Supplementary Information for:

The Influence of Copper Ions on the Transport and Relaxation Properties of Hydrated Eumelanin

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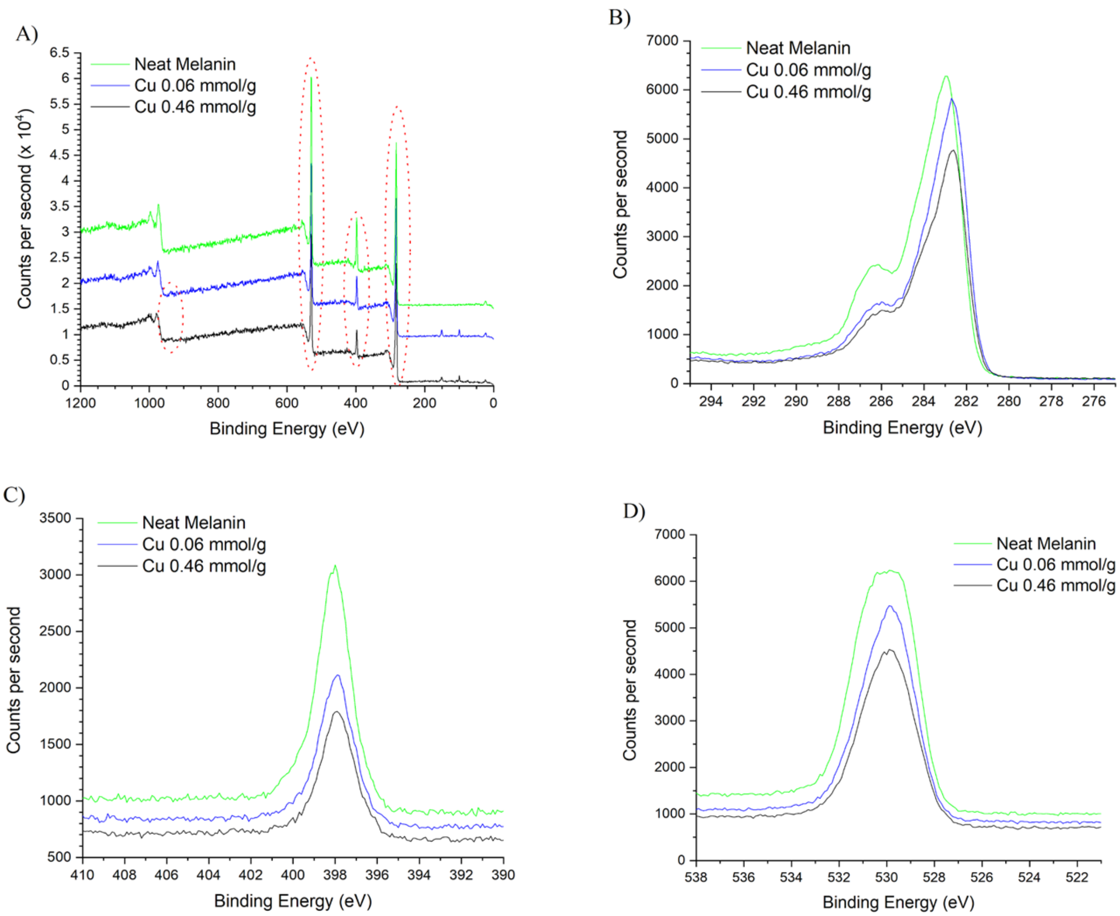
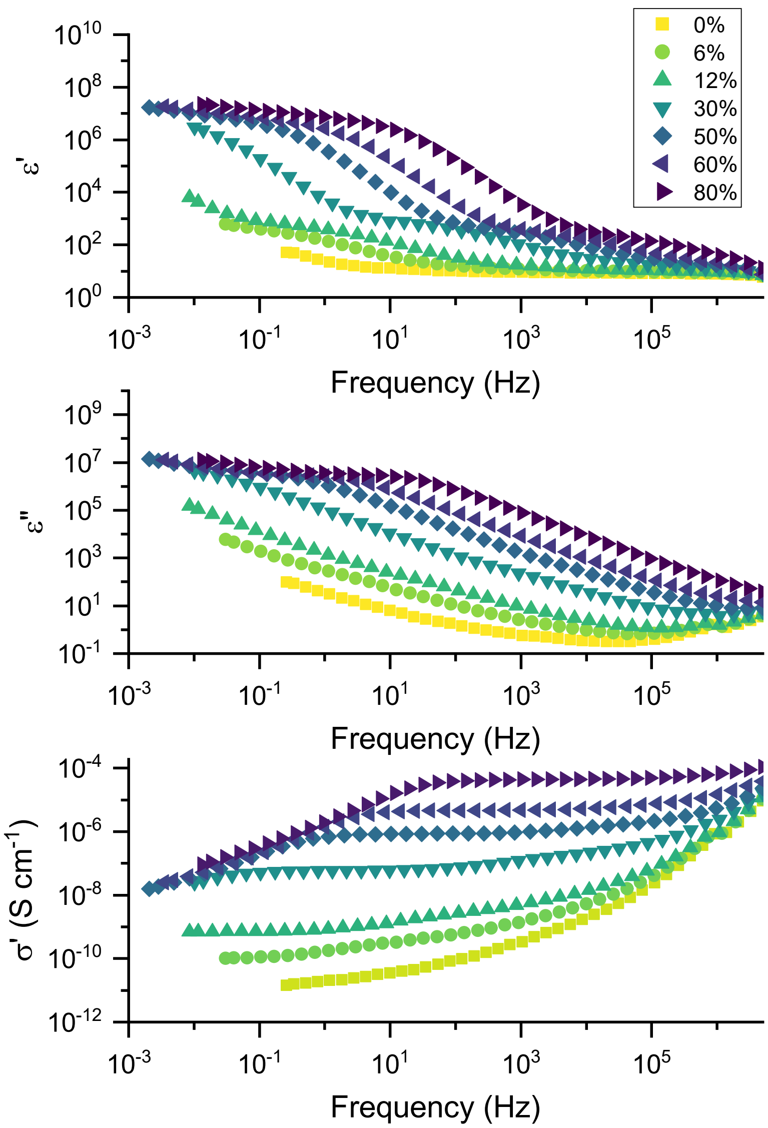
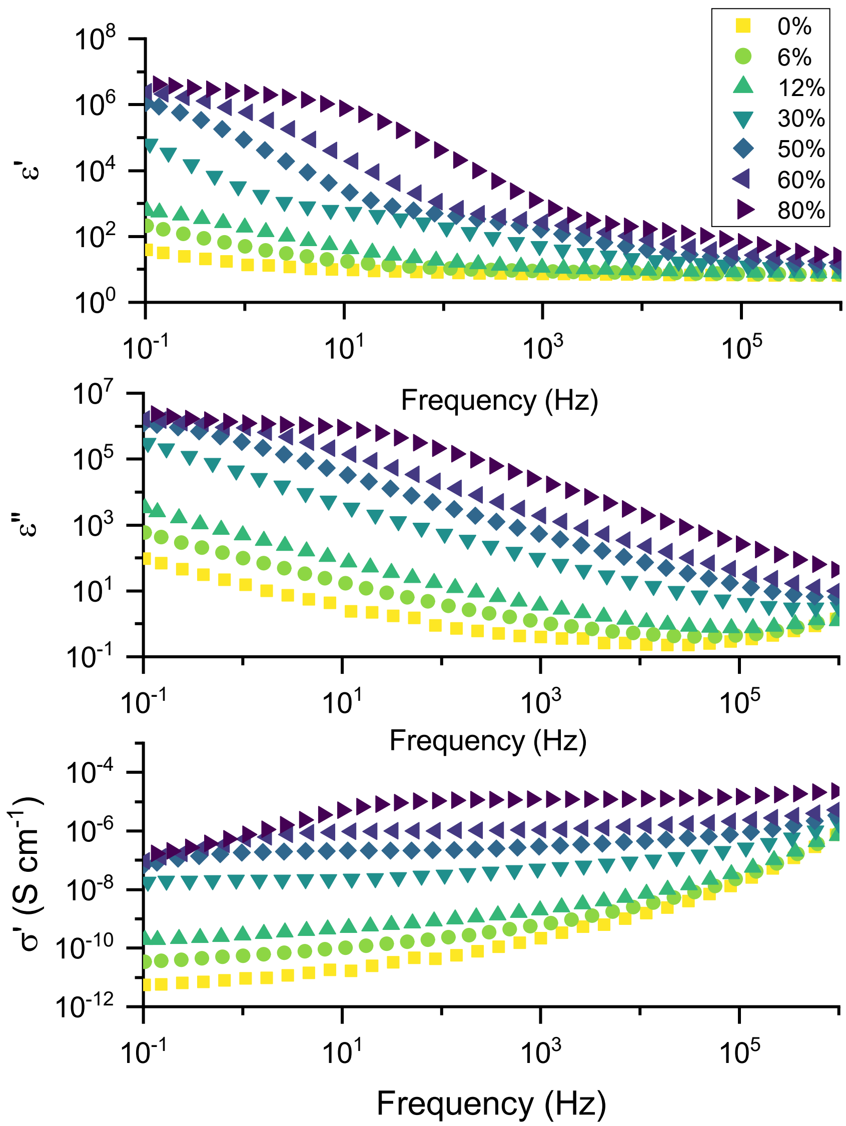


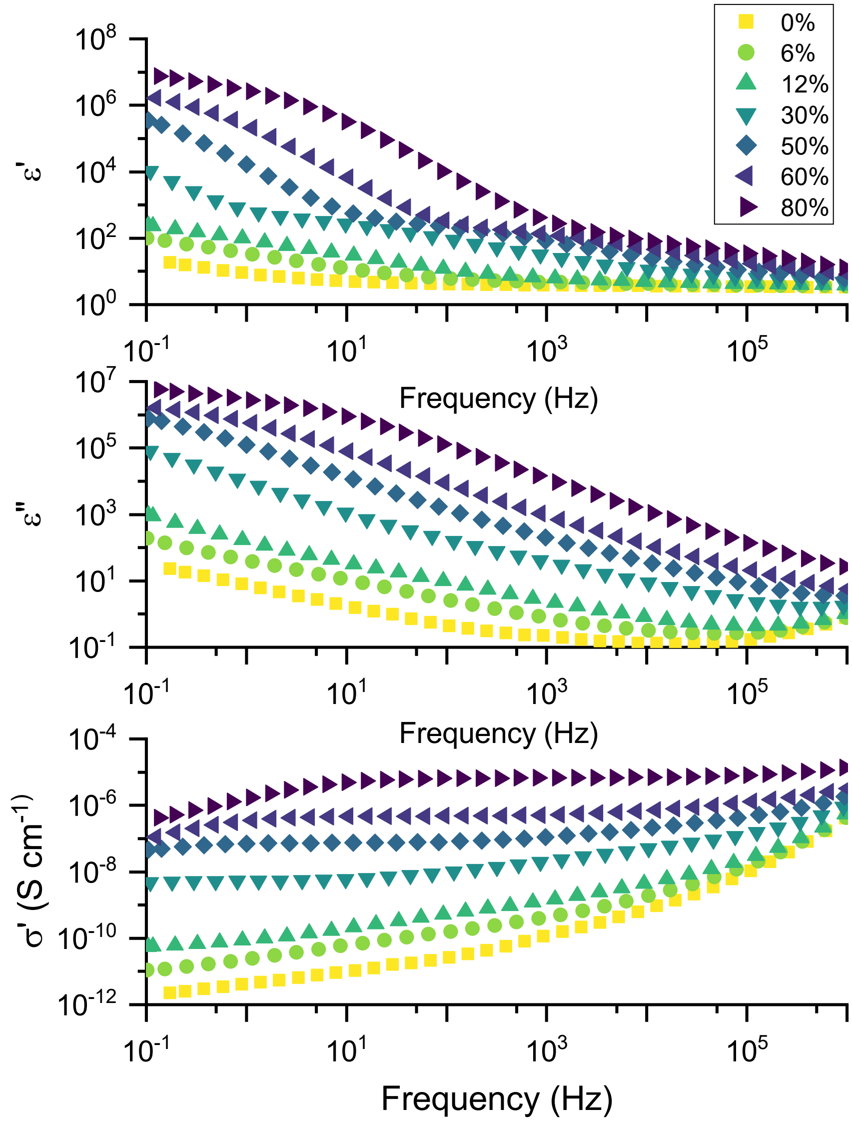
Supplementary Fig. 1. XPS scan of the samples: (A) examples of wide survey scans of the various samples; the red circles highlight the Cu 2p (~930 eV), O 1s (~530 eV), N 1s (~400 eV) and C 1s (~285 eV) peaks; (B) examples of high-resolution scans of the C 1s peak of the various samples; (C) examples of high-resolution scans of the N 1s peak of the various samples; (D) examples of high-resolution scans of the O 1s peak of the various samples.



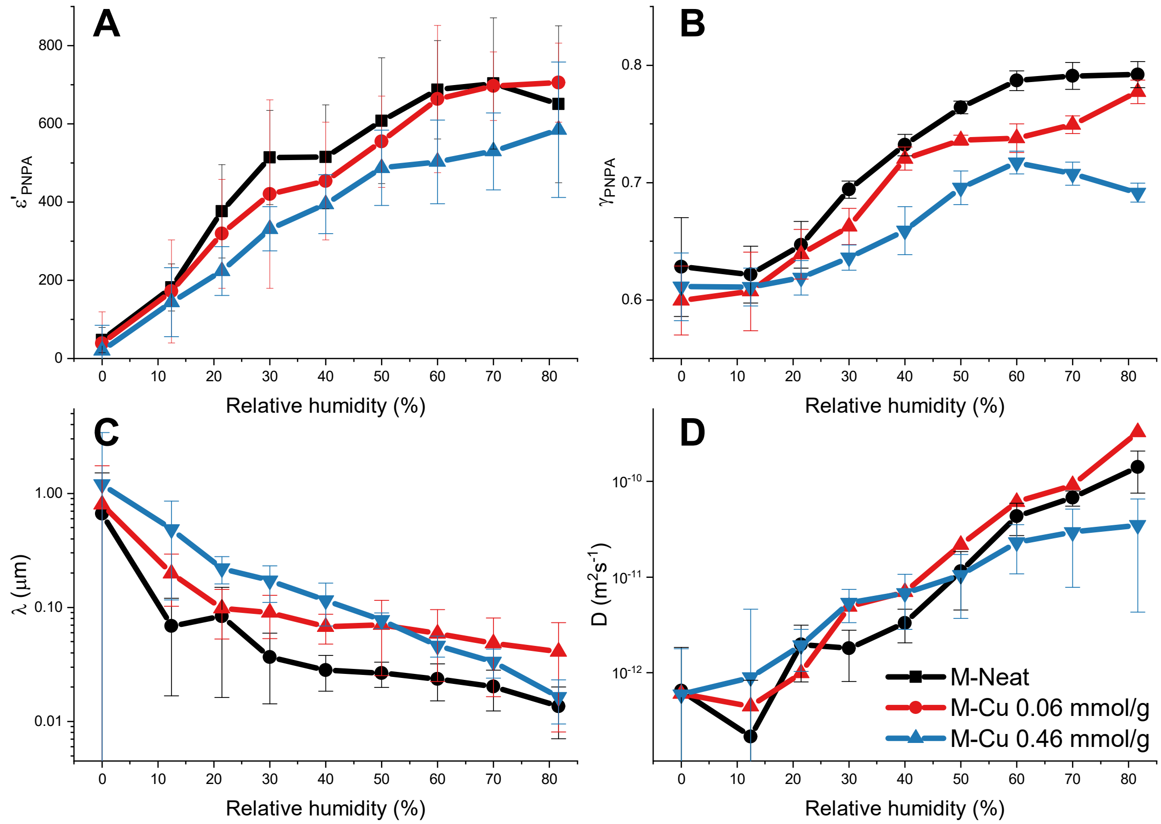
Supplementary Fig. 2. The evolution of neat synthetic eumelanin dielectric properties induced by relative humidity growth at 27°C. We broadened the frequency range for these results in order to show the diffusion origin of the behavior of the dielectric parameters in the lowest frequency range below 10^{-1} Hz. Corresponding values of relative humidity are given in the inset in the upper panel.



Supplementary Fig. 3. The evolution of dielectric properties of synthetic eumelanin containing 0.06 mmol/g Cu induced by relative humidity growth at 27 °C. Corresponding values of relative humidity are given in the inset in the upper panel.



Supplementary Fig. 4. The evolution of dielectric properties of synthetic eumelanin containing 0.46 mmol/g Cu induced by relative humidity growth at 27 °C. Corresponding values of relative humidity are given in the inset in the upper panel.



Supplementary Fig. 5. The dependencies of PNPA model parameters on the level of the relative hydration for the studied materials: (A) ε_{DC} is the dielectric constant; (B) γ is a diffusion exponent; (C) λ is the Debye screening length; (D) D is the diffusion coefficient.

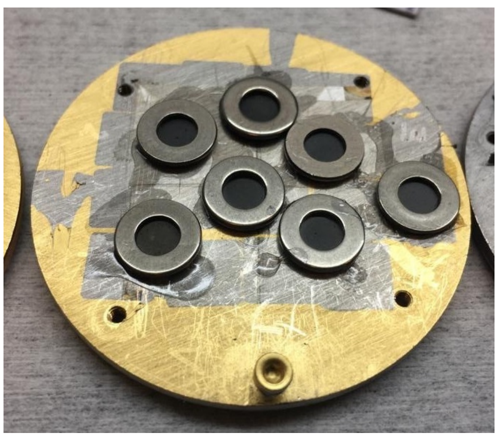
Ultra-high vacuum magnetron sputtering technical information

The first side.
Pre -cleaning:
1 time for 600 seconds with a pause of 1 second;
Residual pressure p = 2,100140E-2;
P = 80 W (step 10); V = 511 V;

Au sputtering:
Residual pressure p = 2.328000E-6;
P = 200 W; V = 165 V;
P(Ar) = 3,9999E-3;
Thickness (according to the sensor) 164,200000 nm, speed 0.195025 nm/s;
Thickness (recalculated) 152.706000 nm, coefficient 0.930000

The second side.

Au sputtering:
Residual pressure p = 1.149000E-6;
P = 200 W; V = 156 V;
P(Ar) = 4,0006E-3;
Thickness (according to the sensor) 164.500000 nm, speed 0.238885 nm/s;
Thickness (recalculated) 152.985000 nm, coefficient 0.930000



Supplementary Fig. 6. The set of prepared eumelanin pellets before carrying out the sputtering procedure.

Supplementary Fig. 7. The general view of the ultra-high vacuum sputtering facility utilized in the study.

Supplementary table 1. Elemental analysis of the synthesized eumelanin utilizing XPS. For reference the underlying monomer building blocks of DHI and DHICA are also listed. It is expected that eumelanin's elemental composition should fall in between DHI and DHICA. Note that the Cu loaded samples have their Cu content excluded to test whether the base polymer is commensurate to a synthetic melanin. Cu content was detected (see SI Fig. 4) but can't be accurately used to determine atomic composition of the bulk, unlike C, O and N [1]. Uncertainties are to 1 SD.

Sample	C (at%)	N (at%)	O (at%)	C/N	O/N	C/O
DHI - Expected	72.7	9.1	18.2	8	2	4
DHICA - Expected	64.3	7.1	29.6	9	4	2.2
Neat synthetic eumelanin sample	69.5±0.3	9.2±0.2	21.2±0.4	7.6±0.2	2.3±0.1	3.3±0.1
0.05 mmol/g Cu sample (Cu doping excluded)	72.4±1.7	6.8±1.4	20.8±0.6	10.6±2.4	3.1±0.7	3.5±0.2
0.5 mmol/g Cu sample (Cu doping excluded)	71.2±1.1	7.6±0.3	21.2±0.9	9.4±0.5	2.8±0.2	3.4±0.2

Supplementary table 2. Elemental analysis of the synthesized eumelanin utilizing inductively coupled plasma atomic emission spectroscopy (ICP-AES) and inductively coupled plasma mass spectrometry (CP-MS).

Element	**Detection limit, mkg/g**	**Concentration, mkg/g**		
		Neat eumelanin	**Cu doped 0.06 mmol/g**	**Cu doped 0.46 mmol/g**
Li	0.01	0.021	0.090	0.034
Be	0.003	< DL	< DL	< DL
B	0.6	26.3	8.4	7.1
Na	4	16.2	15.3	8.1
Mg	3	< DL	13.1	< DL
Al	4	20.6	39.7	31.7
P	10	< DL	< DL	< DL
S	29	145	< DL	< DL
K	3	4.5	10.4	8.1
Ca	22	< DL	122	< DL
Sc	0.1	< DL	< DL	< DL
Ti	2	< DL	< DL	< DL
V	1	< DL	< DL	< DL
Cr	0.5	12.9	6.8	6.8
Mn	0.2	3.3	4.0	3.6
Fe	5	49.5	90.8	70.4
Co	0.1	< DL	< DL	0.17
Ni	0.2	0.89	2.3	1.9
Cu	0.3	15.3	3810	29142
Zn	0.2	7.1	11.2	6.1
Ga	0.05	< DL	< DL	< DL
Ge	0.1	< DL	< DL	< DL

As	0.03	< DL	< DL	< DL
Se	0.8	< DL	< DL	< DL
Rb	0.05	< DL	0.64	< DL
Sr	0.04	0.10	0.50	0.20
Y	0.06	< DL	< DL	< DL
Zr	0.03	1.1	1.0	0.86
Nb	0.08	< DL	< DL	< DL
Mo	0.01	0.38	0.29	0.45
Rh	0.07	< DL	< DL	0.55
Pd	0.08	< DL	< DL	< DL
Ag*	0.1	124	< DL	0.18
Cd	0.02	< DL	0.078	0.045
Sn	0.05	0.89	0.63	4.1
Sb	0.02	0.056	0.051	0.052
Te	0.02	< DL	< DL	< DL
Cs	0.004	< DL	< DL	< DL
Ba	0.01	1.3	2.3	6.4
La	0.002	0.0088	0.025	0.013
Ce	0.003	0.020	0.38	0.093
Pr	0.002	< DL	0.0037	0.0024
Nd	0.002	0.010	0.018	0.011
Sm	0.002	0.0073	0.0036	< DL
Eu	0.003	< DL	< DL	< DL
Gd	0.001	< DL	0.0022	< DL
Tb	0.002	< DL	< DL	< DL
Dy	0.002	< DL	0.0034	< DL
Ho	0.001	< DL	0.00084	< DL

Er	0.001	< DL	0.0025	< DL
Tm	0.001	< DL	< DL	< DL
Yb	0.002	< DL	< DL	< DL
Lu	0.001	< DL	< DL	< DL
Hf	0.01	0.022	0.020	0.020
Ta	0.004	< DL	< DL	< DL
W	0.02	0.19	0.22	0.24
Re	0.002	< DL	< DL	< DL
Ir	0.002	< DL	< DL	< DL
Pt	0.003	< DL	0.014	0.013
Au	0.01	0.031	< DL	< DL
Hg	0.02	0.18	< DL	< DL
Tl	0.003	< DL	< DL	< DL
Pb	0.03	0.30	1.3	2.0
Bi	0.004	0.028	0.043	0.035
Th	0.004	< DL	< DL	< DL
U	0.001	0.0044	0.0065	0.0054

REFERENCES

1 J. V. Paulin, J. D. McGettrick, C. F. O. Graeff and A. B. Mostert, Melanin system composition analyzed by XPS depth profiling, *Surfaces and Interfaces*, 2021, **24**, 101053.