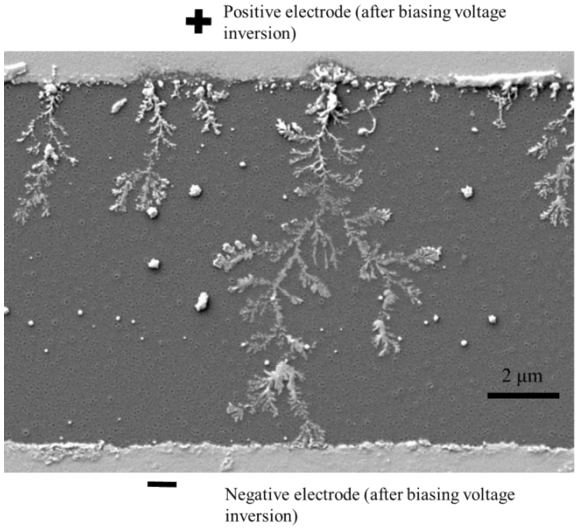

Figure S20. SEM image of the interelectrode region of a thin film of Sigma eumelanin (Cl^- 8% wt.) biased for 12 minutes at 1 V and, immediately after, for 12 hours at -1 V. The dendrites that grew in the first 12 minutes (resistive switch after 6 minutes) were not erased by the inversion of the bias that lasted 12 hours. SEM voltage=5 kV.

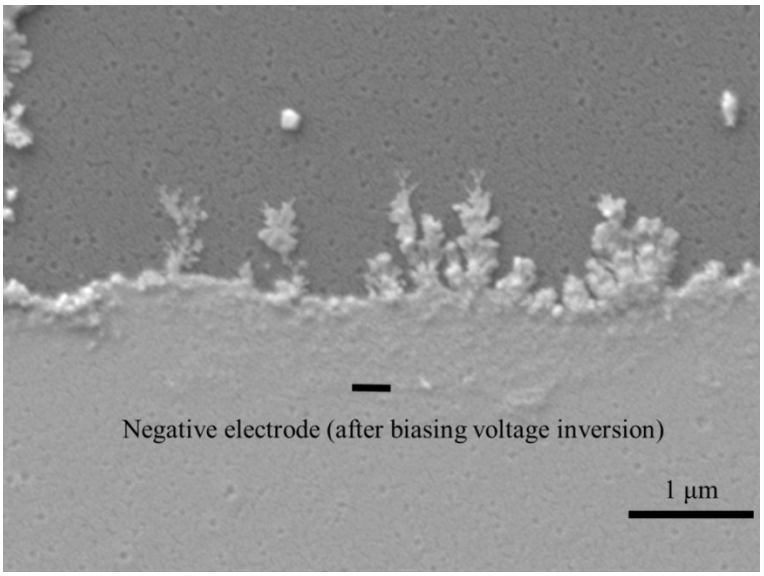

Figure S21. SEM image showing new dendrites starting to nucleate on the negative electrode after the inversion of the polarity of the applied electrical bias, same sample of Figure S20. SEM voltage=5 kV.

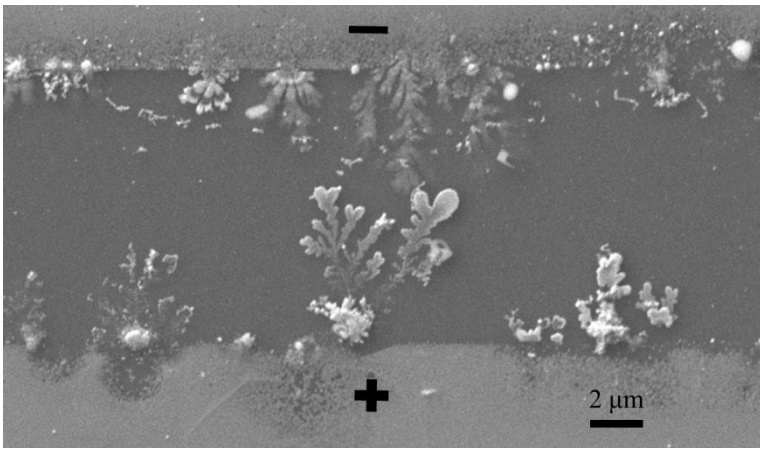

Figure S22. SEM image of dendrites protruding from both Au electrodes. Thin film of Sigma eumelanin (8% wt. Cl^-), hydrated for 1 hour at 90% RH, biased for ≈21 hours, sweeping voltage 2 mV/s. For each cycle, initial and final bias = 0 V, max bias applied |2.5| V, for 15 cycles. The first switch took place after ≈9 minutes at 1.13 V. SEM voltage=10kV.