Supporting information

Tailoring melanins for bioelectronics: polycysteinyldopamine as ion conducting redox-responsive polydopamine variant for pro-oxidant thin films.

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Materials and methods:

X-ray photoelectron spectroscopy (XPS): All the analysis were performed on a Thermo Scientific K-Alpha XPS system (Thermo Fisher Scientific, UK). Spectra were collected using a monochromatized Al-K α radiation (1486.6 eV). The surface emitted photoelectrons were analysed in a double-focusing hemispherical analyser and recorded on a multi-channel detector. All the spectra were acquired in the constant analyser energy mode. The ThermoScientific Avantage software (Thermo Fisher Scientific) was used for digital acquisition and data processing.

Water contact angle assessment (WCA): Static contact angle analyses were performed with 1 μL droplets for water, and carried out on a TBU90E Dataphysics contact angle goniometer.

Atomic Force Microscopy (AFM): Measurements were carried out on air at 298 K by using a Nanoscope V (model MMAFMLN, Digital Instrument Metrology Group). The tips used in all measurements were antimony-doped silicon cantilevers (T = 3.5–4.5 μm, L = 115–135 μm, fo = 271–305 kHz, k = 20–80 N m^{-1}, Bruker) at a resonant frequency of ca. 280 kHz. The collected images were then analysed with WsxM 5.0 software (Nanotec Electronica S. L.) to acquire the cross-sectional values and profiles of the processed images.

Coating experiments : Glass coverslips, quartz slides or the other materials (cuttings of polyethyleneterephthalate (PET) , coins) were dipped in a solution of either dopamine hydrochloride, or cysteinyldopamine at 10 mM concentration in 0.05 M bicarbonate buffer, pH 8.5 and kept under stirring in air. At the proper times the coated materials were rinsed with deionized water and air dried.

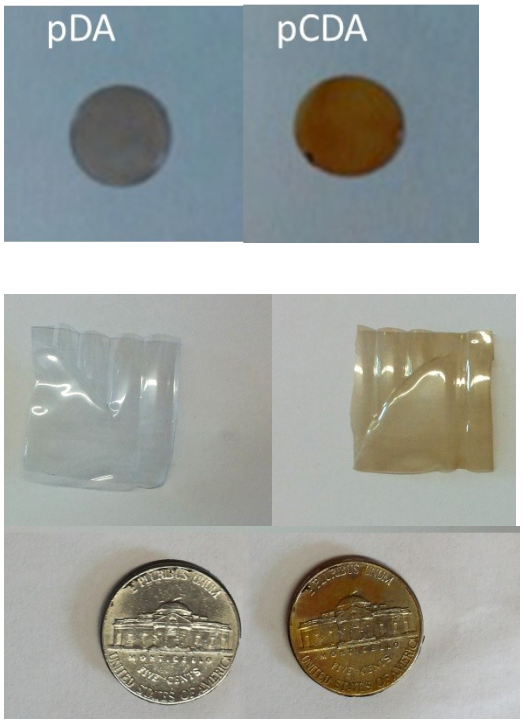


Figure SI-1 . TOP: pDA and pCDA thin films on glass coverslips produced by oxidation of 10 mM DA and CDA for 8h. BOTTOM: pCDA films on cuttings from polyethyleneterephthalate (PET) bottles and metals (right) as obtained by dip- coating into CDA at 10 mM in for 24 h, against controls (left)

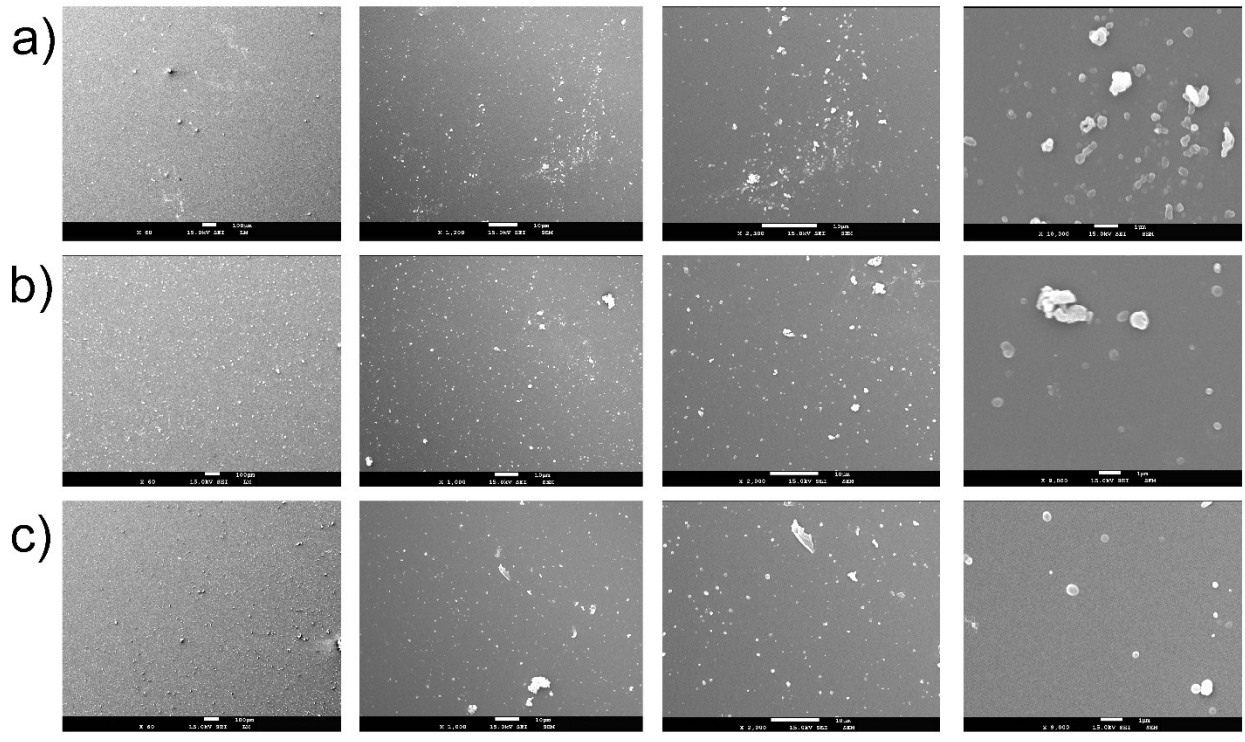


Figure SI-2. Representative SEM of pCD-3h (a), pCD-5h (b) and pCD-8h (c) surfaces, taken at different magnification.

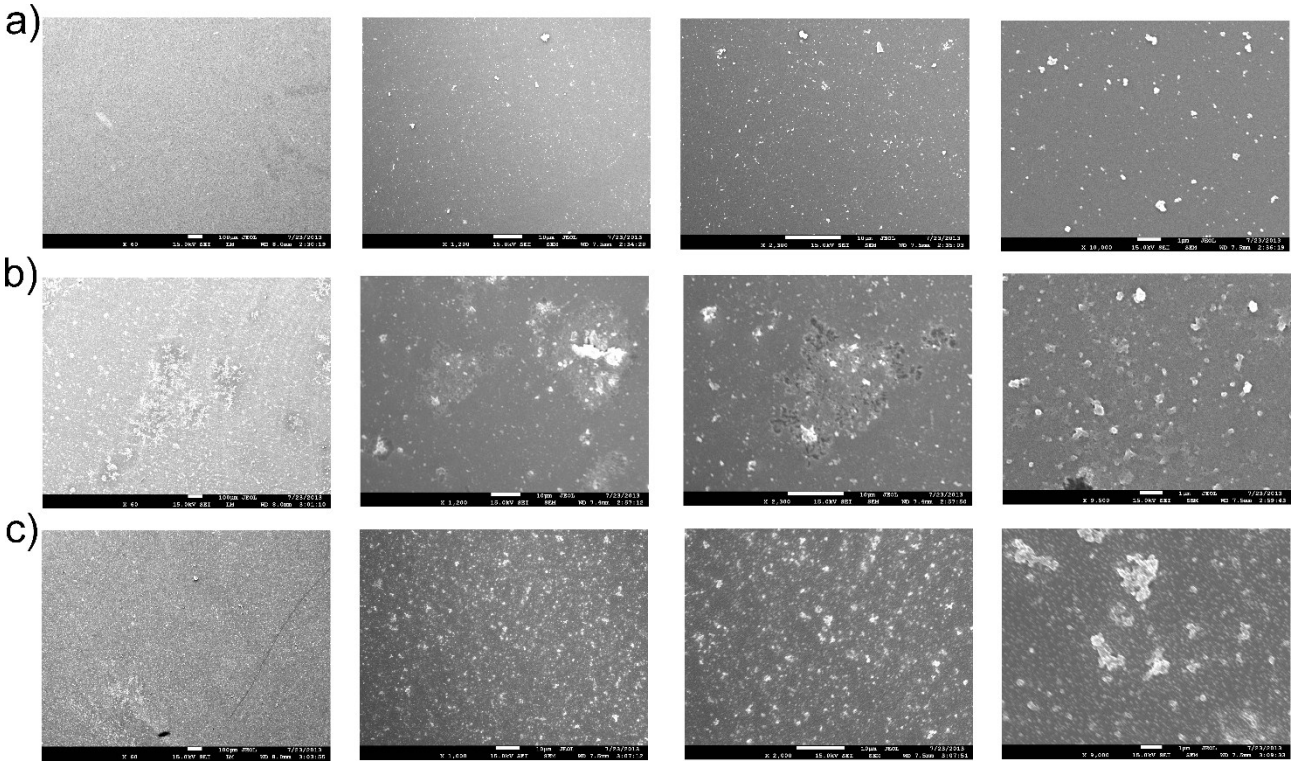


Figure SI-3. Representative SEM of pDA-3h (a), pDA-5h (b) and pDA-8h (c) surfaces, taken at different magnification.

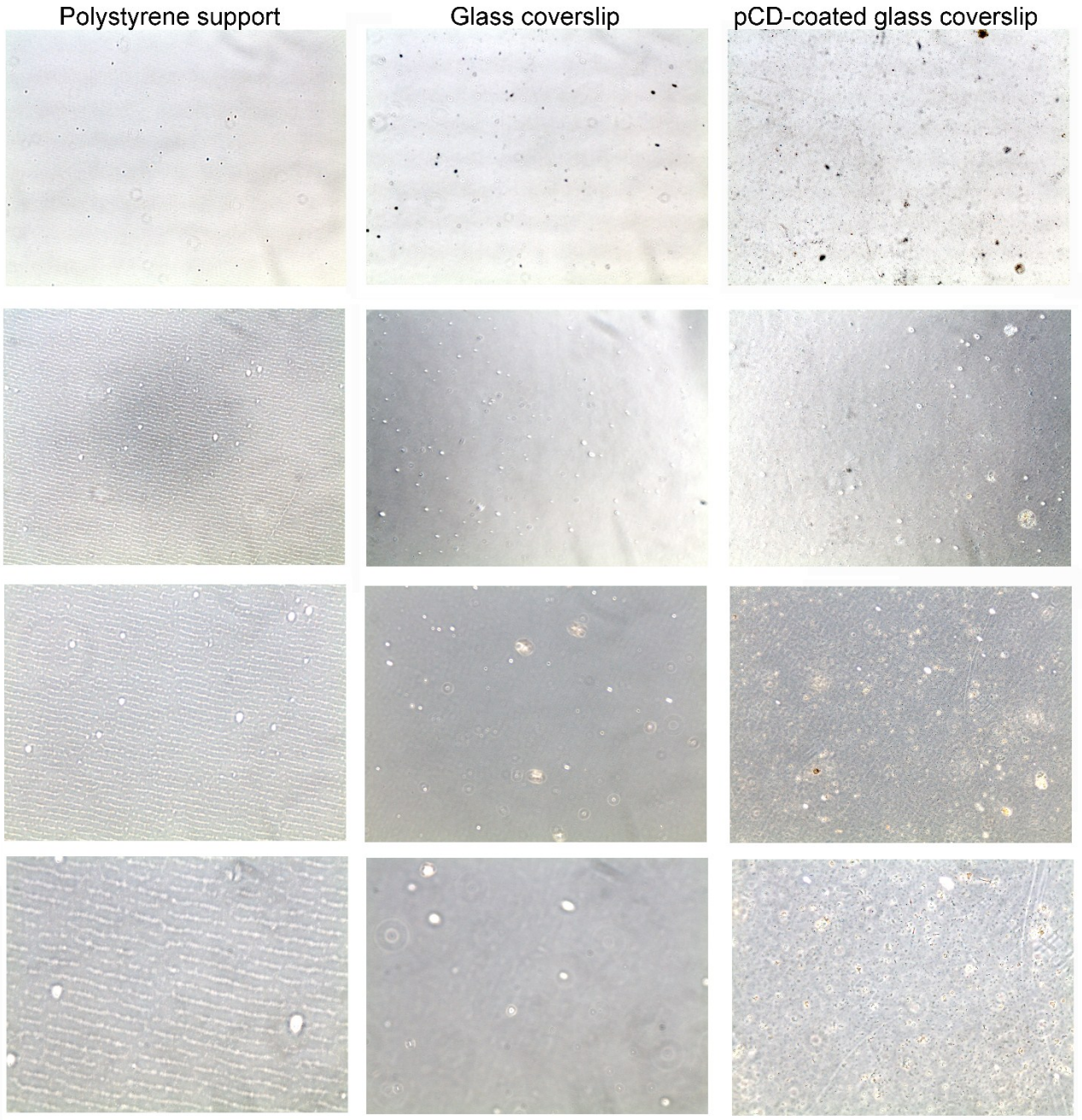


Fig. SI-4. Images taken by phase contrast (first two rows) or optical imaging (last two rows), showing image sizes from 4.7 mm^2 (top) to 0.21 mm^2 (bottom).

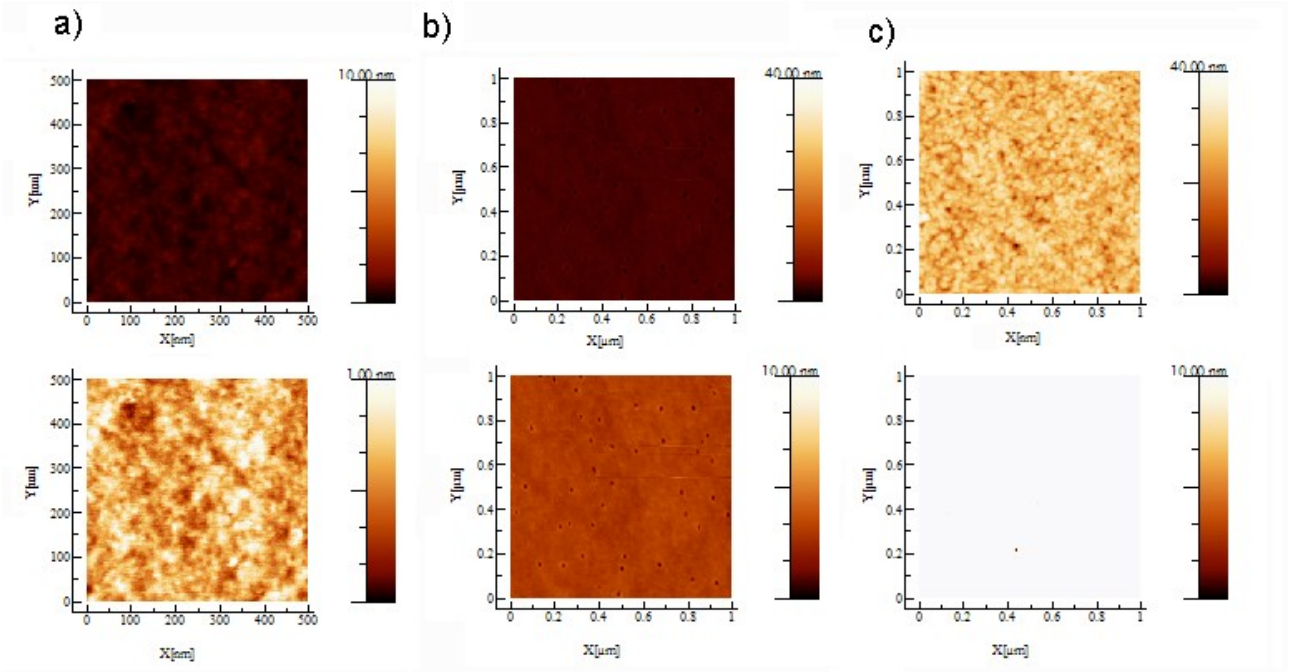


Figure SI-5. Tapping-mode AFM images of a 0.25 µm^2 (a) or 1 µm^2 areas (b, c) of a glass surface before (a,b) or after the coating with pCDA for 8h (c). The z ranges are reported in the range 0-10 nm or 0-40 nm, and scaled by a dark-brown-white colouration at the height values pass from the bottom to the upper height range.

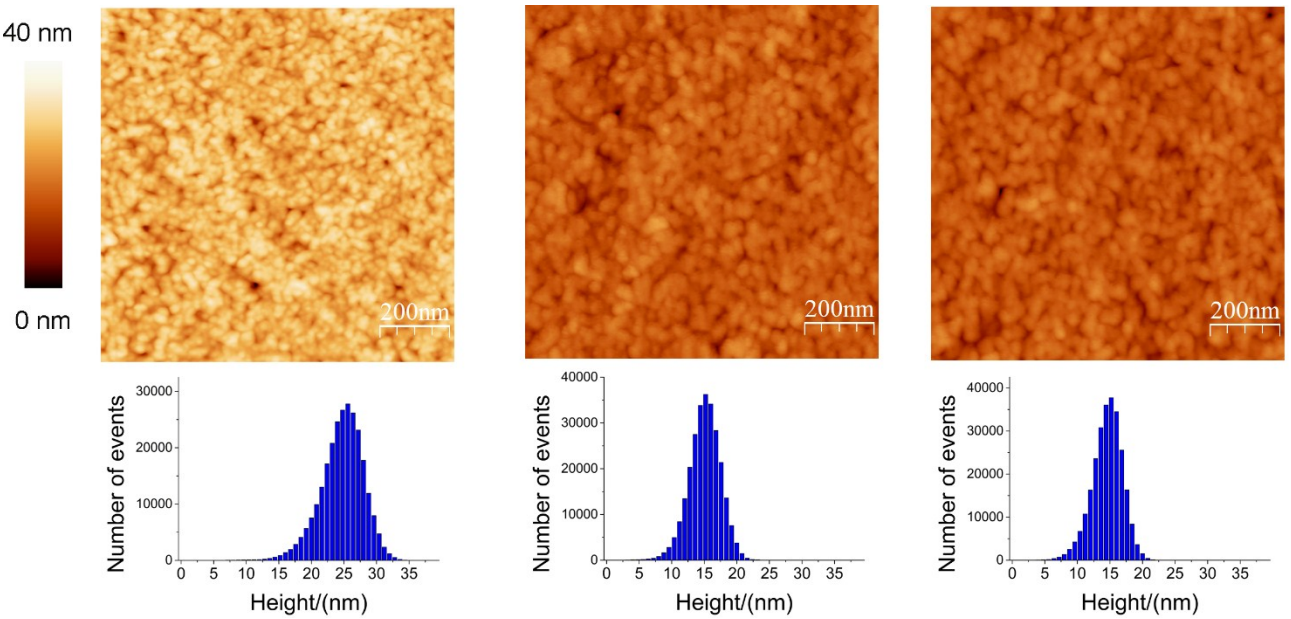


Figure SI-6. Tapping mode AFM images (height channel) of three representative spots (1 X 1 µm^2) of a glass surface 3 hours after CD polymerisation (pCD-3h), along with the surface roughness (bottom).

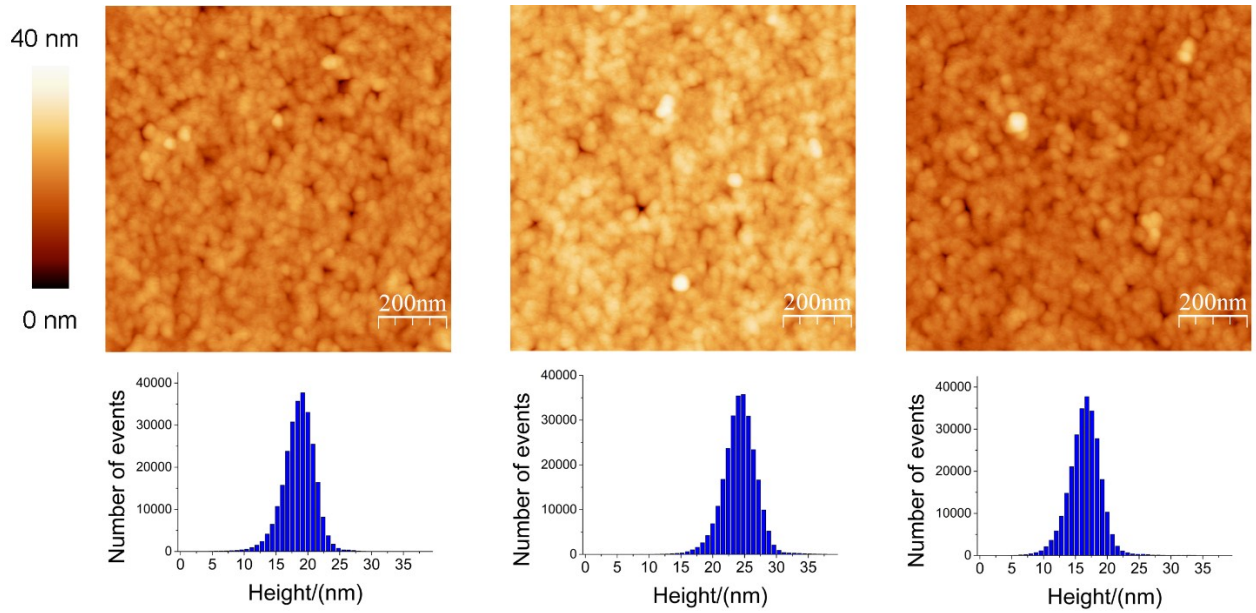


Figure SI-7. Tapping mode AFM images (height channel) of three representative spots (1 X 1 μm^2) of a glass surface 5 hours after CD polymerisation (pCD-5h), along with the surface roughness (bottom).

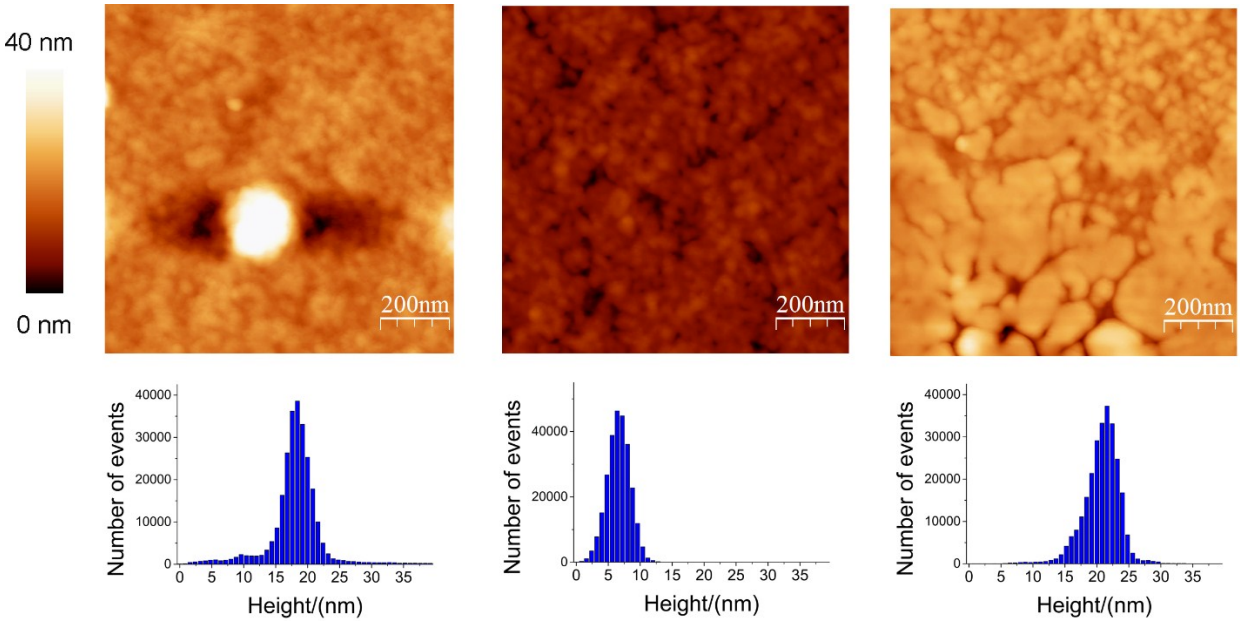


Figure SI-8. Tapping mode AFM images (height channel) of three representative spots (1 X 1 μm^2) of a glass surface 8 hours after CD polymerisation (pCD-8h), along with the surface roughness (bottom).

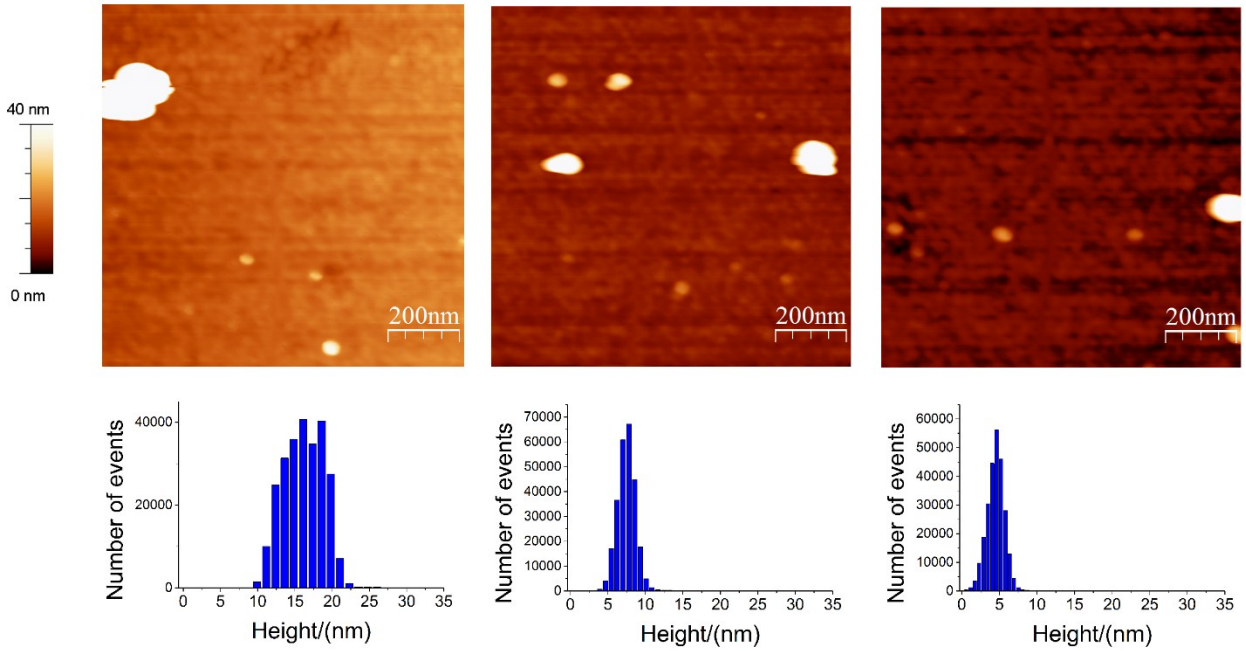


Figure SI-9. Tapping mode AFM images (height channel) of three representative spots (1 X 1 μm^2) of a glass surface 3 hours after DA polymerisation (pDA-3h), along with the surface roughness (bottom).

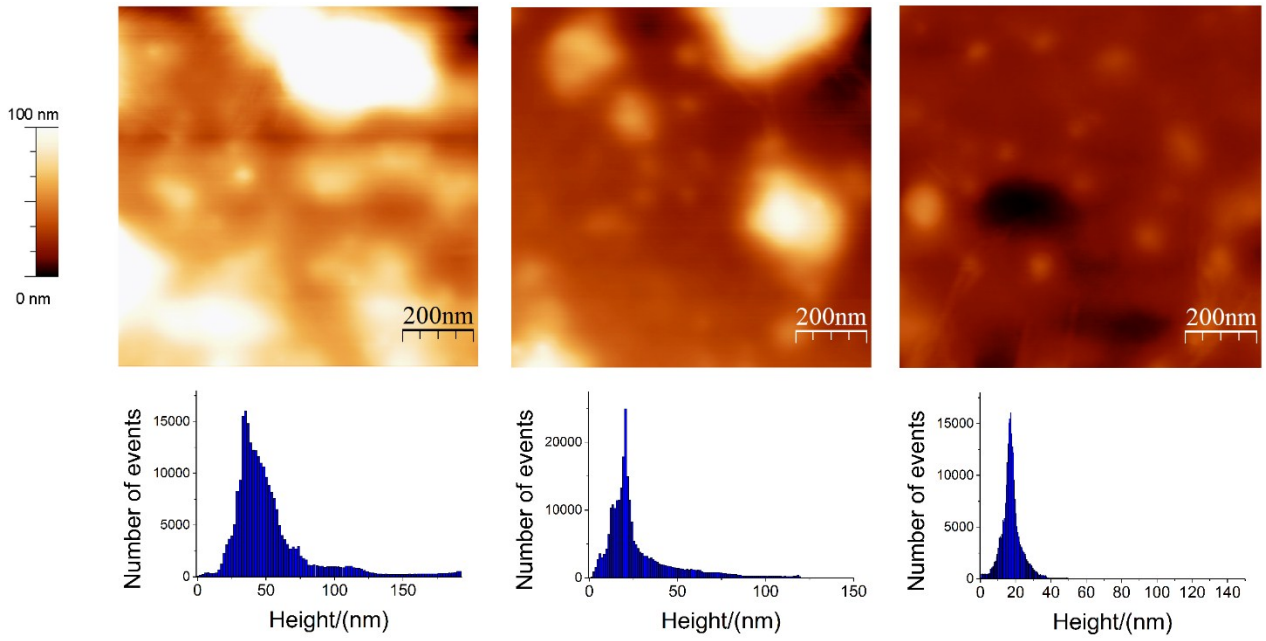


Figure SI-10. Tapping mode AFM images (height channel) of three representative spots (1 X 1 μm^2) of a glass surface 5 hours after DA polymerisation (pDA-5h), along with the surface roughness (bottom).

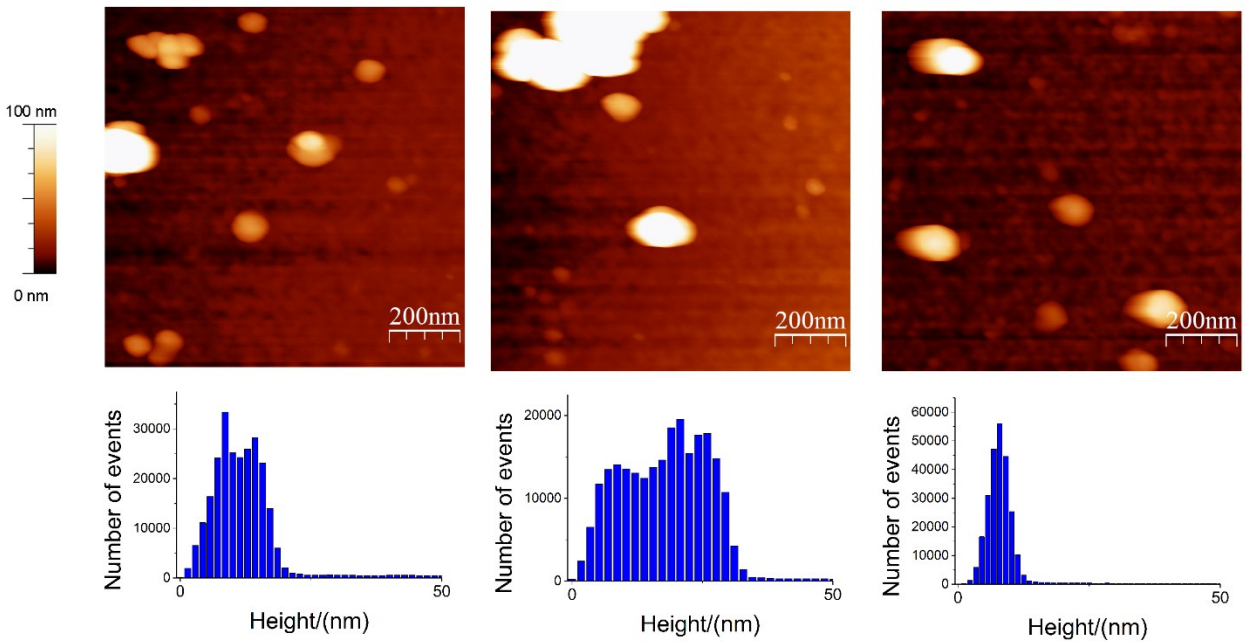
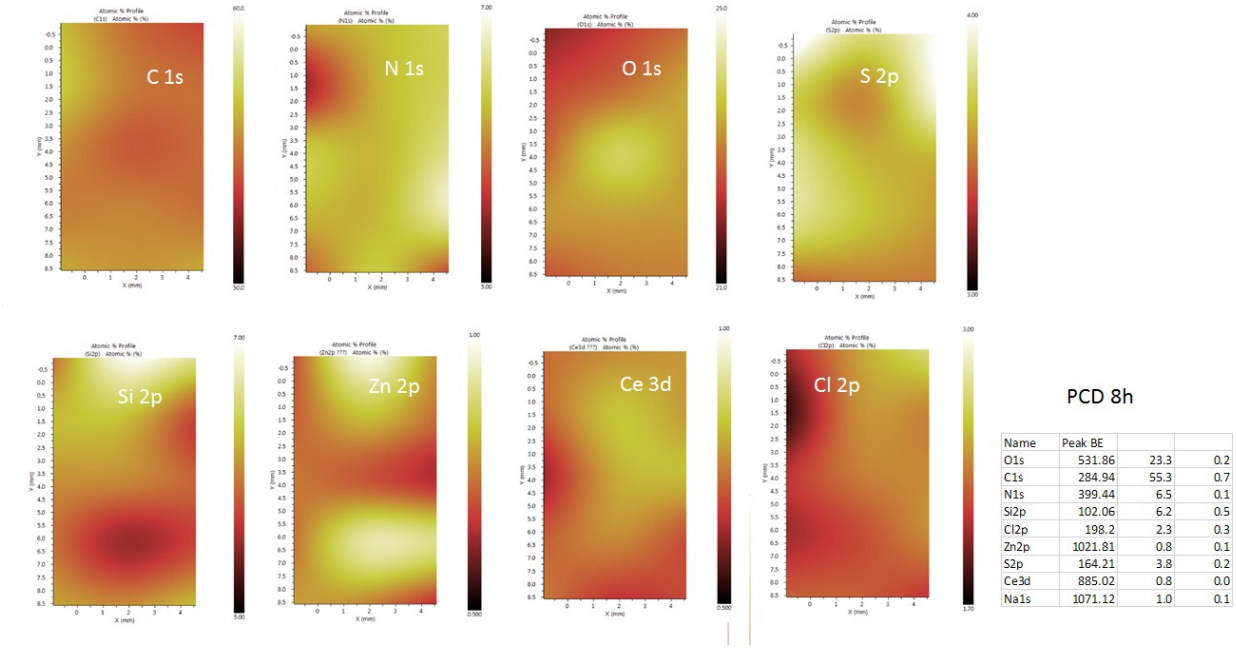


Figure SI-11. Tapping mode AFM images (height channel) of three representative spots (1 X 1 μm^2) of a glass surface 8 hours after DA polymerisation (pDA-8h), along with the surface roughness (bottom).

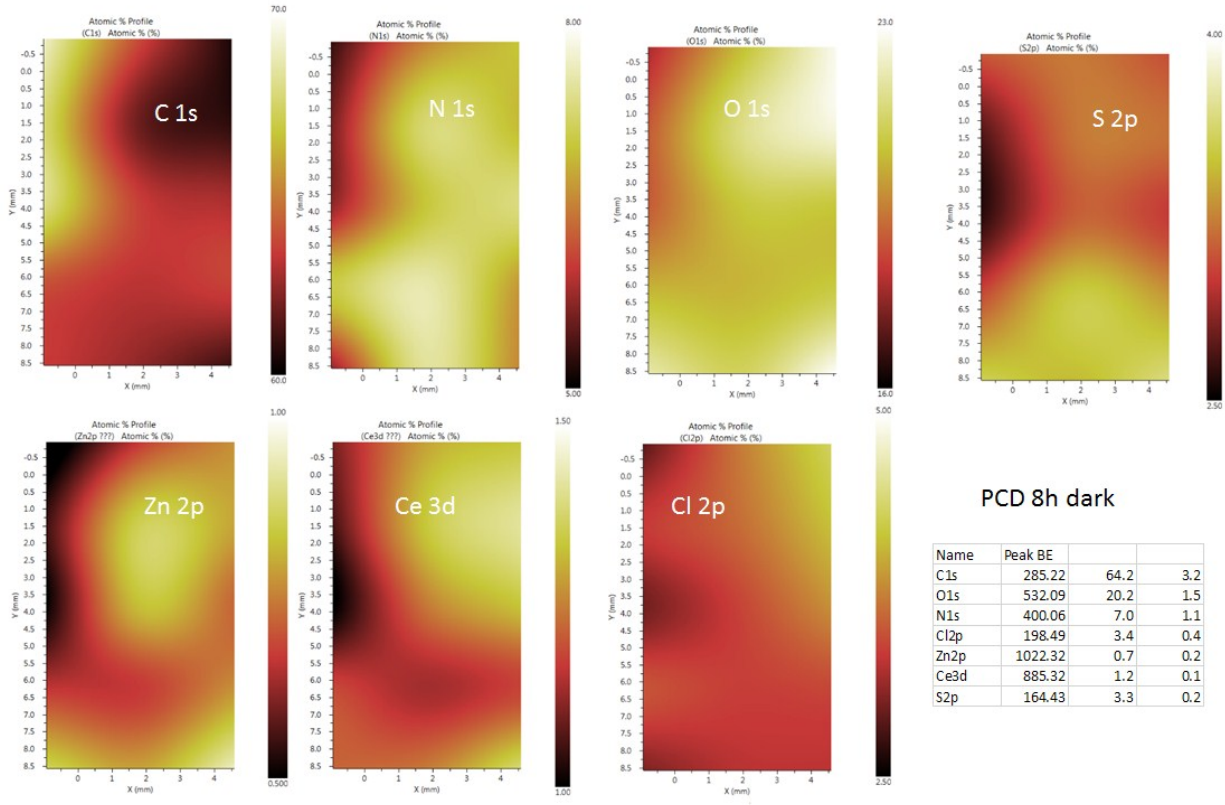
Table S1. Assessment of the organic moiety composition of PCD and PDA films on to glass coverslips after 8 hour of polymerisation.

		PCD 8h		PCD 8h (dark)		PDA 8h	
	eV	mean	s.d.	mean	s.d.	mean	s.d.
C1s	285	62.2	0.7	67.9	3.2	70.7	0.9
N1s	400	7.3	0.1	7.4	1.5	7.2	0.7
O1s	532	26.2	0.2	21.3	1.5	22.2	0.9
S2p	164	4.2	0.2	3.5	0.2	-	-



Name	Peak BE		
O1s	531.86	23.3	0.2
C1s	284.94	55.3	0.7
N1s	399.44	6.5	0.1
Si2p	102.06	6.2	0.5
Cl2p	198.2	2.3	0.3
Zn2p	1021.81	0.8	0.1
S2p	164.21	3.8	0.2
Ce3d	885.02	0.8	0.0
Na1s	1071.12	1.0	0.1

Figure SI-12. Elemental distribution maps of a pCDA surface after 8h of polymerisation on to a glass coverslip.



Name	Peak BE		
C1s	285.22	64.2	3.2
O1s	532.09	20.2	1.5
N1s	400.06	7.0	1.1
Cl2p	198.49	3.4	0.4
Zn2p	1022.32	0.7	0.2
Ce3d	885.32	1.2	0.1
S2p	164.43	3.3	0.2

Figure SI-13. Elemental distribution maps of a pCDA surface after 8h of polymerisation (protected from the light exposure) on to a glass coverslip.

PDA

Name	Peak BE		
C1s	285.03	69.8	0.9
O1s	531.85	21.9	0.9
N1s	399.86	7.1	0.7
Na1s	1071.11	1.3	0.3

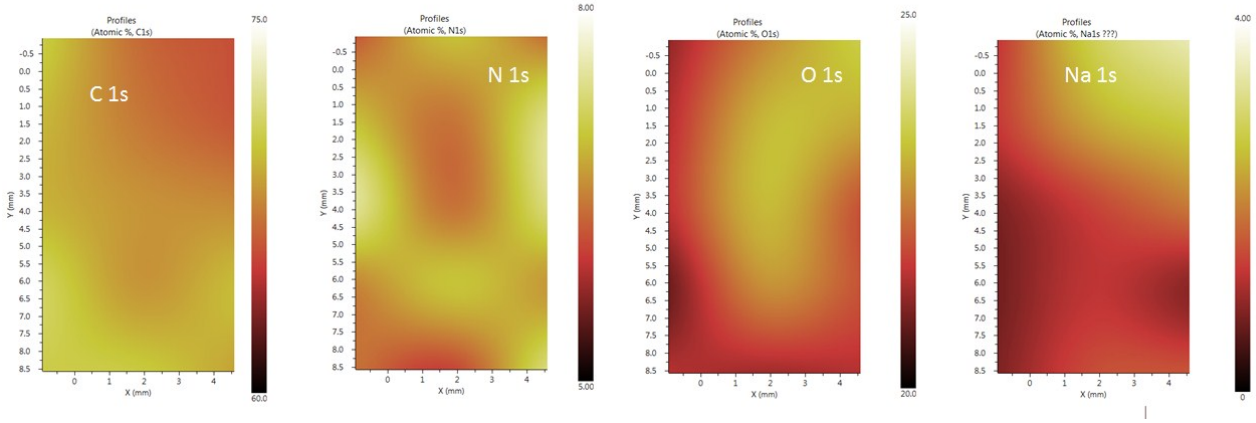


Figure SI-14. Elemental distribution maps of a pDA surface after 8h of polymerisation on to a glass coverslip.

Table S2. WCA values of a set of 18 surfaces coated with pDA by 8h of polymerisation time. Mean WCA for each surface is presented by averaging for each drop (4 drops per surface) with respect of left and right WCA (2 values per drop). Same will apply for all the WCA values of the following images and tables. Red values indicate the highest and lowest WCA values of this data set, where each value is reported as mean ± standard deviation.

	Drop 1	Drop 2	Drop 3	Drop 4	Average		Drop 1	Drop 2	Drop 3	Drop 4	Average
1	37.4	39.3	42.5	45.4	41.0±2.7	10	43.6	45.6	43.7	46.2	44.3±1.1
	39.9	39.3	39.8	44.1			43.1	45.1	43.1	43.9	
2	44.3	39.5	41.3	41.3	42.4±1.4	11	40.5	45.3	49.8	42.9	45.0±1.8
	44.5	43.5	43.3	41.7			47.7	44.5	45.4	44.1	
3	44.5	48.9	50.1	50.1	50.1±1.1	12	44.2	37.5	39.5	50.1	42.1±2.9
	52.5	52.3	52.2	50.0			37.3	41.1	44.7	42.0	
4	42.9	47.1	41.3	43.1	43.8±2.4	13	36.5	36.9	41.0	44.8	38.9±2.6
	45.9	45.9	40.0	44.2			35.5	37.7	41.3	37.3	
5	48.8	39.9	41.4	45.0	43.5±2.9	14	40.0	38.8	31.4	47.0	39.3±5.9
	44.2	39.8	44.0	44.8			41.9	37.8	34.0	47.0	
6	35.9	40.8	44.1	45.1	42.6±3.9	15	43.1	40.2	39.1	39.1	39.9±1.2
	38.9	42.7	45.6	47.3			40.1	39.8	39.8	38.3	
7	44.9	50.1	47.3	45.3	46.5±2.6	16	42.9	40.1	40.1	34.2	39.2±1.8
	48.3	49.2	45.7	41.2			36.3	39.3	41.7	39.2	
8	42.4	41.0	42.8	37.9	40.9±1.3	17	46.3	42.6	33.1	39.9	40.8±5.6
	41.6	41.0	40.0	40.2			49.3	42.6	40.1	32.1	
9	45.4	41.3	42.6	48.8	43.2±1.8	18	44.0	40.0	45.9	48.0	43.5±2.1
	39.2	41.2	46.3	41.1			38.4	45.5	41.8	44.2	

Table S3. WCA values of a set of 8 surfaces coated with pDA by 8h of polymerisation time, kept under air and measured for WCA 24h, 48h, 72h, or 144h after preparation.

After 24 h (air exposure)

	Drop 1	Drop 2	Drop 3	Drop 4	Average of (Av.L-R) ±S.D.	Mean WCA
1	66.6 67.3	66.0 69.1	69.9 69.8	69.5 69.5	68.5±1.4	69.0±0.7
2	68.4 68.3	69.1 68.8	70.5 69.9	71.2 70.0	69.5±1.1	

After 48 h (air exposure)

	Drop 1	Drop 2	Drop 3	Drop 4	Average of (Av.L-R) ±S.D.	Mean WCA
1	65.2 63.2	69.8 69.8	69.1 68.1	65.0 63.0	66.7±3.0	67.5±1.1
2	70.2 71.2	67.3 69.2	67.2 65.4	68.1 67.9	68.3±1.8	

After 72 h (air exposure)

	Drop 1	Drop 2	Drop 3	Drop 4	Average of (Av.L-R) ±S.D.	Mean WCA
1	62.2 63.8	65.3 63.3	63.1 65.1	61.6 65.4	63.7±0.6	63.0±1.0
2	61.1 62.0	62.9 63.3	63.1 60.9	63.1 62.1	62.3±0.7	

After 6 days (air exposure)

	Drop 1	Drop 2	Drop 3	Drop 4	Average of (Av.L-R) ±S.D.	Mean WCA
1	62.5 66.8	66.1 68.1	68.7 67.6	61.3 62.3	65.4±2.8	64.1±1.8
2	61.9 62.1	64.1 65.2	64.1 63.9	61.3 60.2	62.9±1.8	

Table S4. WCA values of a set of 8 surfaces coated with pDA by 8h of polymerisation time, measured for WCA 24h, 48h, 72h, or 120h after storage in water.

After 24 h (in H_2O)						
	Drop 1	Drop 2	Drop 3	Drop 4	Average of (Av.L-R) ±S.D.	Mean WCA
1	62.8 63.8	67.8 69.8	60.8 63.8	63.5 64.8	64.6±2.9	56.6±8.1
2	48.4 45.8	49.2 46.7	47.9 46.9	51.0 53.0	48.6±2.3	
3	60.2 57.2	65.5 63.3	65.2 65.3	55.2 55.3	60.9±4.8	
4	64.8 61.9	64.4 64.5	60.4 64.8	60.7 61.8	62.9±1.3	
5	69.4 67.2	66.4 66.1	63.4 65.2	69.8 70.2	67.2±2.5	
6	48.3 52.0	56.1 58.0	47.7 44.7	53.1 54.0	51.7±4.6	
7	45.1 43.3	57.1 57.0	48.2 52.0	53.2 48.2	50.5±5.3	
8	43.7 49.1	41.4 45.0	48.2 50.1	45.5 47.8	46.4±2.4	

After 48 h (in H_2O)						
	Drop 1	Drop 2	Drop 3	Drop 4	Average of (Av.L-R) ±S.D.	Mean WCA
1	47.6 46.9	48.9 48.8	47.2 47.9	50.1 53.5	48.9±2.1	55.9±9.7
2	47.4 55.4	52.1 55.7	52.3 49.9	47.0 53.0	51.6±1.6	
3	45.4 50.4	46.9 47.2	51.3 53.3	46.2 45.2	48.2±2.9	
4	67.9 66.7	78.1 76.9	65.6 67.2	75.7 74.4	71.6±5.5	
5	48.4 47.8	54.4 55.3	49.5 52.6	48.8 49.2	50.8±3.0	
6	61.0 61.8	54.0 52.0	55.0 49.9	44.7 44.9	52.9±6.8	
7	47.5 52.9	48.8 57.1	61.1 49.7	48.9 48.8	51.9±2.9	
8	80.1 77.7	66.1 71.6	72.0 70.8	73.0 73.1	71.3±4.3	

After 72 h (in H_2O)						
	Drop 1	Drop 2	Drop 3	Drop 4	Average of (Av.L-R) ±S.D.	Mean WCA
1	69.7 53.7	70.2 64.3	59.3 57.2	56.9 68.3	62.5±3.7	57.6±7.5
2	55.4 49.2	58.1 60.1	67.2 61.3	70.1 72.6	61.8±8.1	
3	57.1 49.9	57.3 60.0	61.0 58.4	71.1 75.4	61.3±8.4	
4	64.8 60.3	46.6 51.3	49.7 51.0	50.1 59.7	54.2±6.1	
5	70.1 71.1	69.3 65.7	65.6 65.5	68.8 70.9	68.4±2.3	
6	51.3 50.5	58.1 51.2	63.5 64.3	67.2 63.0	58.6±7.0	
7	44.1 42.3	39.7 45.5	54.1 50.0	43.1 39.8	44.8±4.9	
8	43.2 49.1	51.2 57.0	54.2 47.1	41.3 49.9	49.1±4.0	

After 120 h (in H_2O)						
	Drop 1	Drop 2	Drop 3	Drop 4	Average of (Av.L-R) ±S.D.	Mean WCA
1	88.6 90.9	84.9 85.3	82.1 83.3	73.8 75.0	83.0±6.4	68.1±12.2
2	63.2 62.7	59.3 60.1	51.8 48.7	55.0 55.5	57.0±5.5	
3	49.5 44.5	58.3 57.4	56.6 57.2	57.1 53.4	54.3±5.0	
4	79.2 89.2	89.0 88.6	87.0 86.4	82.8 81.9	85.5±2.8	
5	57.0 56.6	77.4 83.0	79.0 81.2	62.0 66.1	70.3±11.8	
6	65.1 63.9	79.0 78.0	85.0 85.8	69.3 72.5	74.8±9.1	
7	57.8 56.0	55.0 58.3	59.1 57.3	55.3 52.4	56.4±1.8	
8	49.8 52.3	63.5 69.1	68.1 67.5	71.2 70.0	63.9±8.8	

Table S5. WCA values of a set of 2 surfaces coated with pDA by 8h of polymerisation time, measured 72h after air exposure, or air exposure and subsequent rehydration in deionised water (3 hours) and gentle drying under N_2 flow.

After 72 h (air exposure)						
	Drop 1	Drop 2	Drop 3	Drop 4	Average of (Av.L-R) ±S.D.	Mean WCA
1	62.4 63.4	60.9 63.0	65.3 65.3	65.2 65.2	63.8±1.7	64.0±1.3
2	64.7 65.1	64.9 65.0	64.6 61.7	63.2 63.3	64.1±1.0	

After 72 h (air exposure), rehydration (3h) and drying under N_2 flow						
	Drop 1	Drop 2	Drop 3	Drop 4	Average of (Av.L-R) ±S.D.	Mean WCA
1	42.1 46.1	44.2 44.8	44.2 46.7	45.8 46.2	45.0±0.9	45.1±1.5
2	45.2 45.8	44.9 41.9	42.8 44.7	47.8 48.3	45.2±2.1	

Table S6. WCA values of a set of 4 surfaces coated with pCDA by 8h of polymerisation time, and after thermal treatment of 80 °C inside an over under air atmosphere for 3 minutes.

t=8h						
	Drop 1	Drop 2	Drop 3	Drop 4	Average of (Av.L-R) ±S.D.	Mean WCA
1	55.4 56.4	50.3 55.4	56.3 54.9	52.8 54.5	58.1±1.1	57.8±0.5
2	59.6 57.8	59.9 59.8	55.0 53.1	57.8 53.5	57.1±0.6	
3	58.3 57.0	60.3 61.4	58.6 57.1	55.0 58.3	58.1±1.1	
4	57.9 58.1	58.4 57.4	56.3 58.0	57.8 59.1	57.8±0.5	

t=8h (T=80° for 3')						
	Drop 1	Drop 2	Drop 3	Drop 4	Average of (Av.L-R) ±S.D.	Mean WCA
1	68.9 68.9	67.8 68.9	73.3 72.2	72.4 73.9	70.8±2.5	69.8±1.5
2	69.8 68.9	72.2 72.7	73.1 70.9	70.8 72.1	71.3±1.4	
3	68.4 68.8	69.1 65.9	68.6 69.8	69.0 69.0	68.6±0.8	
4	67.7 67.8	68.1 68.7	67.6 68.9	70.7 70.5	68.8±1.3	

Table S7. WCA values of a set of 2 surfaces coated with pCDA by 8h of polymerisation time, measured 72h after air exposure, or air exposure and subsequent rehydration in deionised water (3 hours) and gentle drying under N_2 flow.

After 72 h (air exposure)						
	Drop 1	Drop 2	Drop 3	Drop 4	Average of (Av.L-R) ±S.D.	Mean WCA
1	76.4 73.4	75.8 76.3	76.0 75.1	74.9 71.3	74.9±1.3	73.8±1.1
2	71.5 73.9	72.7 74.7	72.5 71.2	72.0 72.1	72.6±0.8	

After 72 h (air exposure), rehydration (3h) and drying with N_2						
	Drop 1	Drop 2	Drop 3	Drop 4	Average of (Av.L-R) ±S.D.	Mean WCA
1	51.4 52.1	54.0 52.0	52.0 48.8	48.2 50.9	51.2±1.5	51.3±2.0
2	53.7 48.8	49.2 46.8	53.2 52.3	54.5 52.9	51.4±2.5	

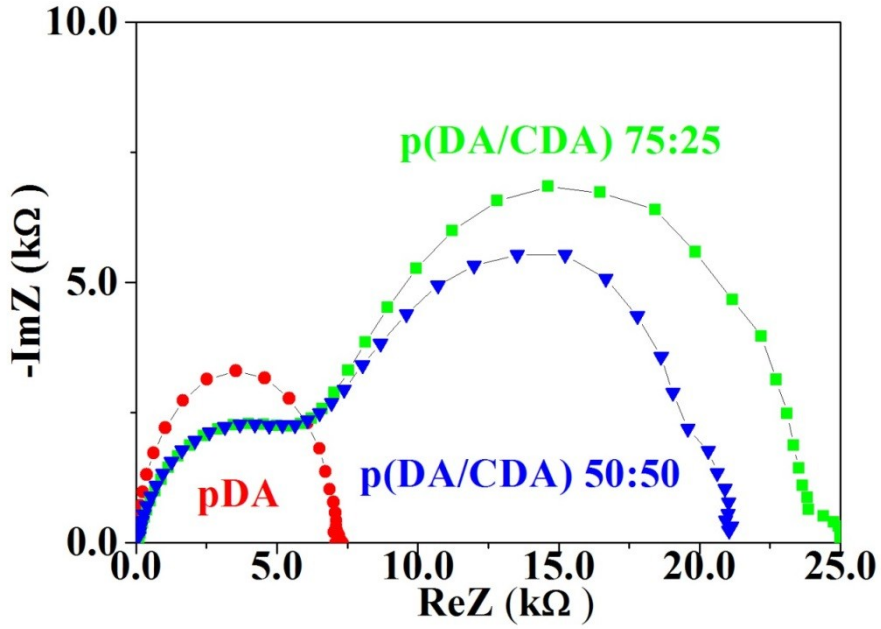


Figure SI-15. Nyquist plot as resulting from impedance data on mixed p(DA/CDA) –based MIS device. It is noteworthy to observe the presence of a second semicircle representing the loosing of the electron blocking behavior and occurrence in the copolymer of charge exchange reaction