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SUPPORTING INFORMATION

Melanin thin-films: perspective on optical and electrical properties

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Table S1. The atomic composition (atomic concentration %) and atomic ratios determined from spin-coated thin-films of soluble non-functionalized and soluble sulfonated melanin samples.

Solvent	Samples	Atomic concentration (at%)				Atomic ratio			
		C	O	N	S	N/C	N/O	O/C	N/S
Not applicable: Theoretical	NF-DHI	72.7	18.2	9.1	#	0.13	0.50	0.25	#
	NF-DHICA	64.3	29.6	7.1	#	0.11	0.24	0.46	#
	S-DHI	60.1	26.7	6.7	6.7	0.11	0.25	0.44	1.00
	S-DHICA	55.6	33.3	5.6	5.6	0.10	0.17	0.60	1.00
H_2O+NH_3	NFMel-I	62.1	26.8	12	#	0.19	0.45	0.43	#
	NFMel -S	62.3	25.2	15.5	#	0.25	0.62	0.40	#
	NFMel -6P	57.9	29.4	12.7	#	0.22	0.43	0.51	#
H_2O	NFMel -S	64	25.5	10.5	#	0.16	0.41	0.40	#
	NFMel -6P	61.1	27.9	11	#	0.18	0.39	0.46	#
DMSO	SMel	66.1	29.4	3.3	1.1	0.05	0.11	0.44	3.00
	SMel -T	64.7	29.9	3.9	1.6	0.06	0.13	0.46	2.44
	SMel -4P	56.4	34.8	6.9	1.8	0.12	0.20	0.62	3.83
	SMel -8P	57.4	35.1	6.4	1	0.11	0.18	0.61	6.40
DMF	SMel	74.1	22.1	2.9	0.9	0.04	0.13	0.30	3.22
	SMel -T	67	26.8	4.3	1.9	0.06	0.16	0.40	2.26
	SMel -4P	66.5	27.3	4.5	1.7	0.07	0.16	0.41	2.65
	SMel -8P	67.7	26.3	4.4	1.6	0.06	0.17	0.39	2.75
NMP	SMel	61.5	34	3.5	1.1	0.06	0.10	0.55	3.18
	SMel -T	60.4	33.4	4.6	1.7	0.08	0.14	0.55	2.71
	SMel -4P	56.5	36.1	5.6	1.8	0.10	0.16	0.64	3.11
	SMel -8P	58.1	33.9	6.1	1.9	0.10	0.18	0.58	3.21

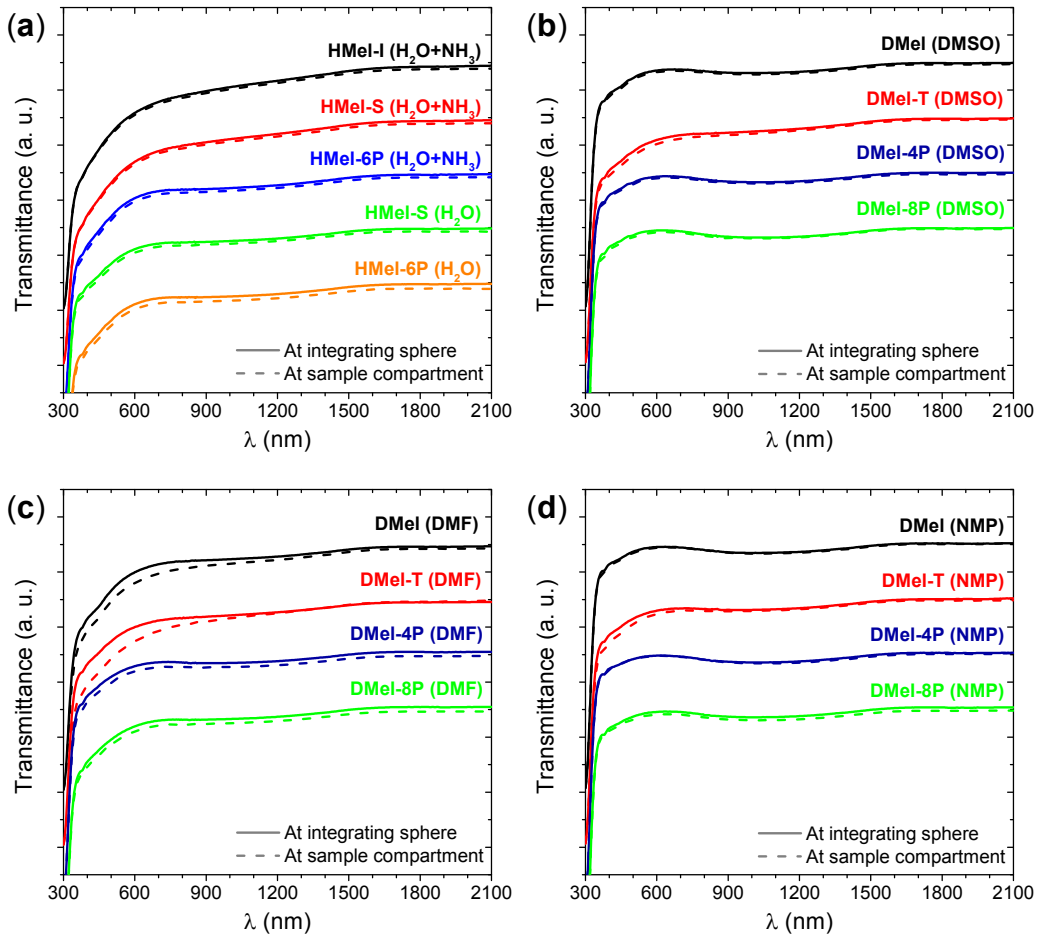

Figure S1. Transmittance spectra of melanin derivatives thin-films at different positions at the UV-Vis-NIR spectrophotometer. The small variation in the intensity between the two parts (about 30 cm) indicates that the scattering is neglectable in these samples.

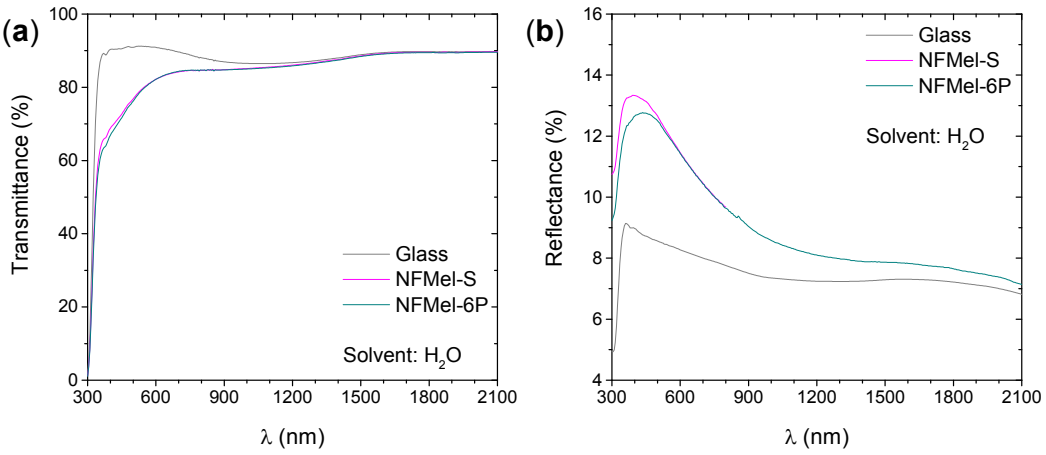

Figure S2. (a) Transmittance and (b) reflectance spectra of NF-melanin in water-only solution (i.e., neutral solution). NFMeI-I is insoluble in water-only solution, hindering its thin-film deposition.

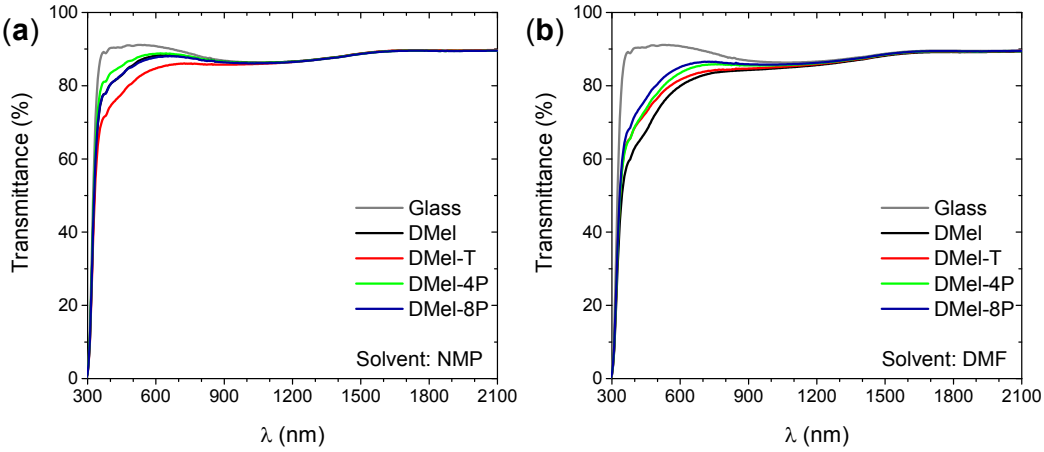

Figure S3. Transmittance spectra of S-melanin in (a) NMP and (b) DMF solutions.

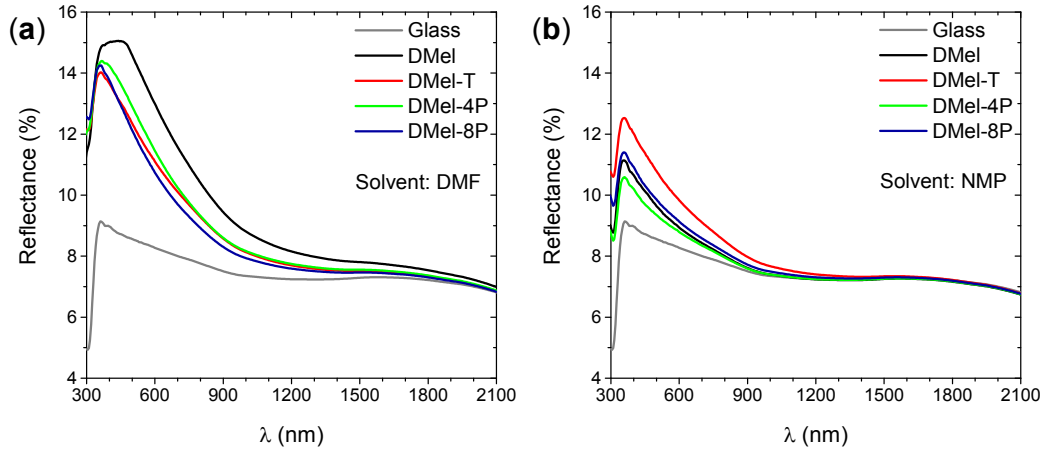

Figure S4. Reflectance spectra of S-melanin in (a) DMF and (b) NMP solutions.

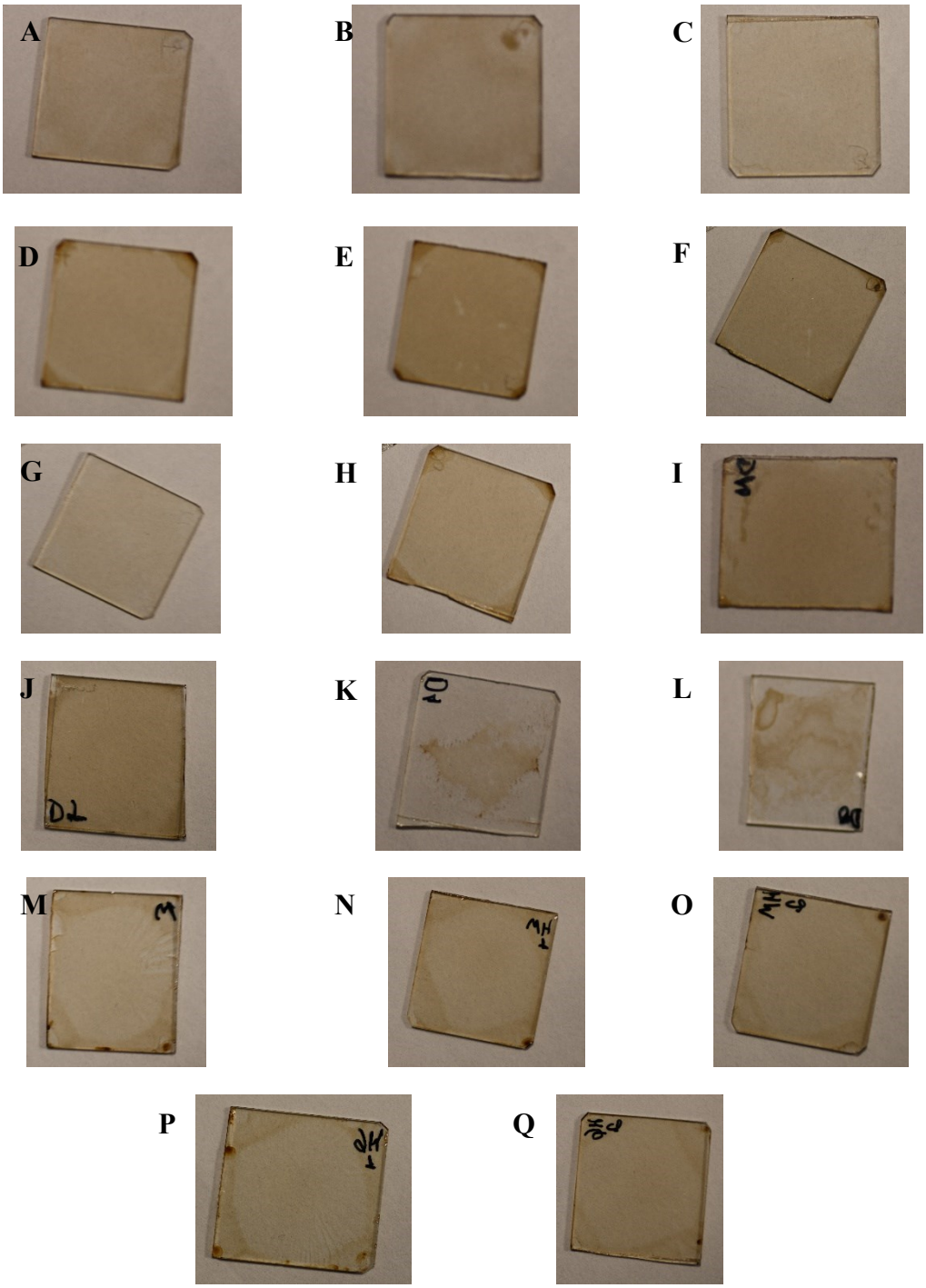

Figure S5. Optical images of different melanin thin-films deposited on a glass substrate. These images are merely a guide to indicate consistent brown color. True spectra is given in the optical profiles. A) SMel out of DMSO. B) SMel-T out of DMSO. C) SMel-4P out of DMSO. D) SMel-8P out of DMSO. E) SMel out of DMF. F) SMel-T out of DMF. G) SMel-4P out of DMF. H) SMel-8P out of DMF. I) SMel out of NMP. J) SMel-T out of NMP. K) SMel-4P out of NMP. L) SMel-8P out of NMP. M) NFMel-I out of H_2O+NH_3. N). NFMel-S out of H_2O+NH_3 O). O) NFMel-S out of H_2O.P) NFMel-6P out of H_2O+NH_3. Q) NFMel-6P out of H_2O.

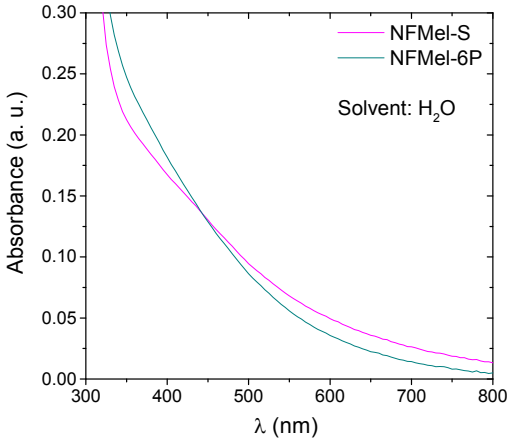

Figure S6. Absorbance spectra of NF-melanin in water-only solution (i.e., neutral solution). NFMel-I is insoluble in water-only solution, hindering its thin-film deposition.

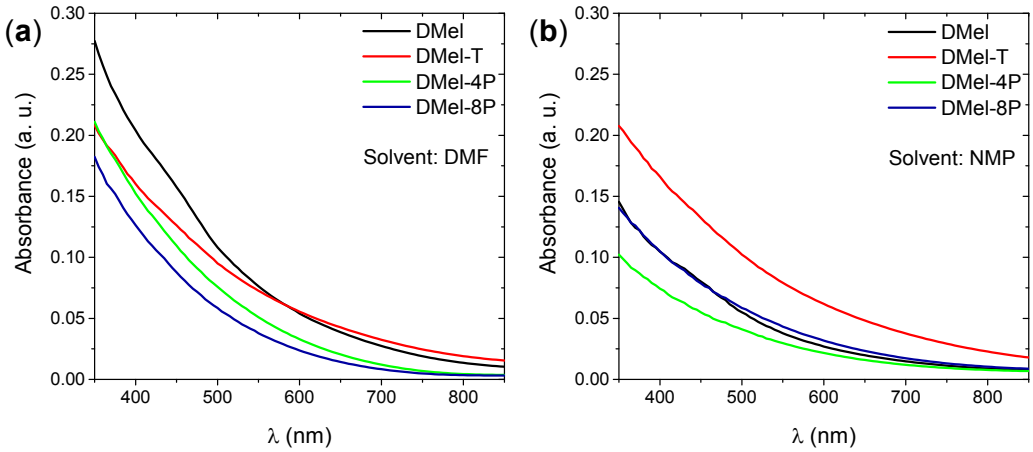

Figure S7. Absorbance spectra of S-melanin in (a) DMF and (b) NMP solutions.

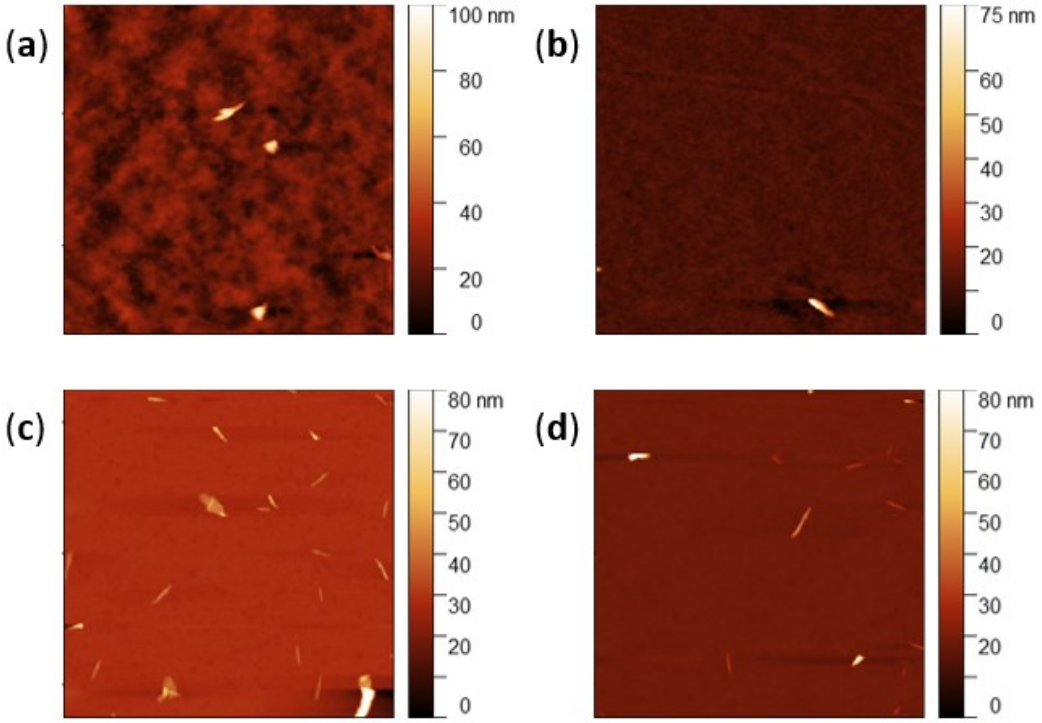

Figure S8. AFM images for S-melanins spin coated out of DMSO. All images are 5x5 μm^2. (a) SMel sample. (b) SMel-T sample. (c) SMel-4P sample. (d) SMel-8P sample. The underlying films are smooth, but does exhibit features that are reminiscent of "grains of rice". Similar features have recently been reported for other melanin films.[1]

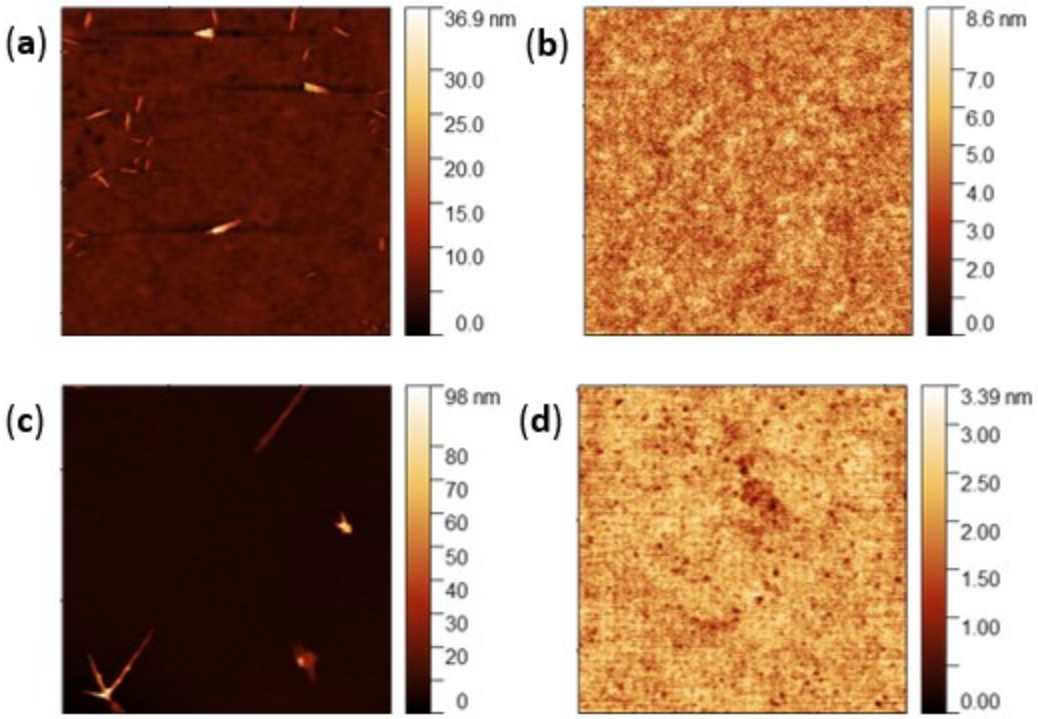

Figure S9. AFM images for S-melanins spin coated out of DMF. All images are 5x5 μm^2. (a) SMel sample. (b) SMel-T sample. (c) SMel-4P sample. (d) SMel-8P sample. The underlying films are smooth, but does exhibit features that are reminiscent of "grains of rice". Similar features have recently been reported for other melanin films.[1]

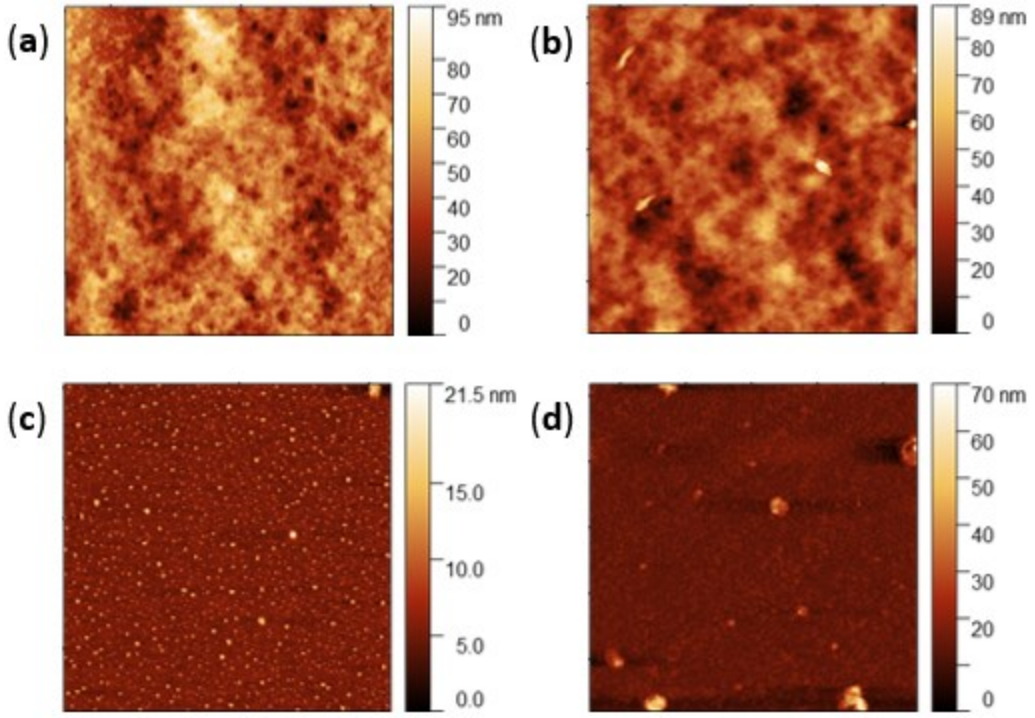

Figure S10. AFM images for S-melanins spin coated out of NMP. All images are 5x5 μm^2. (a) SMel sample. (b) SMel-T sample. (c) SMel-4P sample. (d) SMel-8P sample. The underlying films are smooth, but some exhibit features that are reminiscent of "grains of rice". Similar features have recently been reported for other melanin films.[1]

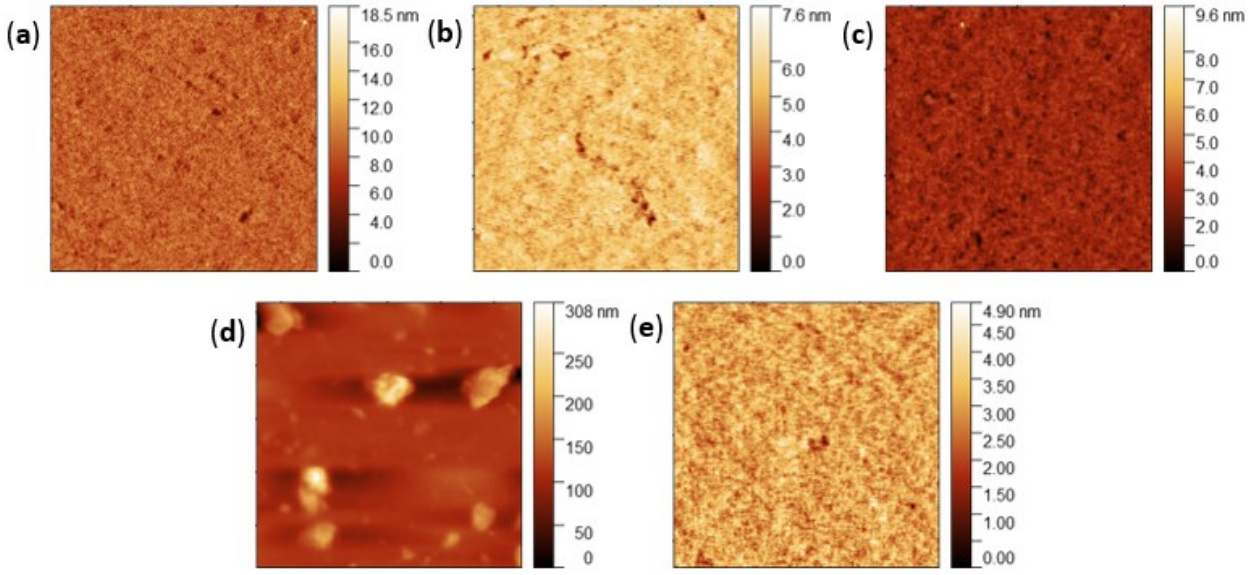

Figure S11. AFM images for NF-melanins in (a, b, c) H_2O+NH_3 solution and (d, e) H_2O solution. All images are 5x5 μm^2. (a) NFMel-I sample, (b) NFMel-S sample, (c) NMel-6P sample, (d) NFMel-S sample and (e) NMel-6P sample. The underlying films are smooth, but some exhibit features that are large granules, indicating i) melanin particles that were not fully dispersed and ii) aggregates formed during de-wetting process.[1] The size of around 100 nm for the solubilized melanins has been reported from TEM work.[2]

Table S2. The average roughness calculations for the melanin films. Both mean roughness (S_a) and root mean square roughness (S_q) are shown. Furthermore, analysis was done on the films including and excluding the prominent features in order to obtain the underlying film smoothness as well.

Solvent	Samples	Overall roughness (nm)		Underlying Film Roughness (nm)	
		S_a	S_q	S_a	S_q
H_2O+NH_3	**NFMel-I**	1.2	1.5	1.2	1.5
	NFMel-S	4.9	10.2	1.0	1.4
	NFMel-6P	0.5	0.6	0.5	0.6
H_2O	**NFMel-S**	7.8	15.3	3.0	3.7
	NFMel-6P	1.4	1.8	1.2	1.5
DMSO	**SMel**	4.8	6.4	3.9	4.7
	SMel -T	1.4	3.1	1.1	1.4
	SMel -4P	0.9	2.4	0.5	0.7
	SMel -8P	0.6	2.0	0.3	0.3
DMF	**SMel**	0.8	1.7	0.6	0.7
	SMel -T	1.4	4.1	0.9	1.1
	SMel -4P	0.8	2.1	0.5	0.7
	SMel -8P	0.4	0.5	0.4	0.5
NMP	**SMel**	9.8	12.2	7.3	9.0
	SMel -T	7.5	9.6	5.3	6.5
	SMel -4P	0.9	1.5	0.9	1.5
	SMel -8P	3.1	7.4	1.5	1.9

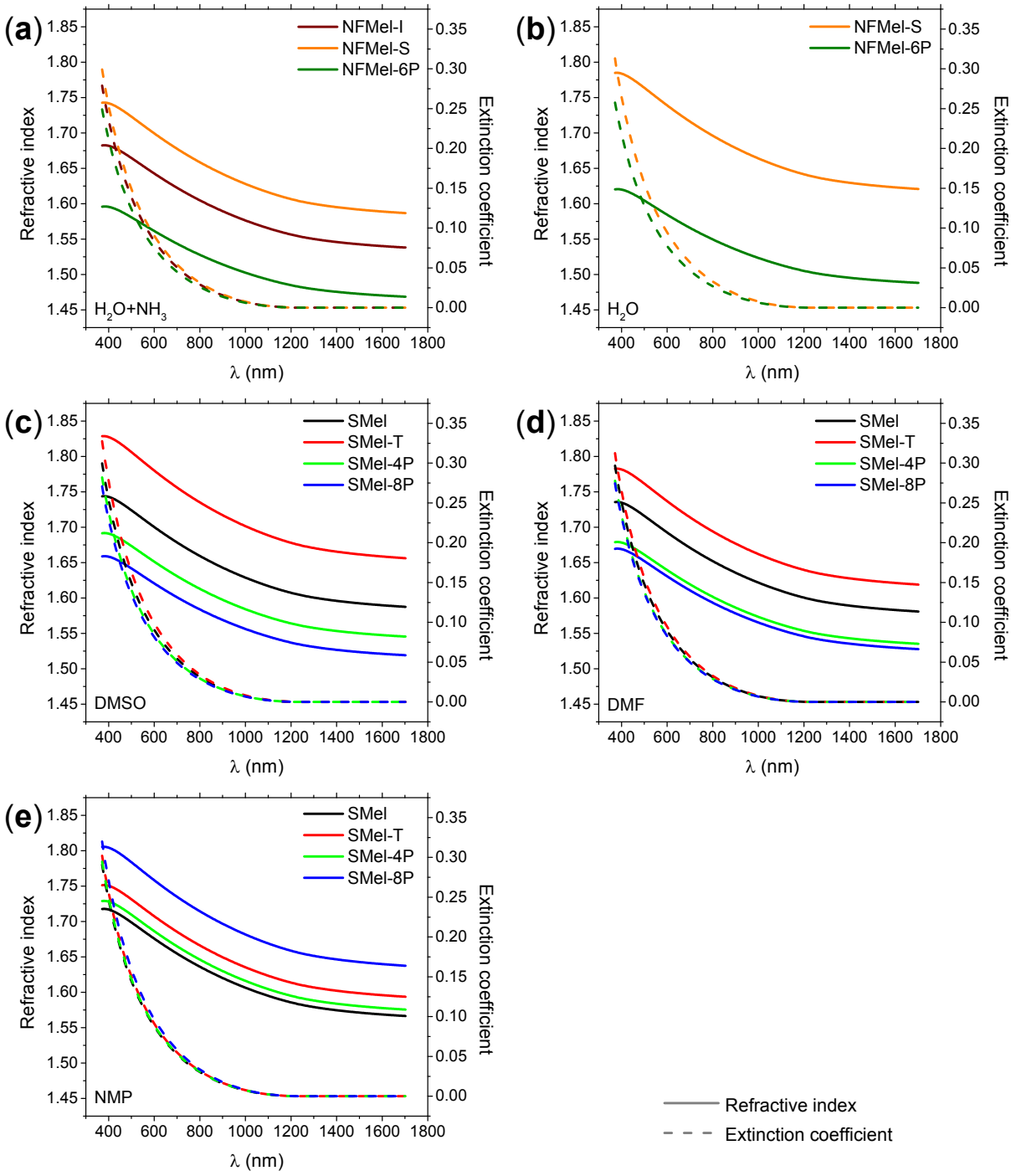

Figure S12. Optical constants of all NF and S-melanin derivatives for the different films (see legend). Solid line represents the refractive index and dash line the extinction coefficient.

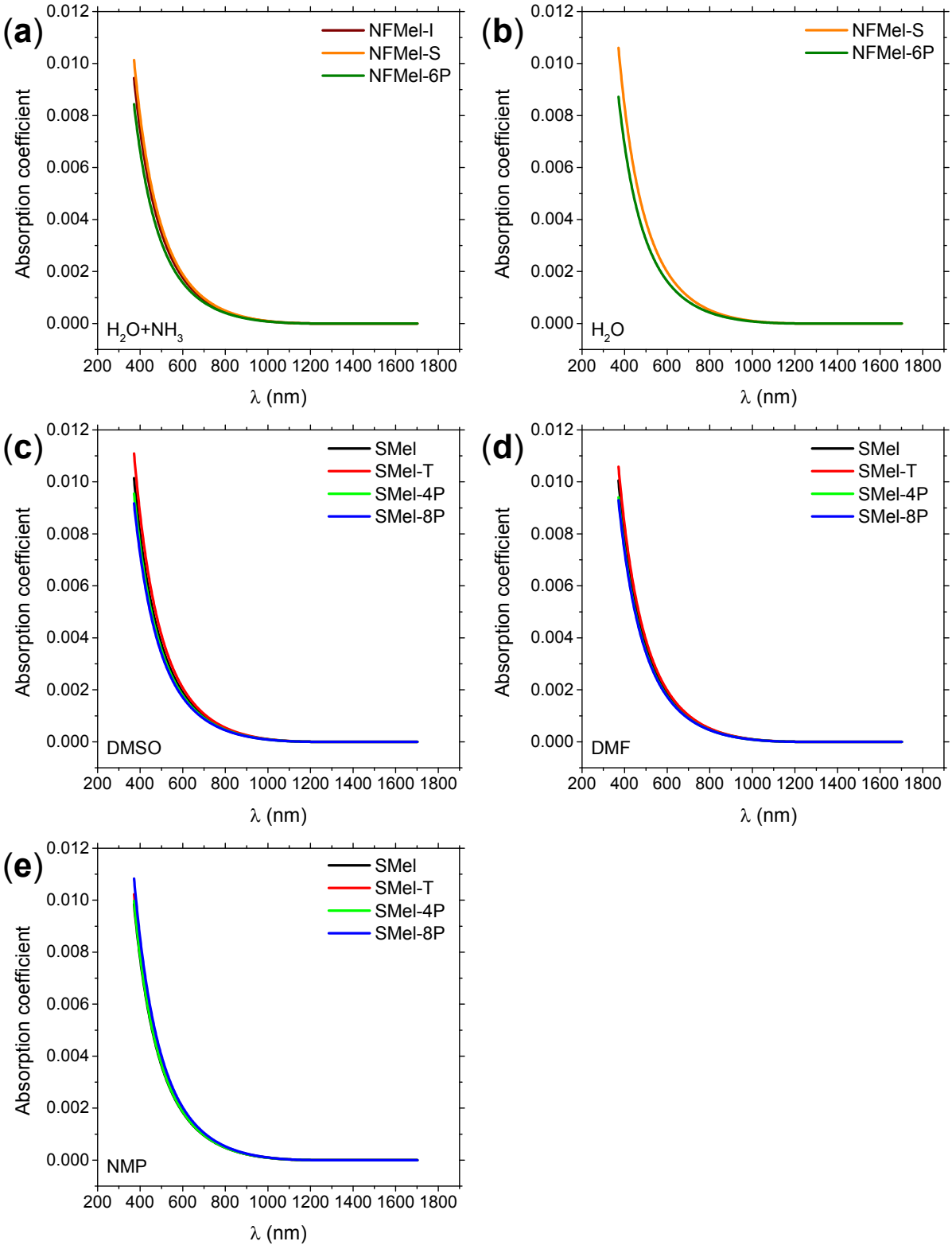

Figure S13. Films' absorption coefficient of all NF and S-melanin derivatives.

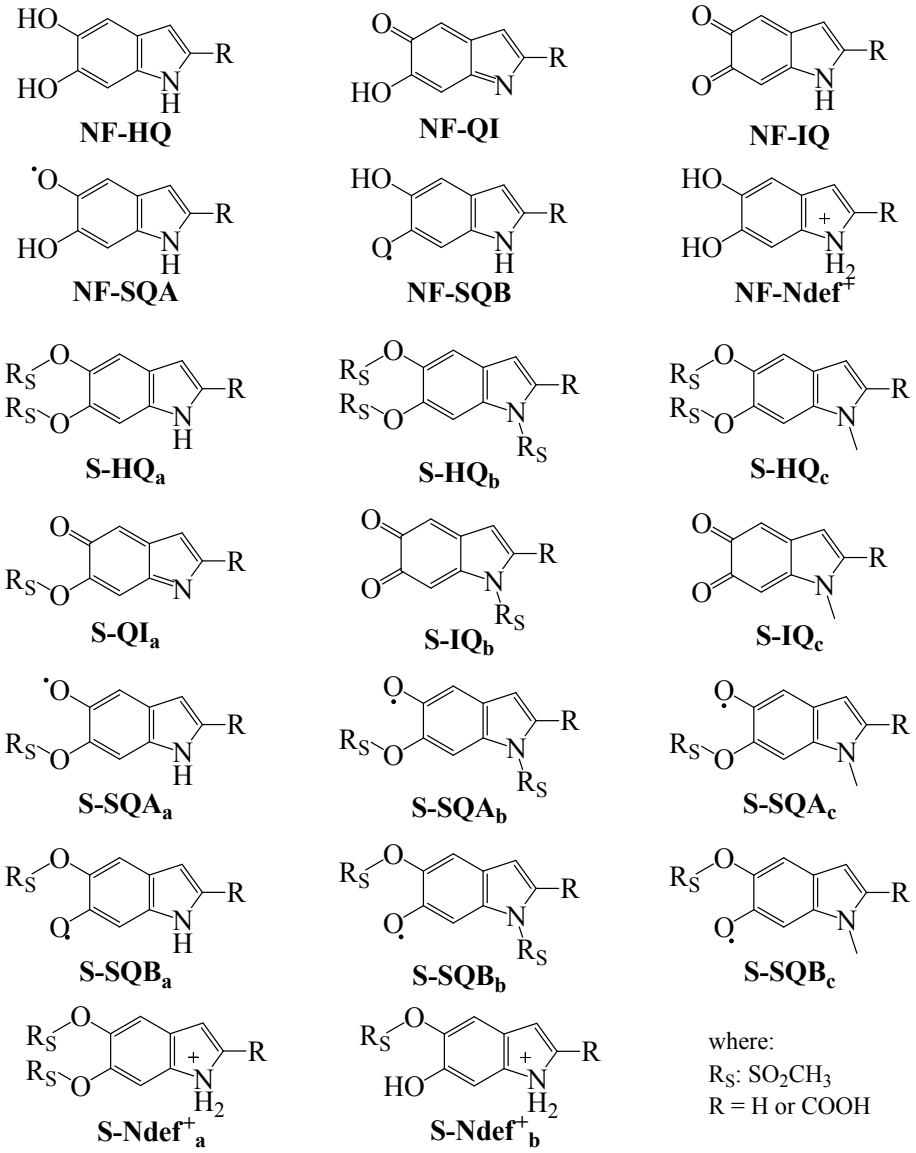

Figure S14. Different NF and S-melanin units.

Table S3. Abbe's number for the different films.

	Abbe's number for the different films				
	$H_2O + NH_3$	**H_2O**	**DMSO**	**DMF**	**NMP**
NFMel-I	17.78	#	#	#	#
NFMel-S	17.91	18,01	#	#	#
NFMel-6P	19.59	17,64	#	#	#
SMel	#	#	17.91	17.90	17.86
SMel-T	#	#	18.10	18.00	17.93
SMel-4P	#	#	17.80	17.77	17.88
SMel-8P	#	#	17.73	17.75	18.05

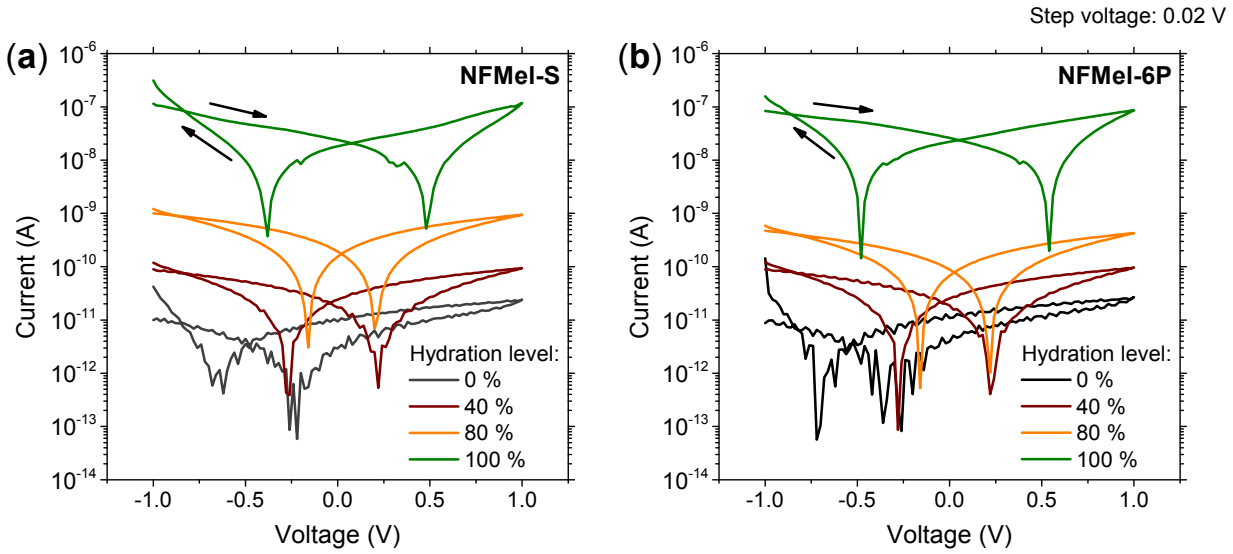

Figure S15. Current as a function of voltage for (a) NFMel-S and (b) NFMel-6P in H_2O-NH_3 at different hydration levels on a log-linear scale. The films were deposited using a mixture of pure water and ammonia (H_2O+NH_3) solution.

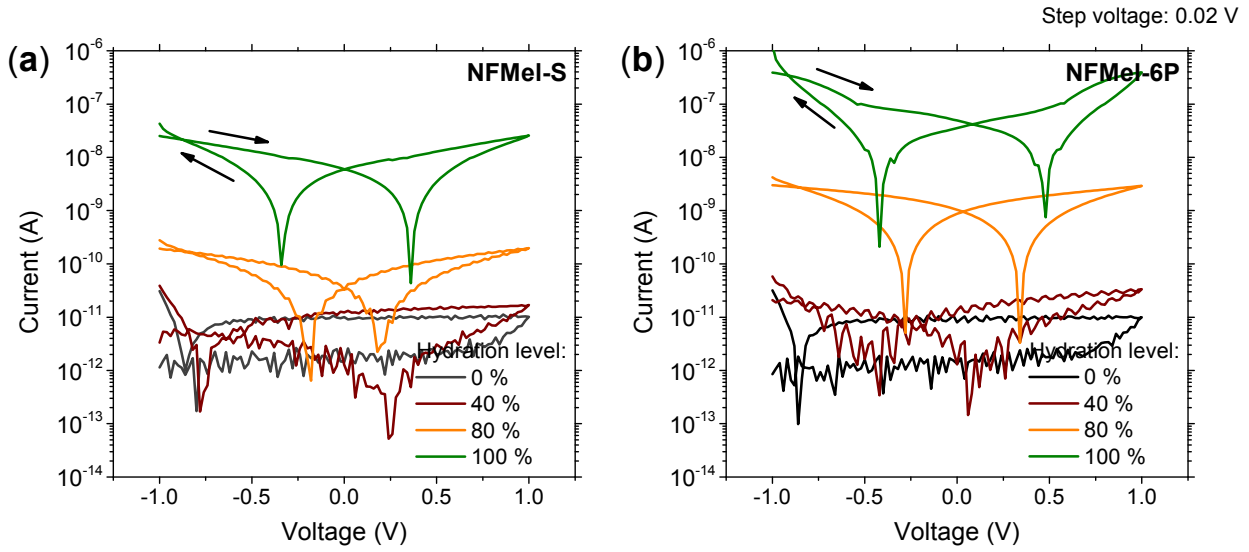

Figure 16 Current as a function of voltage for (a) NFMel-S and (b) NFMel-6P in H_2O at different hydration levels on a log-linear scale. The films were deposited using pure water solution.

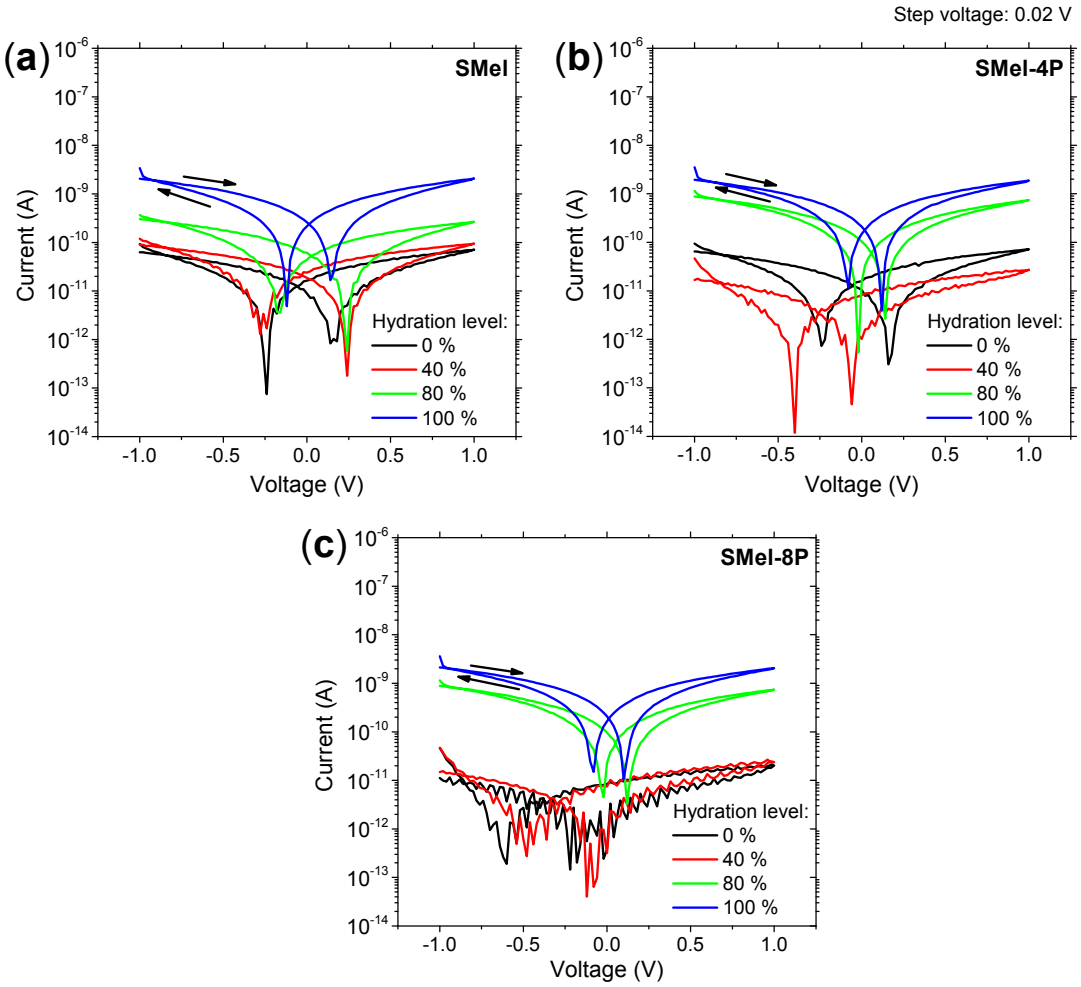

Figure S17. Current as a function of voltage for (a) SMel, (b) SMel-4P and (c) SMel-8P in DMSO at different hydration levels on a log-linear scale. The films were deposited using DMSO solution.

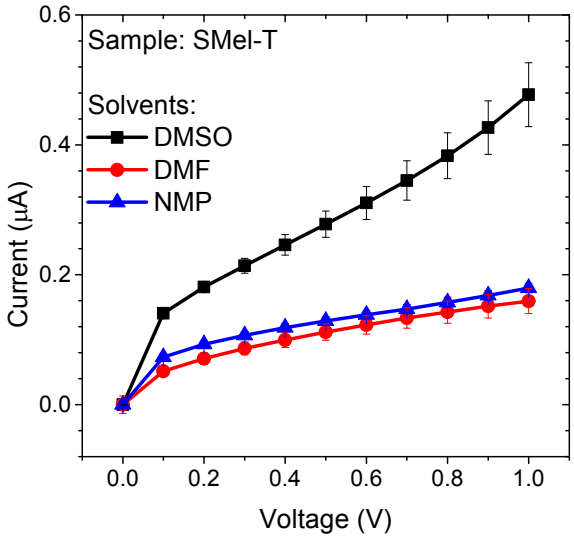

Figure S18. Current *vs.* voltage curve for SMel-T in different solvents at room atmosphere.

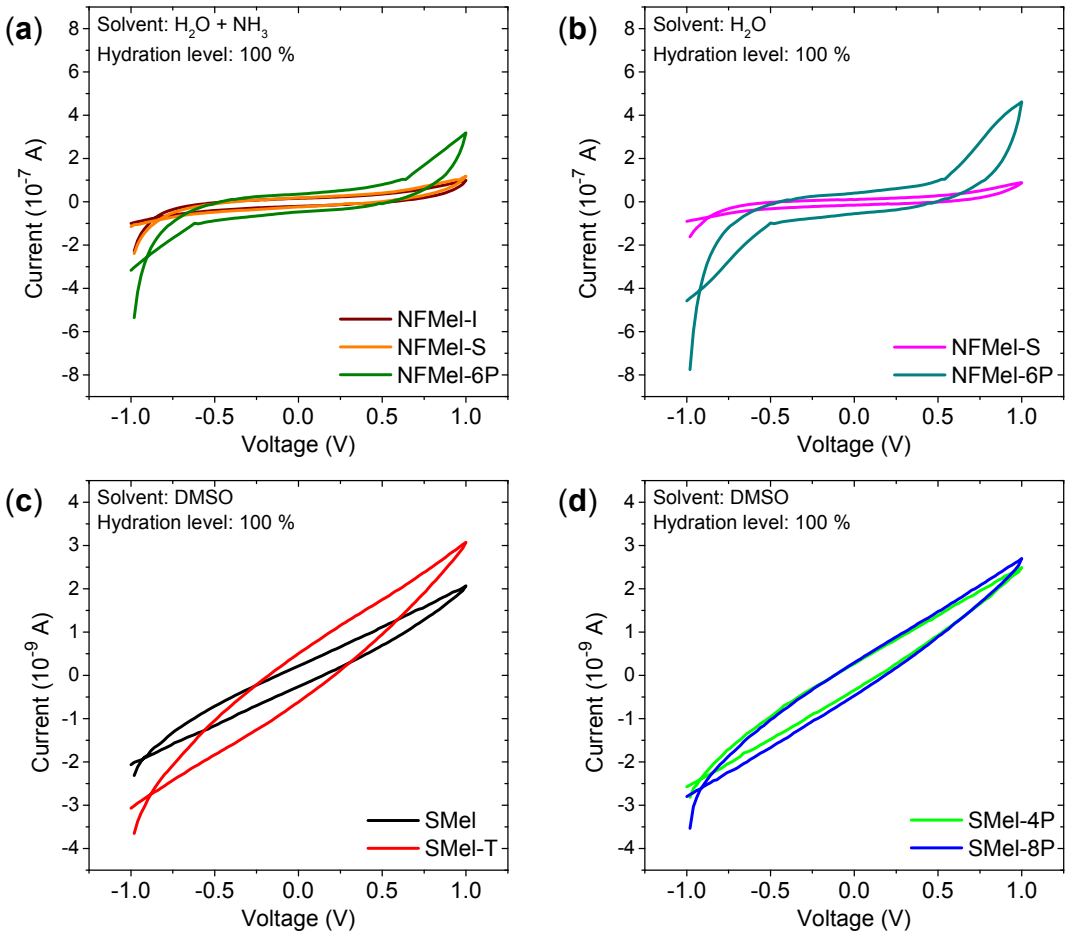

Figure S19. Current as a function of voltage at saturation condition with y-axis in linear scale.

Table S4. Area of the JV curve normalized by the electrode geometry to estimate the hysteresis at different hydration.

NF-Melanin	Hydration 0 % ($10^{-6} \pm 10^{-6}$) cm^{-1}	40 % ($10^{-6} \pm 10^{-6}$) cm^{-1}	80 % ($10^{-4} \pm 10^{-4}$) cm^{-1}	100 % ($10^{-3} \pm 10^{-3}$) cm^{-1}
H_2O+NH_3				
NFMel-I	4.36 ± 3.37	7.62 ± 3.37	3.48 ± 3.26	7.44 ± 1.14
NFMel-S	7.54 ± 2.82	7.57 ± 3.64	2.90 ± 3.88	9.77 ± 1.53
NFMel-6P	7.22 ± 2.82	5.77 ± 3.37	3.46 ± 3.85	16.01 ± 5.45
H_2O				
NFMel-S	1.47 ± 2.97	1.80 ± 3.64	2.72 ± 4.33	3.49 ± 2.44
NFMel-6P	1.48 ± 2.98	2.28 ± 3.65	11.45 ± 3.89	26.47 ± 8.49
S-Melanin	**Hydration 0 %** ($10^{-6} \pm 10^{-6}$) cm^{-1}	**40 %** ($10^{-6} \pm 10^{-6}$) cm^{-1}	**80 %** ($10^{-5} \pm 10^{-6}$) cm^{-1}	**100 %** ($10^{-5} \pm 10^{-6}$) cm^{-1}
DMSO				
SMel	8.01 ± 3.37	4.60 ± 3.99	1.56 ± 3.64	8.41 ± 3.95
SMel-T	7.19 ± 3.64	5.27 ± 3.99	1.60 ± 4.46	12.86 ± 3.33
SMel-4P	2.74 ± 3.16	2.17 ± 3.64	1.20 ± 5.15	7.82 ± 3.61
SMel-8	2.69 ± 3.16	2.27 ± 3.37	1.34 ± 3.37	7.57 ± 3.35

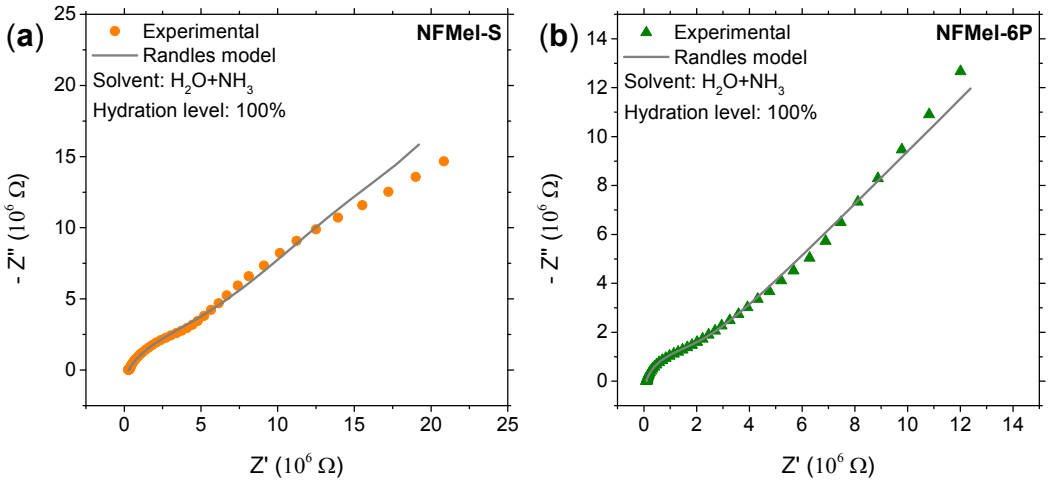

Figure S20. Nyquist plot of the EIS measurement of NF-melanin using H_2O+NH_3 as a solvent at 100% hydration level.

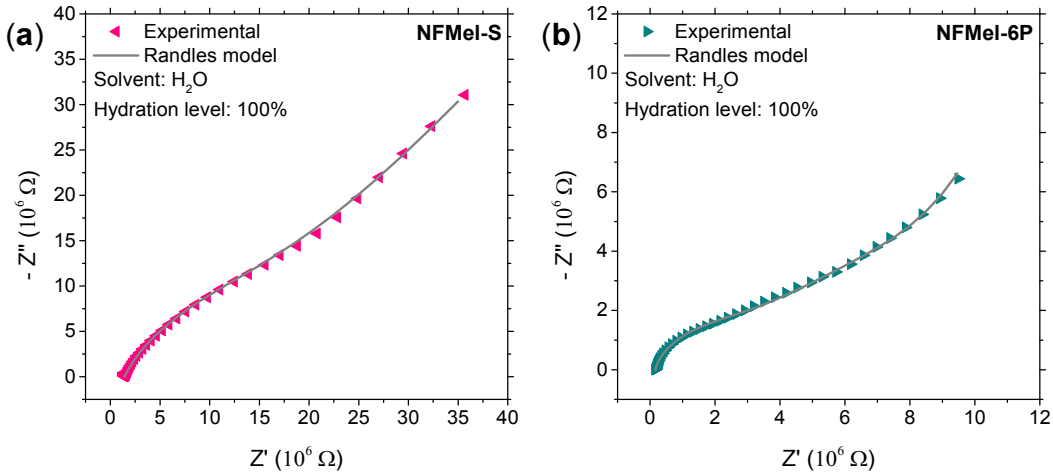

Figure S21. Nyquist plot of the EIS measurement of NF-melanin using H_2O as a solvent at 100% hydration level.

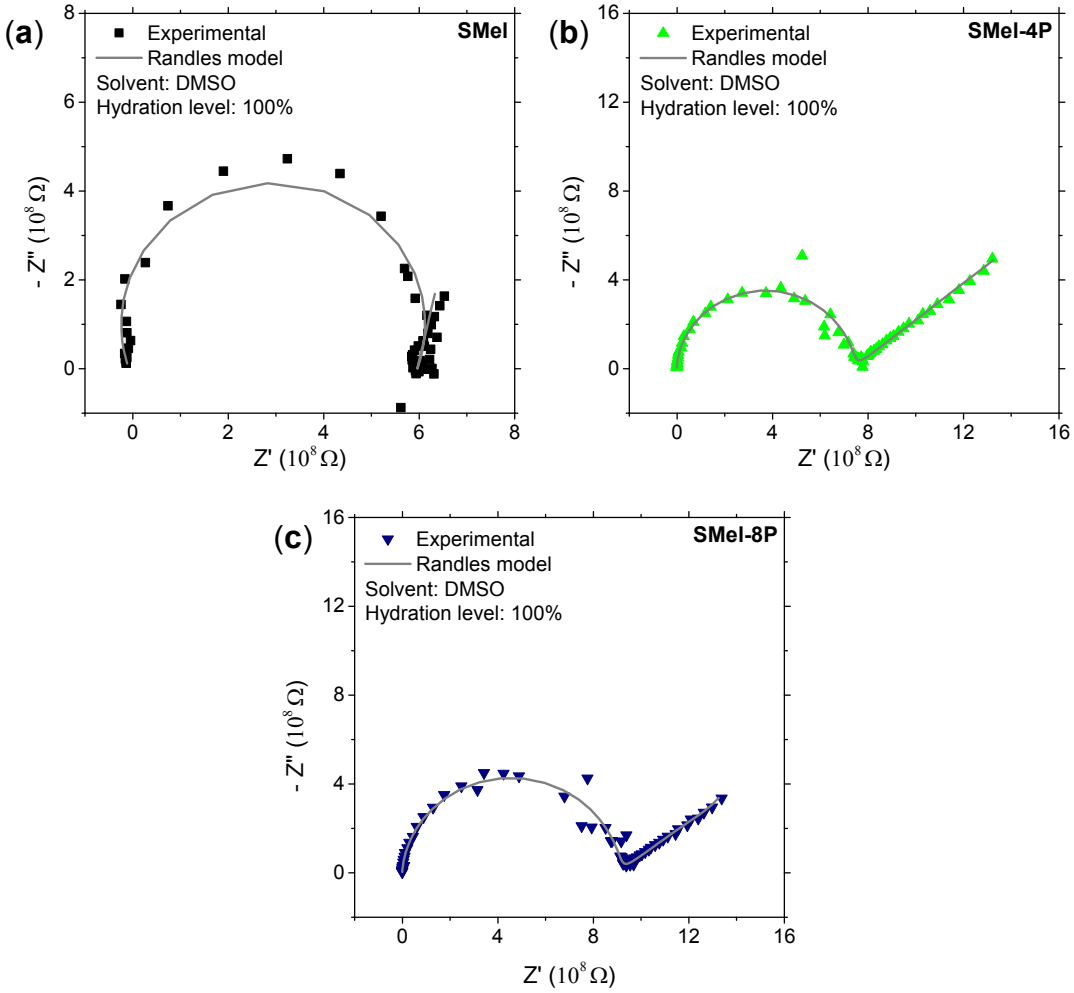

Figure S22. Nyquist plot of the EIS measurement of S-melanin using DMSO as a solvent at 100% hydration level.

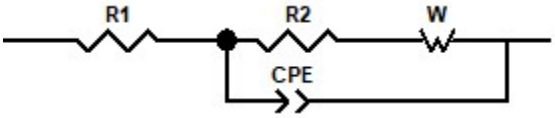

Figure S23. Randle circuit was used as an equivalent circuit for the representation of the melanin derivatives impedance between gold interdigitated electrodes. R1 represents the contact resistance, R2 represents the ionic flow with the Warburg element W capturing the ionic/electrode effects. The CPE, or constant phase element, captures the capacitive effects of the rest of the material.

Table S5. Fitting parameters used to fit the data according to the equivalent circuit (Figure S15) for all samples at 100% hydration level. The Warburg diffusion element (given by $Z_W = \sigma\omega^{-1/2} - j\sigma\omega^{-1/2}$, with σ representing the Warburg coefficient, ω the angular frequency and j the imaginary unit) is divided in W-R represents the diffusion impedance, W-T is the system diffusion time and W-P is an exponential factor. For Warburg diffusion, W-P = 0.5.

Sample	R1 (Ω)	R2 (Ω)	W-R (Ω)	W-T (s)	W-P (unitless)	Q (Ω^{-1})	η (unitless)
H_2O+NH_3							
NFMel-I	8.99E+05	1.73E+07	9.03E+07	8.65E+01	6.25E-01	6.81E-08	7.38E-01
NFMel-S	2.87E+05	5.84E+06	6.57E+07	1.06E+02	4.92E-01	4.91E-08	7.06E-01
NFMel-6P	1.02E+05	2.01E+06	1.39E+05	1.71E-03	2.62E-01	3.75E-08	8.68E-01
H_2O							
NFMel-S	1.41E+06	2.39E+07	9.06E+05	1.69E-02	2.82E-01	9.45E-08	7.12E-01
NFMel-6P	1.62E+05	2.11E+06	2.02E+07	7.79E+01	4.00E-01	4.25E-08	8.64E-01
DMSO							
SMel	7.80E+06	6.04E+08	2.10E+03	3.22E-05	4.32E-01	8.56E-16	1.00E+00
SMel-T	1.95E+06	3.58E+08	3.74E+08	2.44E+01	4.15E-01	4.19E-13	9.69E-01
SMel-4P	1.61E+06	7.36E+08	4.55E+10	1.69E+05	4.41E-01	4.68E-13	9.68E-01
SMel-8	1.07E+06	9.05E+08	1.35E+09	1.24E+02	4.24E-01	6.57E-13	9.60E-01

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2 E. S. Bronze-Uhle, J. V. Paulin, M. Piacenti-Silva, C. Battocchio, M. L. M. Rocco and C. F. de O. Graeff, *Polym. Int.*, 2016, **65**, 1339–1346.