Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information for: The structural impact of water sorption on device-quality melanin thin films

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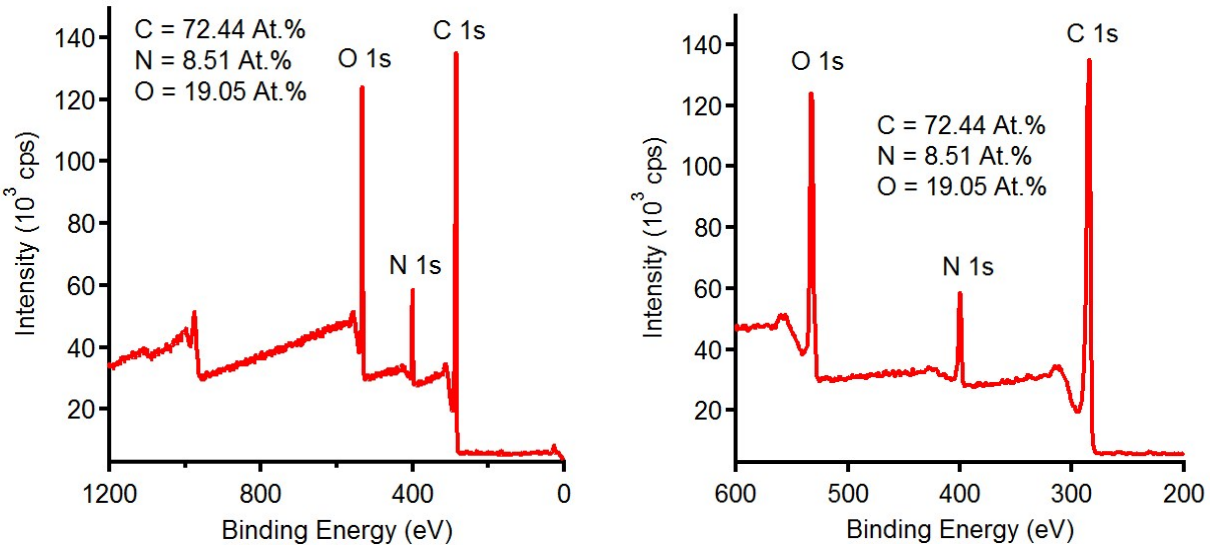

Figure S1 XPS of a melanin film under high vacuum. Referenced to the N 1s signal of poly(9-vinylcarbazole), which has a binding energy of 400.22 eV according to Beamson, G.; Briggs, D., *High Resolution XPS of Organic Polymers: The Scienta ESCA300 Database*. John Wiley & Sons: Chichester, England, UK, **1992**.

Table S1 NR fitting parameters for the film exposed to H_2O. Layer 1 = air interface layer, Layer 2 = bulk layer and Layer 3 = substrate interface layer. Tx = thickness of layer x, ρx = scattering length density of layer x, R1 = interfacial roughness between layer 1 and air, R2 = interfacial roughness between layer 2 and layer 1, R3 = interfacial roughness between layer 2 and layer 3. RS = interfacial roughness between layer 3 and the silicon substrate. Fixed parameters: T1 = 65 Å, T3 = 28 Å, R1 = 10 Å, R2 = 15 Å, R3 = 15 Å, RS = 8.3.

p(H_2O) (mbar)	**Exposed / Evacuated**	**Thickness 2 (Å)**	**ρ 1 (10^{-6} Å^{-2})**	**ρ 2 (10^{-6} Å^{-2})**	**ρ 3 (10^{-6} Å^{-2})**
0.0	Evacuated	342 ± 1	3.22 ± 0.07	3.35 ± 0.06	3.20 ± 0.10
2.3	Exposed	348 ± 1	3.17 ± 0.07	3.29 ± 0.06	3.21 ± 0.09
	Evacuated	341 ± 1	3.20 ± 0.07	3.37 ± 0.06	3.28 ± 0.10
6.2	Exposed	362 ± 1	3.07 ± 0.07	3.19 ± 0.06	3.08 ± 0.09
	Evacuated	343 ± 1	3.19 ± 0.07	3.36 ± 0.06	3.35 ± 0.09
15.5	Exposed	395 ± 2	2.89 ± 0.07	2.94 ± 0.06	2.80 ± 0.10
	Evacuated	350 ± 1	3.14 ± 0.07	3.30 ± 0.06	3.24 ± 0.09
24.8	Exposed	437 ± 2	2.66 ± 0.07	2.69 ± 0.06	2.49 ± 0.10
	Evacuated	352 ± 1	3.05 ± 0.07	3.27 ± 0.06	3.25 ± 0.09

Table S2 NR fitting parameters for the film exposed initially to D_2O and then to H_2O to regenerate/back exchange the H/D moieties. Layer 1 = air interface layer, Layer 2 = bulk layer and Layer 3 = substrate interface layer. Tx = thickness of layer x, ρx = scattering length density of layer x, R1 = interfacial roughness between layer 1 and air, R2 = interfacial roughness between layer 2 and layer 1, R3 = interfacial roughness between layer 2 and layer 3, RS = interfacial roughness between layer 3 and the silicon substrate. Fixed parameters: T1 = 52 Å, T3 = 40 Å, R1 = 12 Å, R2 = 15 Å, R3 = 15 Å, RS = 8.5 Å.

p(D_2O/H_2O) (mbar)	**Exposed / Evacuated**	**T2 (Å)**	**ρ1 (10^{-6} Å^{-2})**	**ρ2 (10^{-6} Å^{-2})**	**ρ3 (10^{-6} Å^{-2})**
0.0	Evacuated	327 ± 1	3.24 ± 0.07	3.37 ± 0.06	3.23 ± 0.08
2.0 (D_2O)	Exposed	333 ± 1	3.75 ± 0.08	4.03 ± 0.06	3.75 ± 0.08
	Evacuated	327 ± 1	3.63 ± 0.08	3.81 ± 0.06	3.68 ± 0.09
5.4 (D_2O)	Exposed	344 ± 1	4.46 ± 0.09	4.78 ± 0.06	4.48 ± 0.10
	Evacuated	328 ± 1	4.22 ± 0.08	4.38 ± 0.06	4.25 ± 0.09
13.5 (D_2O)	Exposed	373 ± 1	5.18 ± 0.09	5.31 ± 0.06	4.95 ± 0.11
	Evacuated	335 ± 1	4.42 ± 0.09	4.74 ± 0.06	4.54 ± 0.10
21.6 (D_2O)	Exposed	411 ± 1	5.65 ± 0.11	5.66 ± 0.06	5.23 ± 0.14
	Evacuated	339 ± 1	4.41 ± 0.10	4.88 ± 0.06	4.73 ± 0.11
24.8 (H_2O)	Exposed	423 ± 1	3.03 ± 0.07	2.99 ± 0.06	2.85 ± 0.08
	Evacuated	344 ± 1	3.21 ± 0.08	3.52 ± 0.06	3.46 ± 0.09

Table S3 Total thickness, average SLD of the film exposed to H_2O calculated from the data in Table S1 and the corresponding values of ρ_{Matrix} calculated using equation (2).

p(H_2O) (mbar)	Exposed / Evacuated	Total Thickness (Å)	Average ρ_{Film} (10^{-6} Å^{-2})	ρ_{Matrix} (10^{-6} Å^{-2})
0.0	Evacuated	436 ± 1	3.32 ± 0.05	3.32 ± 0.05
2.3	Exposed	442 ± 1	3.26 ± 0.05	3.31 ± 0.05
	Evacuated	435 ± 1	3.34 ± 0.05	3.33 ± 0.05
6.2	Exposed	456 ± 1	3.16 ± 0.05	3.33 ± 0.05
	Evacuated	437 ± 1	3.32 ± 0.05	3.33 ± 0.05
15.5	Exposed	489 ± 2	2.92 ± 0.05	3.34 ± 0.06
	Evacuated	444 ± 1	3.27 ± 0.05	3.34 ± 0.05
24.8	Exposed	531 ± 2	2.67 ± 0.05	3.37 ± 0.06
	Evacuated	446 ± 1	3.23 ± 0.05	3.32 ± 0.05

Table S4 Total thickness, average SLD of the film exposed to D_2O calculated from the data in Table S2 and the corresponding values of ρ_{Matrix} calculated using equation (2).

p(D_2O/H_2O) (mbar)	Exposed / Evacuated	Total Thickness (Å)	Average ρ_{Film} (10^{-6} Å^{-2})	ρ_{Matrix} (10^{-6} Å^{-2})
0.0	Evacuated	421 ± 1	3.34 ± 0.05	3.34 ± 0.05
2.0 (D_2O)	Exposed	427 ± 1	3.97 ± 0.05	3.94 ± 0.05
	Evacuated	421 ± 1	3.77 ± 0.05	3.77 ± 0.05
5.4 (D_2O)	Exposed	438 ± 1	4.72 ± 0.05	4.65 ± 0.05
	Evacuated	422 ± 1	4.34 ± 0.06	4.34 ± 0.06
13.5 (D_2O)	Exposed	467 ± 1	5.27 ± 0.05	5.15 ± 0.06
	Evacuated	429 ± 1	4.68 ± 0.07	4.65 ± 0.07
21.6 (D_2O)	Exposed	505 ± 1	5.63 ± 0.05	5.48 ± 0.06
	Evacuated	433 ± 1	4.80 ± 0.07	4.76 ± 0.07
24.8 (H_2O)	Exposed	517 ± 1	2.98 ± 0.05	3.78 ± 0.06
	Evacuated	438 ± 1	3.47 ± 0.05	3.63 ± 0.05