

Supporting Information

Eumelanin, from the Molecular State to Film

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Table S1. Height of crystal-like aggregates of AC-L-DHI films and their vertical formation rate.

AC-L-DHI: Crystal-like Aggregates		
Time of observation (h)	Height $z(t)$ (nm)	Vertical formation rate (nm h ⁻¹)
24	132 ± 2	27 ± 1
25	159 ± 3	30 ± 1
26	192 ± 2	26 ± 1
27	211 ± 2	19 ± 1

Table S2. Height, width, surface density, root mean square roughness and vertical formation rate ($v_z(t)$) of rod-shaped structures of AC-L-DHICA films.

AC-L-DHICA: Rod-Shaped Structures					
Time from deposition (h)	Height $z(t)$ (nm)	Width (nm)	Surface density (μm ⁻²)	Root mean square roughness (nm)	$v_z(t)$ (nm h ⁻¹)
1.0	68 ± 1	94 ± 1	3.3 ± 0.3	15 ± 1	6.8 ± 0.1
1.2	70 ± 2	113 ± 2	4.9 ± 0.3	22 ± 1	3.7 ± 0.1
11.0	71 ± 1	133 ± 1	7.7 ± 0.3	32 ± 2	0.5 ± 0.1
38.0	83 ± 2	147 ± 2	8.7 ± 0.3	29 ± 1	0.2 ± 0.1
168.0	95 ± 1	179 ± 1	11.8 ± 0.2	36 ± 1	0.2 ± 0.1
504.2	175 ± 3	264 ± 1	4.0 ± 0.4	56 ± 2	0.1 ± 0.1
672.0	181 ± 3	270 ± 1	3.7 ± 0.1	65 ± 2	0 ± 0.1

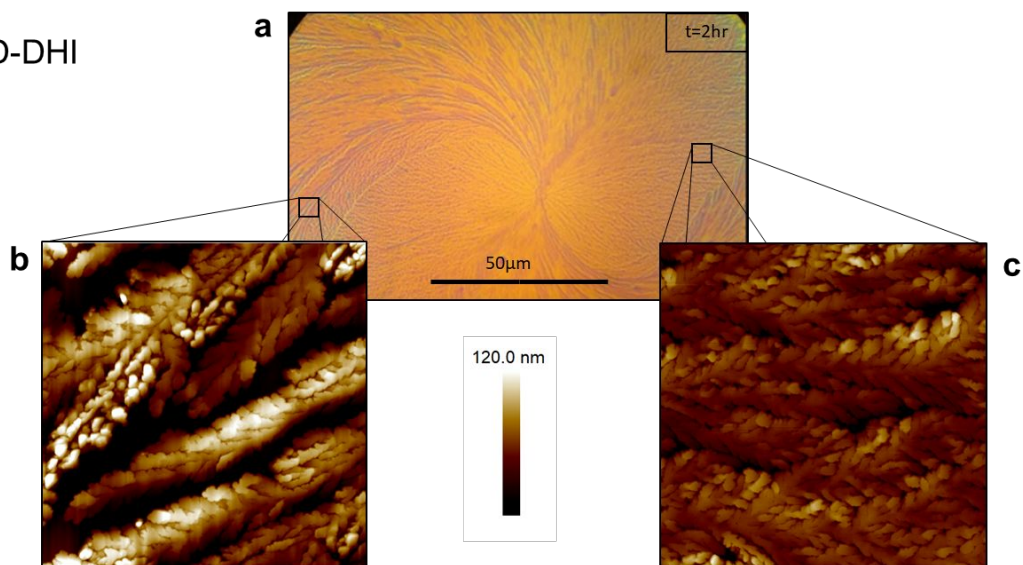
Table S3. Absorption wavelength and optical energy gap evaluated over time by the Tauc Model for AC-L-DHI, AC-L-DHICA, AISSP-L-DHI and AISSP-L-DHICA films.

Name	Time	Absorption wavelength (nm)	Optical energy gap (eV)
AC-L-DHI	As prepared (1 h)	307 ± 1	1.19 ± 0.25
	One day	305 ± 1	1.06 ± 0.19
	4 days	306 ± 1	0.98 ± 0.16
	7 days	306 ± 1	0.94 ± 0.19
AC-L-DHICA	As prepared (1 h)	364 ± 1	2.41 ± 0.23
	One day	363 ± 1	2.39 ± 0.05
	4 days	363 ± 1	2.24 ± 0.04
	7 days	359 ± 1	2.20 ± 0.04
AISSP-L-DHI	As prepared (1 h)	×	×
	3 days	×	×
AISSP-L-DHICA	As prepared (1 h)	351 ± 1	×
	3 days	351 ± 1	×

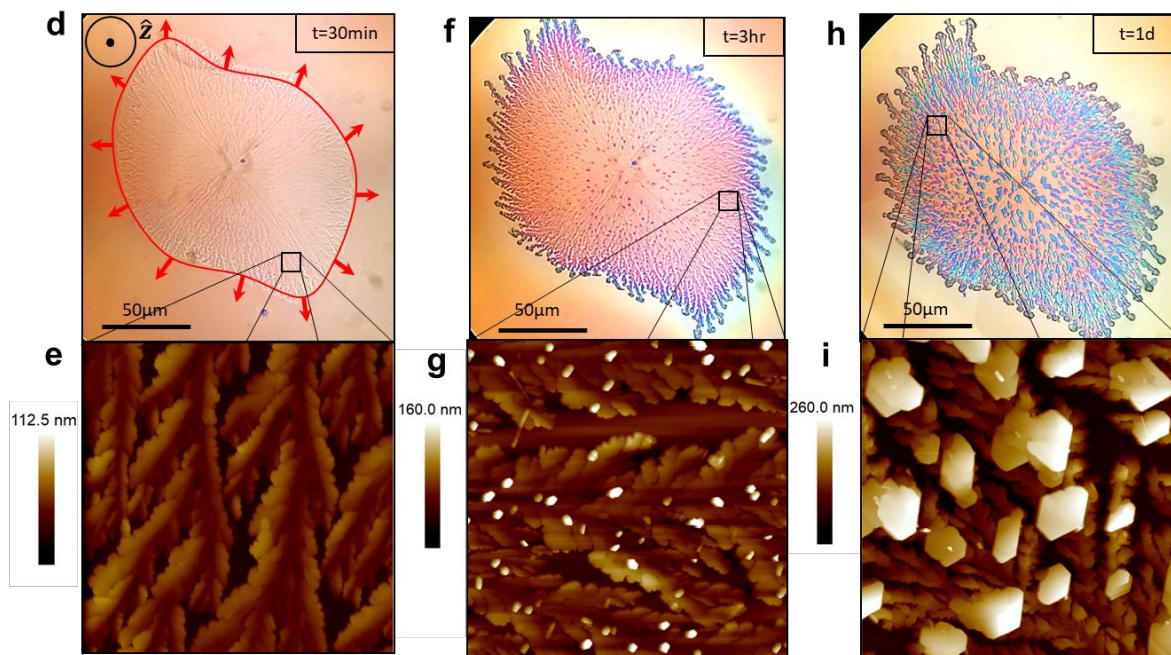
Table S4. Positive and negative current densities at zero voltage ($J_+(V=0)$, $J_-(V=0)$), positive and negative voltage at zero current density ($V_+(I=0)$, $V_-(I=0)$), charge stored (q) at the Au/DHICA and Au/DHI interfaces and room temperature electrical conductivity (σ) at 1.5 V as a function the voltage scan rate.

Electrical hysteresis of AC-L-DHICA and AC-L-DHI Films								
Building block	Voltage scan rate (mVs^{-1})	$J_+(V=0)$ ($\mu\text{A cm}^{-2}$)	$J_-(V=0)$ ($\mu\text{A cm}^{-2}$)	$V_+(J=0)$ (V)	$V_-(J=0)$ (V)	q (μC)	Hysteresis area (nA V)	σ at 1.5 V (S cm^{-1})
DHICA	25	0.20	-0.20	1.1	-1.1	2.4	60	4.6×10^{-11}
	50	0.50	-0.20	0.4	-0.8	1.5	75	6.8×10^{-11}
DHI	25	0.05	-0.06	1.2	-1.2	0.2	3.8	1.1×10^{-11}
	50	0.08	-0.09	1.1	-1.1	0.1	5.6	1.4×10^{-11}

AC-D-DHI



AC-L-DHI



Scheme S1. Morphological evolution of AC-DHI films over a period of 1 day. In **(a)** optical image of AC-D-DHI spiral-like shapes 2 h after deposition and in **(b)** and **(c)** AFM images in different regions of the spiral-like shape revealing the different density of ferns as a function of the distance from the center of the spiral. In **(d)** an optical image of AC-L-DHI spiral-like shapes (red arrows denoting the front propagation direction and the flow of solvent according to the coffee-ring effect, dark dot circle is the \hat{z} direction) and **(e)** its nanoscale structure revealed by AFM image 30 minutes after the deposition. Optical images of AC-DHI spiral-like shapes after **(f)** 3 h and **(h)** 1 day after the deposition at AC-L, with their respective AFM height images **(g)** and **(i)**. Pillar-like and crystal-like aggregates forming on top of fern-like structures are shown respectively in **(g)** and **(i)**. The size of the AFM images is $10\ \mu\text{m} \times 10\ \mu\text{m}$. AC-DHI films feature an average number of spiral-like shapes of about 10.

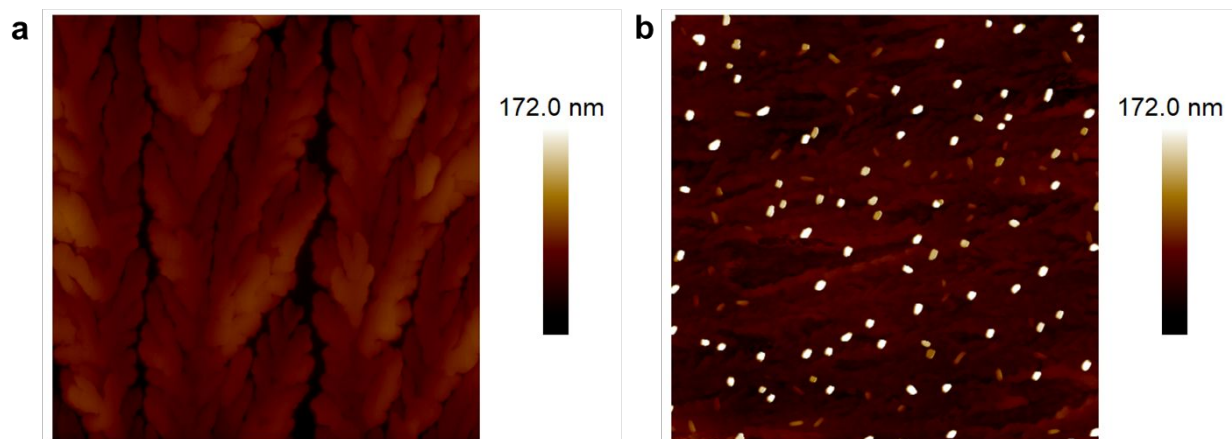


Figure S1. 10 $\mu\text{m} \times 10 \mu\text{m}$ AFM height image showing the morphologies of AC-DHI films **(a)** stored one day in the dark and **(b)** exposed one day to laboratory daylight (see Experimental).

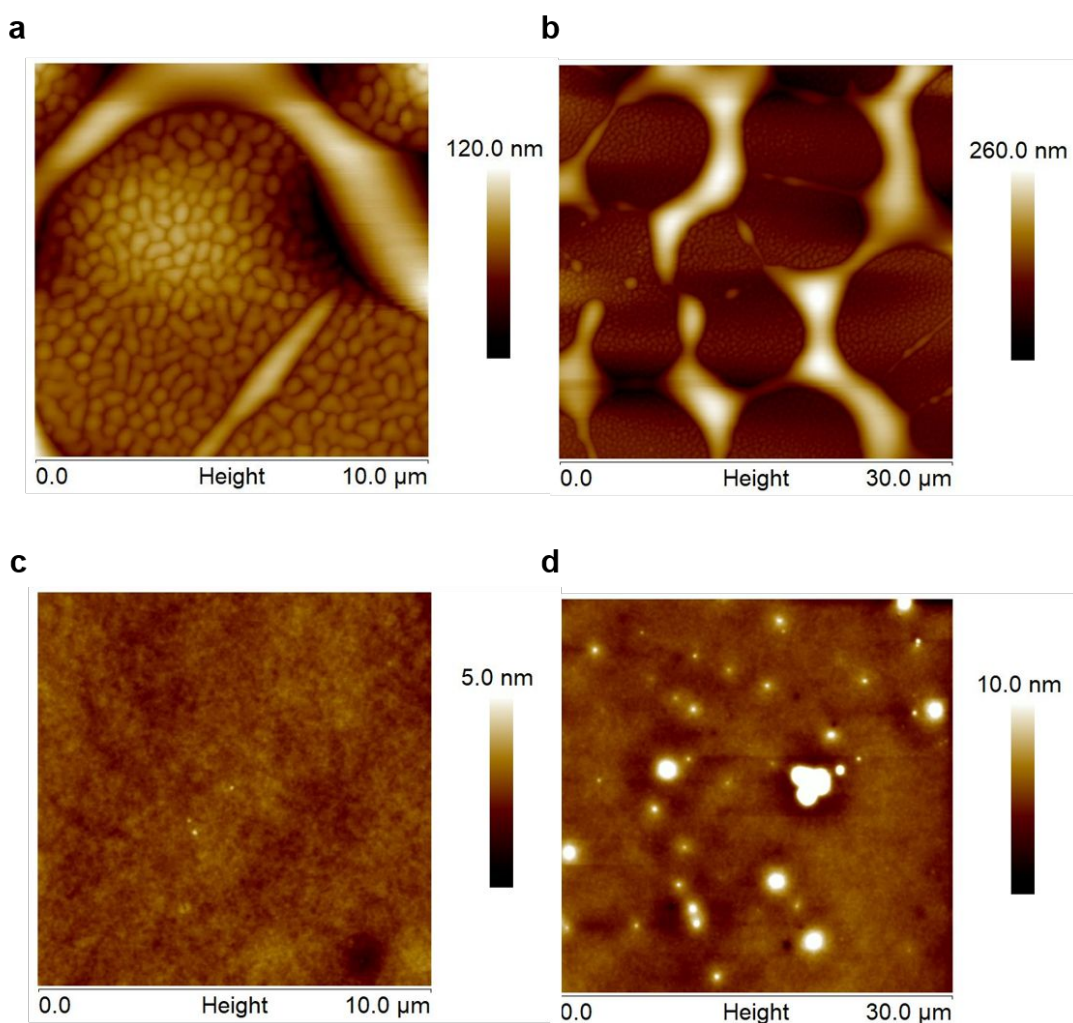


Figure S2. AFM height images of spin-coated AISSP-D-DHI films from powders received after: **(a)** and **(b)** 10 day-shipping; and **(c)** and **(d)** 30 day-shipping.

We cannot exclude that an aging of the DHI powder takes place during its shipping (e.g. because of changes in the oxidation state of DHI), possibly affecting the morphology of DHI-based films (see Experimental, Main File). De-wetting processes are observed for AISSP-D-DHI films fabricated from powders received after a shipping time of ten days (Figure S2 (a), (b)). On the other hand, AISSP-D-DHI films fabricated from powders received after a shipping time of thirty days are smooth and featureless, in agreement with literature¹ (Figure S2 (c), (d)).

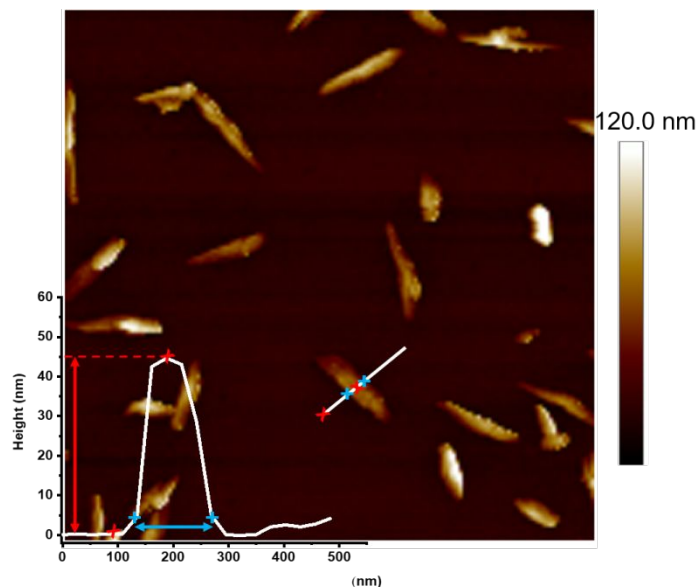


Figure S3. 3 μm×3 μm AFM height image of AC-L-DHICA showing the profile of rod-shaped like structures forming at ambient conditions after 1 h from fabrication.

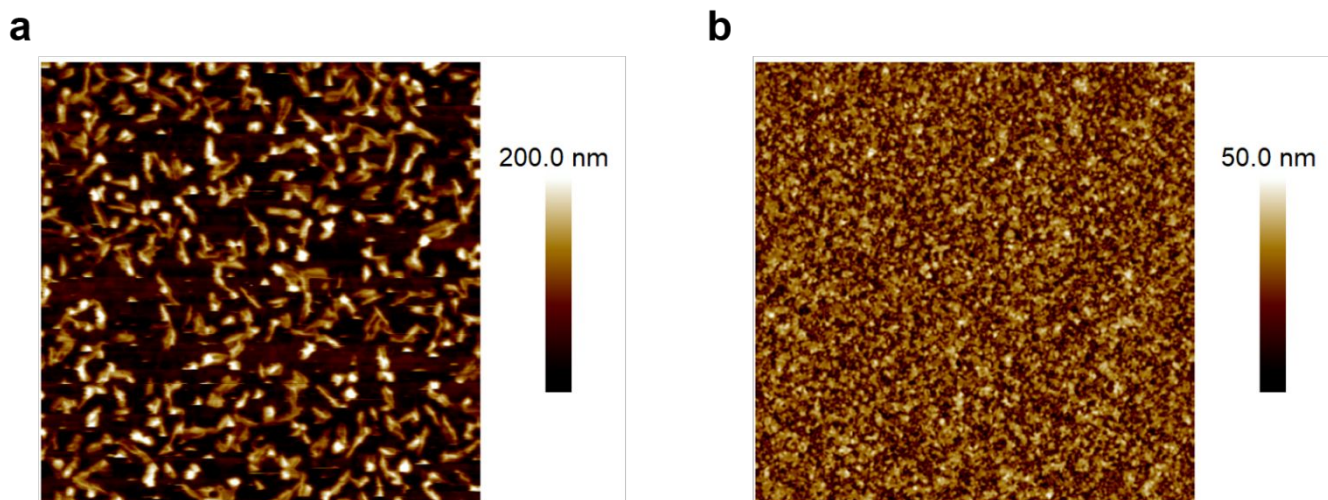


Figure S4. 10 μm×10 μm AFM height image showing the morphologies of (a) AC-D-DHICA and (b) AISSP-D-DHICA films stored one day in the dark.

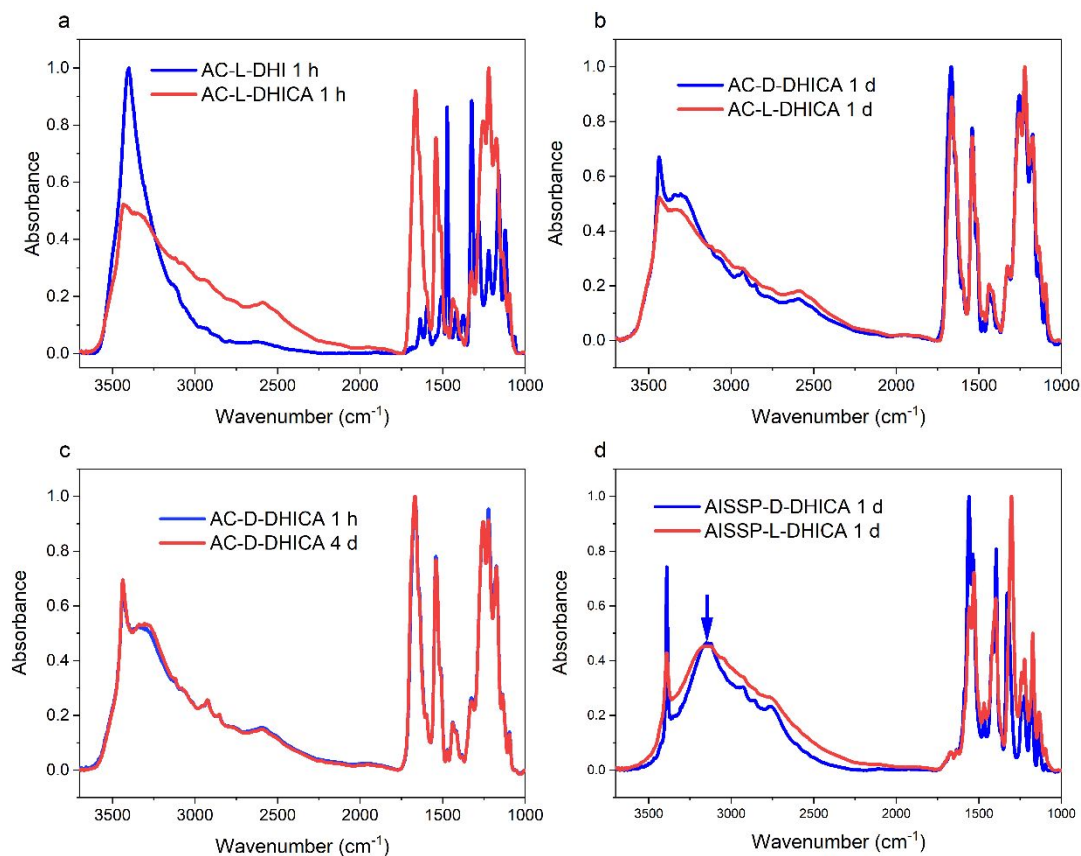


Figure S5. IR spectra of (a) AC-L-DHI and AC-L-DHICA films recorded after 1 h, (b) AC-L and D-DHICA films recorded after one day, (c) AC-D-DHICA films at different stages of formation and (d) AISSP-D-DHICA films acquired after one day. DHI spectra were normalized to the O-H stretching band peak (3400 cm^{-1}) while DHICA spectra were normalized to the maximum peak (ca. 1300 cm^{-1}). For further details on abbreviations see Table 1 and experimental section.

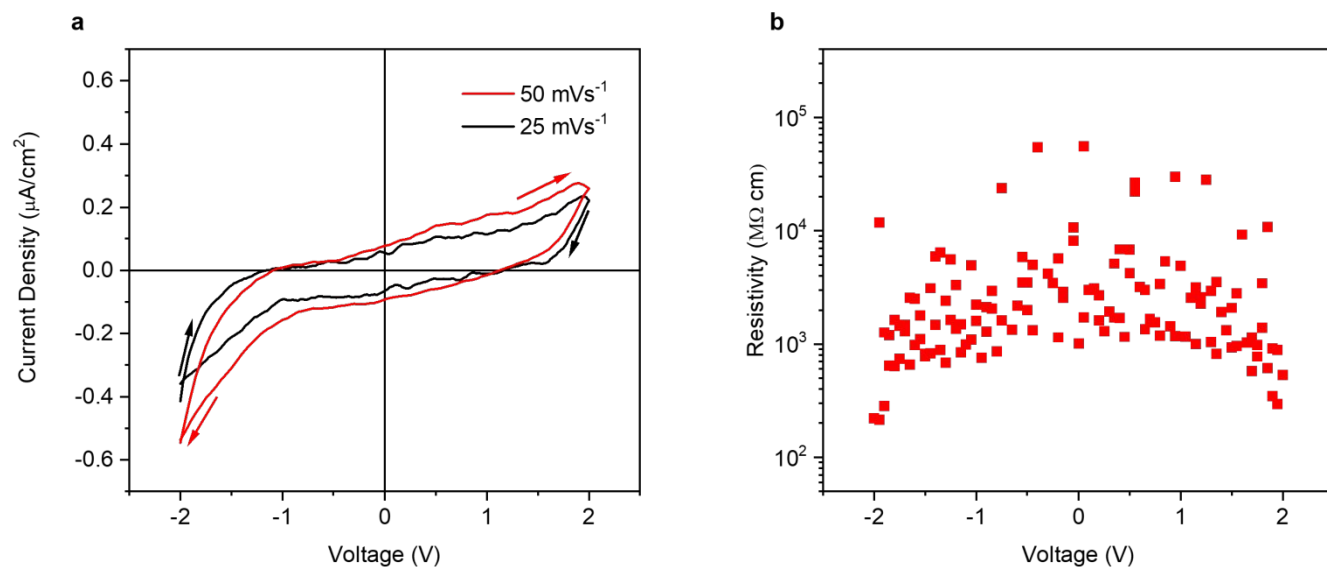


Figure S6. AC-L-DHI films (a) J-V hysteresis at different voltage scan rates on circular interdigitated Ti/Au electrodes ($W=24.5\text{ mm}$, $L=10\text{ }\mu\text{m}$). In (b) Resistivity vs voltage at 50 mVs^{-1} .

References

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