Supporting Information

An Environmental Friendly Fluorinated Oligoamide for Producing Non-Wetting Coatings with High Performance on Porous Surfaces

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Materials characterization

Ethyl ester of PFPE-acid (PFPE-ester)

FT-IR (neat): 2994 (w), 1793 (s), 1381 (m), 1308 (m), 1238 (vs), 1192 (s), 1138 (vs), 983 (s), 892 (m), 745 (m) (cm^{-1}).

^{1}H-NMR (neat): δ 1.42 (t, J_{H-H}=7.13 Hz, 3H, $\underline{CH_3}$-CH$_2$-O-CO-), δ 4.45 (q, J_{H-H}=7.12 Hz, 2H, CH$_3$-$\underline{CH_2}$-O-CO-).

^{13}C-NMR (neat): δ 11.9 ($\underline{CH_3}$-CH$_2$-O-CO-), δ 63.4 (CH$_3$-$\underline{CH_2}$-O-CO-), δ from 113.2 to 128.2 (Rf group = CF$_3$-O-(CF$_2$-CF(CF$_3$)-O)$_m$-(CF$_2$O)$_n$-CF$_2$), δ 157.1 (-$\underline{C}$O-).

^{19}F-NMR (neat): δ -57.7 ($\underline{CF_3}$-O-), δ -76.8 (-O-$\underline{CF_2}$-CO-OEt), δ -81.8 (-O$\underline{CF_2}$-CF($\underline{CF_3}$)-O-), δ from -86.4 to -88.2 ($\underline{CF_3}$-$\underline{CF}$OR(OCF$_3$), ($\underline{CF_3}$-$\underline{CF_2}$-O), δ -146.3 (-O-CF$_2$-$\underline{CF}$(CF$_3$)-O).

Oligo(ethylenesuccinamide) (SC2)

FT-IR (neat): 3295 (vs), 3084-2937 (m), 1636 (vs), 1561 (s), 1448-1419 (m), 1240 (m), 729 (m) (cm^{-1}).

^{1}H-NMR (D$_2$O): δ 2.54 and 2.56 (s, 4H, -CO-($\underline{CH_2}$)$_2$-CO-) , 2.75 (t, J_{H-H} = 6.16 Hz, 8H, -CO-NH-CH$_2$-$\underline{CH_2}$-NH$_2$), 3.27 (t, J_{H-H} = 6.16 Hz, 8H, -CO-NH-$\underline{CH_2}$-CH$_2$-NH$_2$), 3.31 (s, 4H, -CO-NH-($\underline{CH_2}$)$_2$-NH-CO-).

^{13}C-NMR (D$_2$O): δ 31.0 (–CO-$\underline{(CH_2)_2}$-CO–), δ 37.0 (–CO-NH-$\underline{(CH_2)_2}$-NH-CO–),δ 39.7 (–CO-NH-CH$_2$-$\underline{CH_2}$-NH$_2$), δ 41.4 (–CO-NH-$\underline{CH_2}$-CH$_2$-NH$_2$), δ 174.9 (–$\underline{C}$O–).

Oligo(ethylenesuccinamide) with pendant perfluoropolyether segments (SC2-PFPE)

FT-IR (neat): 3298 (s), 3087-2940 (w), 1705 (m), 1638 (s), 1556 (m), 1448-1422 (w), from 1400 to 900 (vs) (cm^{-1}).

^{1}H-NMR (CD$_3$OD:D$_2$O, 95:5 w/w): δ 2.47 (m, 8H, –CO-$\underline{(CH_2)_2}$-CO–), δ 3.03 (m, 4H, –CO-NH-$\underline{(CH_2)_2}$-NH-CO–), δ 3.38 (m, 4H, –CH$_2$-$\underline{CH_2}$-NH-CO-Rf), δ 3.45 (m, 4H, –$\underline{CH_2}$-CH$_2$-NH-CO-Rf).

^{19}F-NMR (CD$_3$OD:D$_2$O, 95:5 w/w): δ -57.0 ($\underline{CF_3}$-O–), δ -76.8 and -77.3 (–O-$\underline{CF_2}$-CO-NH-R), δ -81.4 (–O-$\underline{CF_2}$-CF($\underline{CF_3}$)-O–), δ from -85.9 to -87.6 ($\underline{CF_3}$-$\underline{CF}$OR(OCF$_3$), $\underline{CF_3}$-$\underline{CF_2}$O–), δ -146.0 (–O-CF$_2$-$\underline{CF}$(CF$_3$)-O–).

Vapor Diffusivity in Lecce stone

The water vapor effective diffusion coefficient (D_{eff}) in Lecce stone was measured following the UNI-EN 15803-2010 method,[1] also applied for the determination of the Residual Diffusivity (*RD*).   In fact, in these conditions, the

diffusive flux of vapor through the porous medium can be calculated in accordance to the Fick's Law,[2] and D_{eff} is related to the molecular diffusion coefficient of vapor, the porosity and tortuosity of the porous material. The found value for vapor D_{eff} in Lecce stone is $1.8 \cdot 10^{-2}$ cm^2/s.[3]

Computation of the pore space volume reduction

The reduction of vapor diffusivity in a porous medium coated with a hydrophobic product is usually due to the filling of the pore spaces from the mass of product. Therefore, knowing the mass of product applied and its density, the reduction of the volume of the pore space in fixed stone thicknesses can be computed when a simple model (piston like) for the ingress of the product is assumed. In this specific case, considering that the mass of product applied on a 5x5 cm^2 surface is $\leq$ 40 mg (density $>$ 0.8 g/cm^3) and the porosity of stone is about 40%, the calculated reduction of the volume of the porous space is less than 5% for a penetration depth of the compound of 1 mm, and less than 10% for a depth of 0.5 mm (Table S1). The very low volume reduction is in accordance with a high Residual Diffusivity.

Table S1. **Calculated reduction of the volume of the pore space for different stone thicknesses due to the presence of the hydrophobic product**

Penetration depth of the product (mm)	Volume reduction (%)
0.1	≤50
0.5	≤10
1	≤5
20	< 0.3

Table S2. **Water mass per dry mass (%) absorbed by the samples of Figures 1 and 3 before any coating.**

Stone sample #	Product	$(\Delta m_w(30\ \text{min})/m_0)$ $\times 100\ (\%)$	$(\Delta m_w(1\ \text{h})/m_0)$ $\times 100\ (\%)$
APL_1	SC2-PFPEsol	7.490	9.980
APL_2	SC2-PFPEsusp	6.266	9.023
APL_6	N215	5.826	8.387
APL_16	NT	5.253	8.309

$\Delta m_w(30\ \text{min})$ = amount of water absorbed at 30 minutes; $\Delta m_w(1\ \text{h})$ = amount of water absorbed at 1 hour; m_0 = dry mass of the sample.

Table S3. Ageing Effect (AE) on Lecce stone samples coated with SC2-PFPE and N215 due to different artificial ageing stresses.

Sample	Treatment	$WIE_{t=0}$ (%)		Wet-dry cycles	$WIE_{3\ years}$ (%)		AE (%)	
		30 min	1 h		30 min	1 h	30 min	1 h
APL_1	SC2-PFPEsol	95.2 ± 0.7	93.3 ± 0.9	SA	64.0 ± 0.9	57.0 ± 0.9	31	36
APL_4		90.9 ± 2.2	88.3 ± 1.9	WA	89.3 ± 2.2	85.1 ± 3.3	2	3
APL_2	SC2-PFPEsusp	96.9 ± 0.1	96.5 ± 0.2	SA	51.7 ± 1.7	45.6 ± 0.9	45	51
APL_8		97.0 ± 0.2	96.5 ± 0.3	WA	96.3 ± 0.6	95.3 ± 0.7	1	1
APL_6	N215	70.7 ± 6.3	64.3 ± 4.8	SA	25.2 ± 9.9	20.0 ± 9.7	45	44
APL_14		53.5 ± 4.6	48.1 ± 4.2	WA	40.1 ± 1.5	35.9 ± 2.6	13	12
APL_16	NT	0.0 ± 4.7	-0.8 ± 2.7	SA	-82.1 ± 2.8	-46.8 ± 1.3	82	46
APL_17		7.2 ± 3.2	-2.5 ± 1.6	WA	-31.8 ± 1.9	-6.4 ± 0.9	39	4
APL_26		13.5 ± 4.5	10.1 ± 4.0	WA	-27.5 ± 3.5	-11.2 ± 1.2	41	21

$WIE_{t=0}$ = WIE at time zero (after treatment and before ageing); $WIE_{3\ years}$ = WIE after 3 years from the beginning of the experiment; AE = aging effect; WA = weak ageing = the samples underwent 3 tests (3 wet dry-cycles) of water capillary absorption (wca); SA = strong ageing = WA+ the samples were water saturated by capillarity during 7 days (2 wet-dry cycles) for MRI analyses, then they underwent two saturations under vacuum (2 wet-dry cycles) and further 4 tests (4 wet-dry cycles) of wca having a typical duration of 1 hour; after vacuum saturation the specimens were left wet for 5 days before drying at room conditions. The wca tests carried out before the treatment are not considered because all the samples underwent the same number of absorption tests.
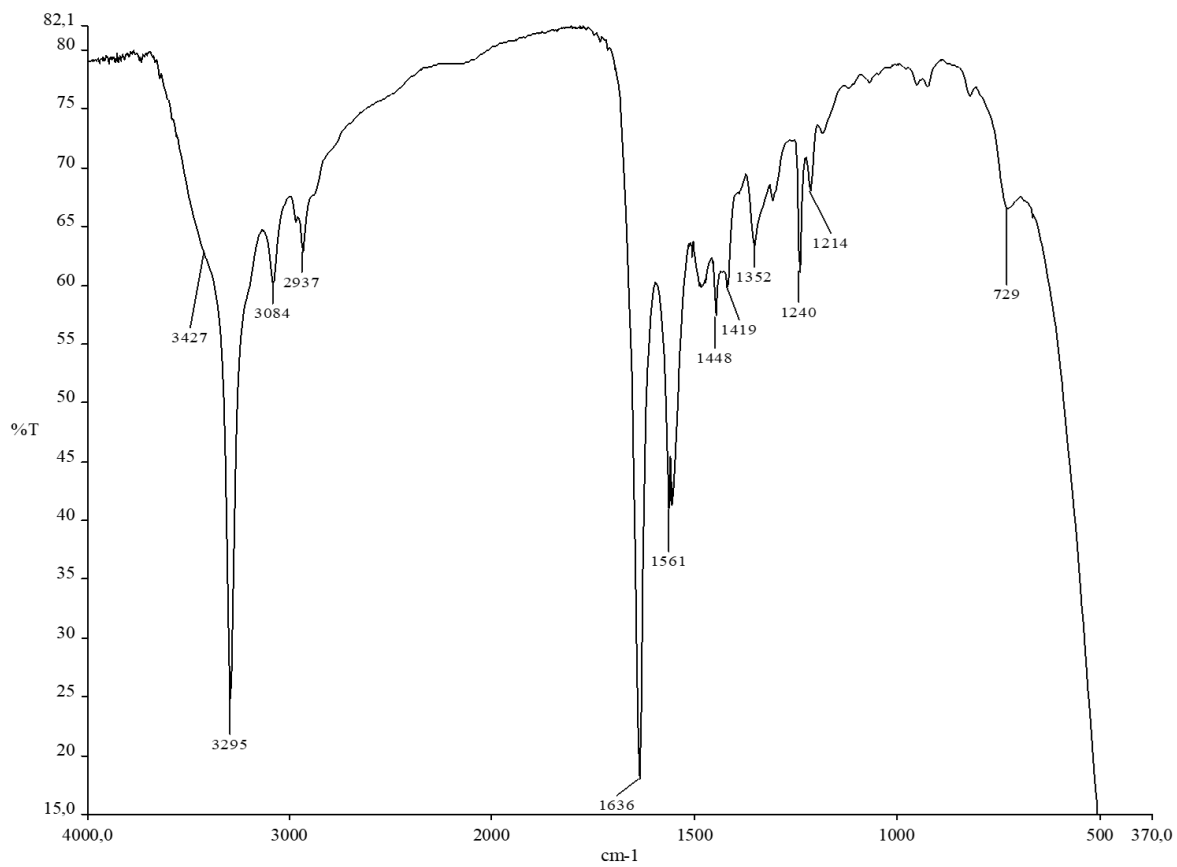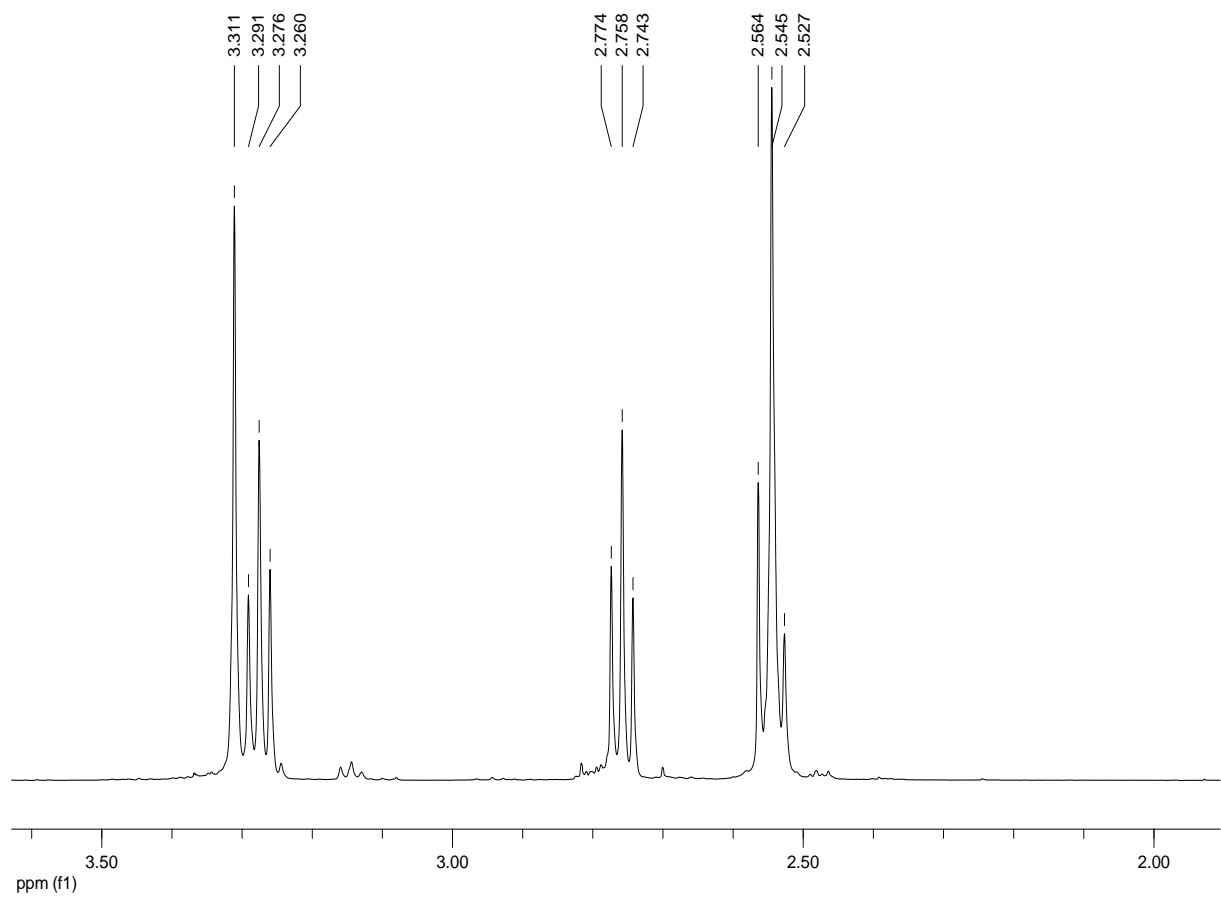
Figure S1. FT-IR spectrum of SC2.
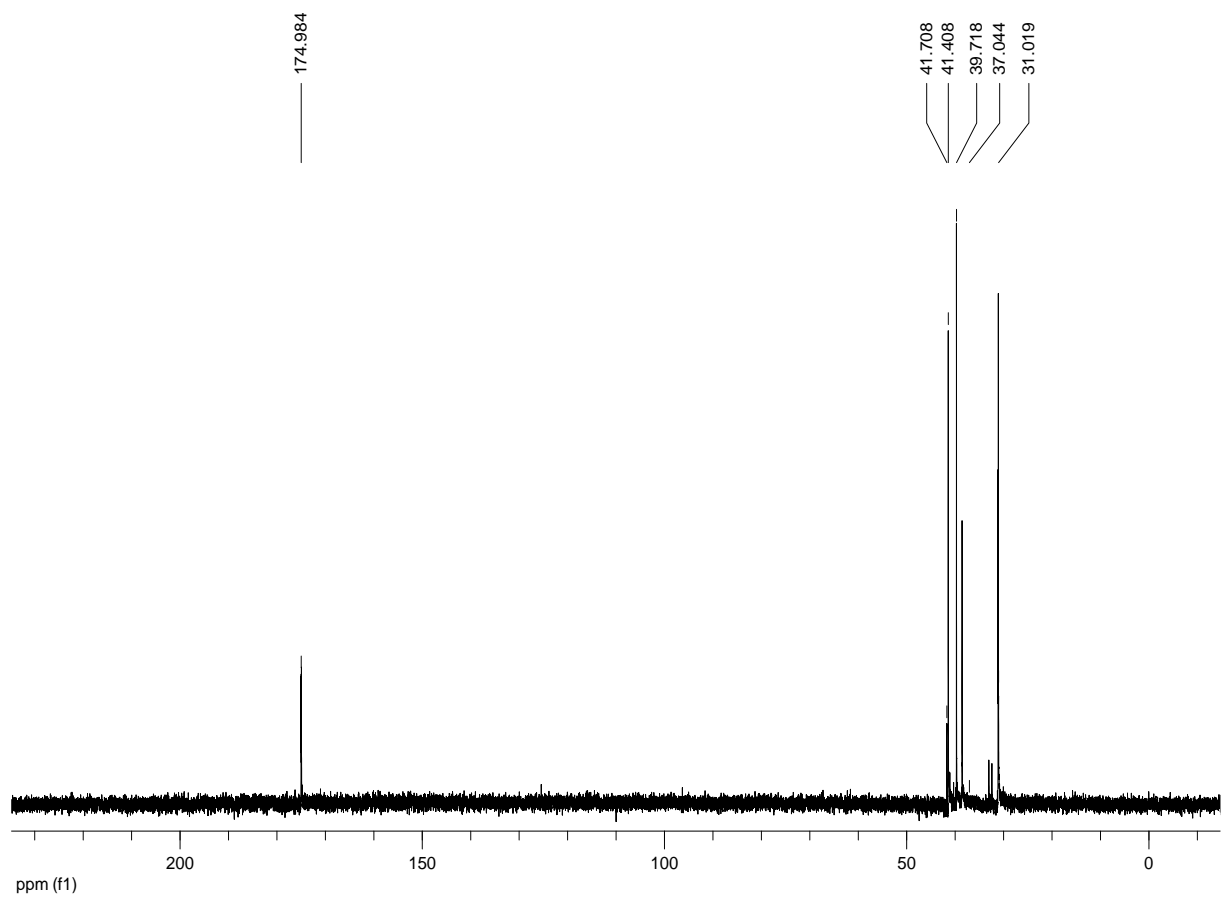
Figure S2. ^{1}H-NMR spectrum of SC2 in D$_2$O.

Figure S3. ^{13}C-NMR spectrum of SC2 in D$_2$O.
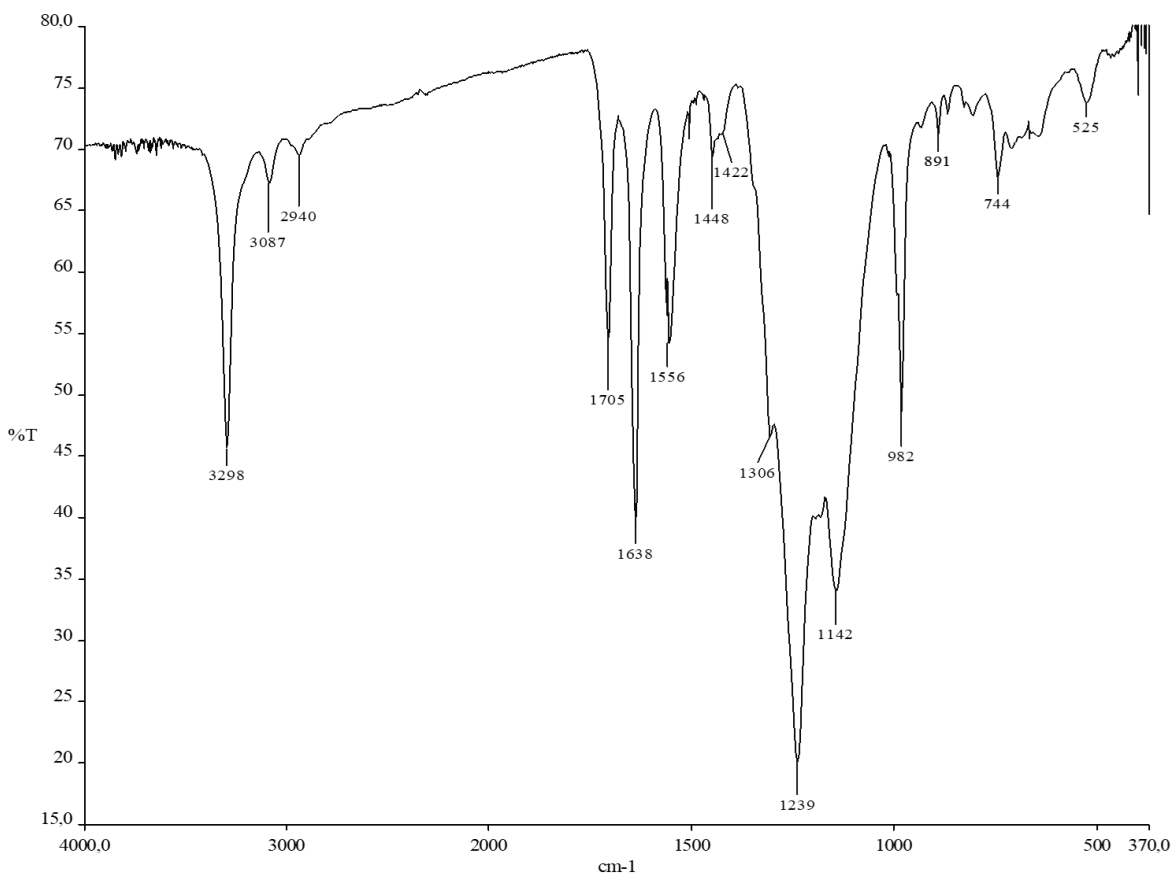
Figure S4. FT-IR spectrum of SC2-PFPE.
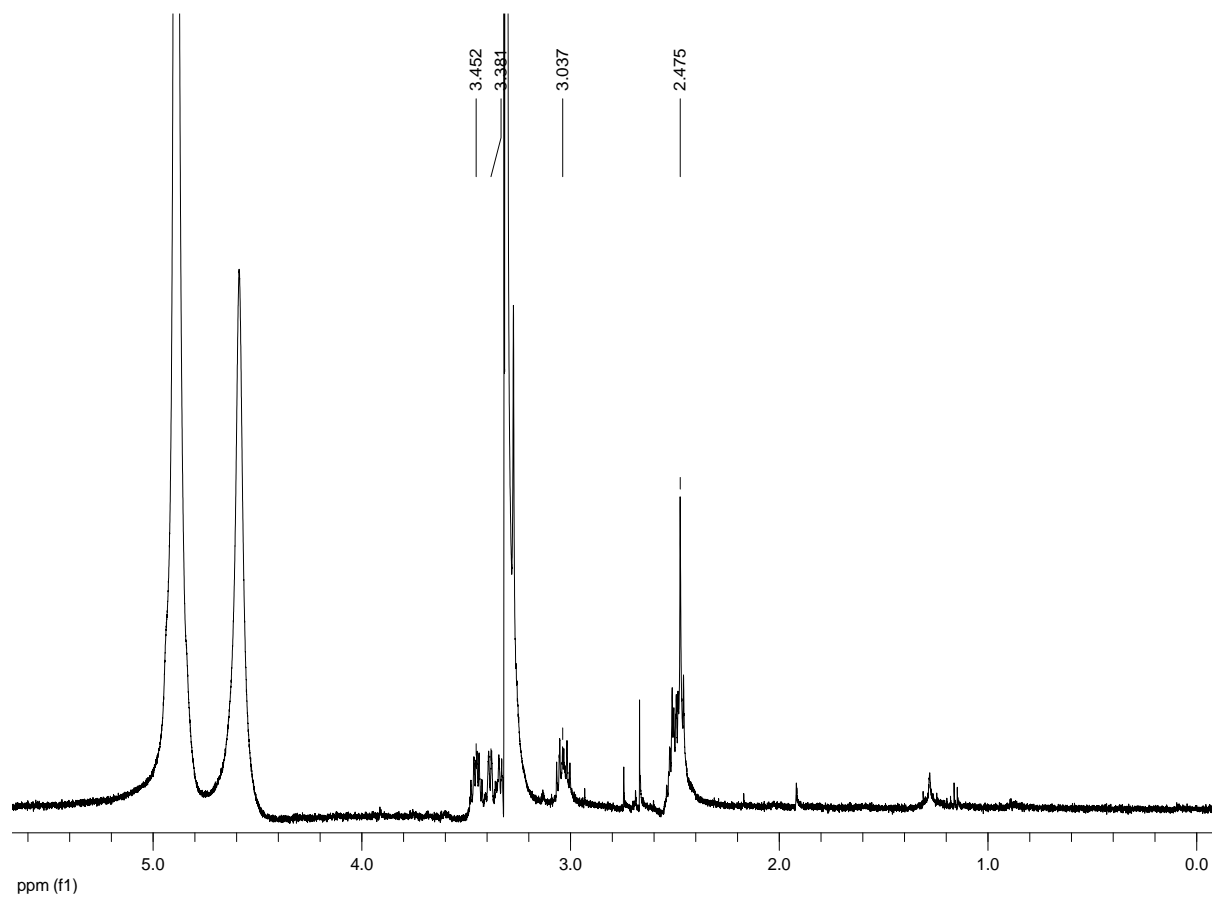
Figure S5. ^{1}H-NMR spectrum of SC2-PFPE in CD$_3$OD/D$_2$O (95/5 w/w).
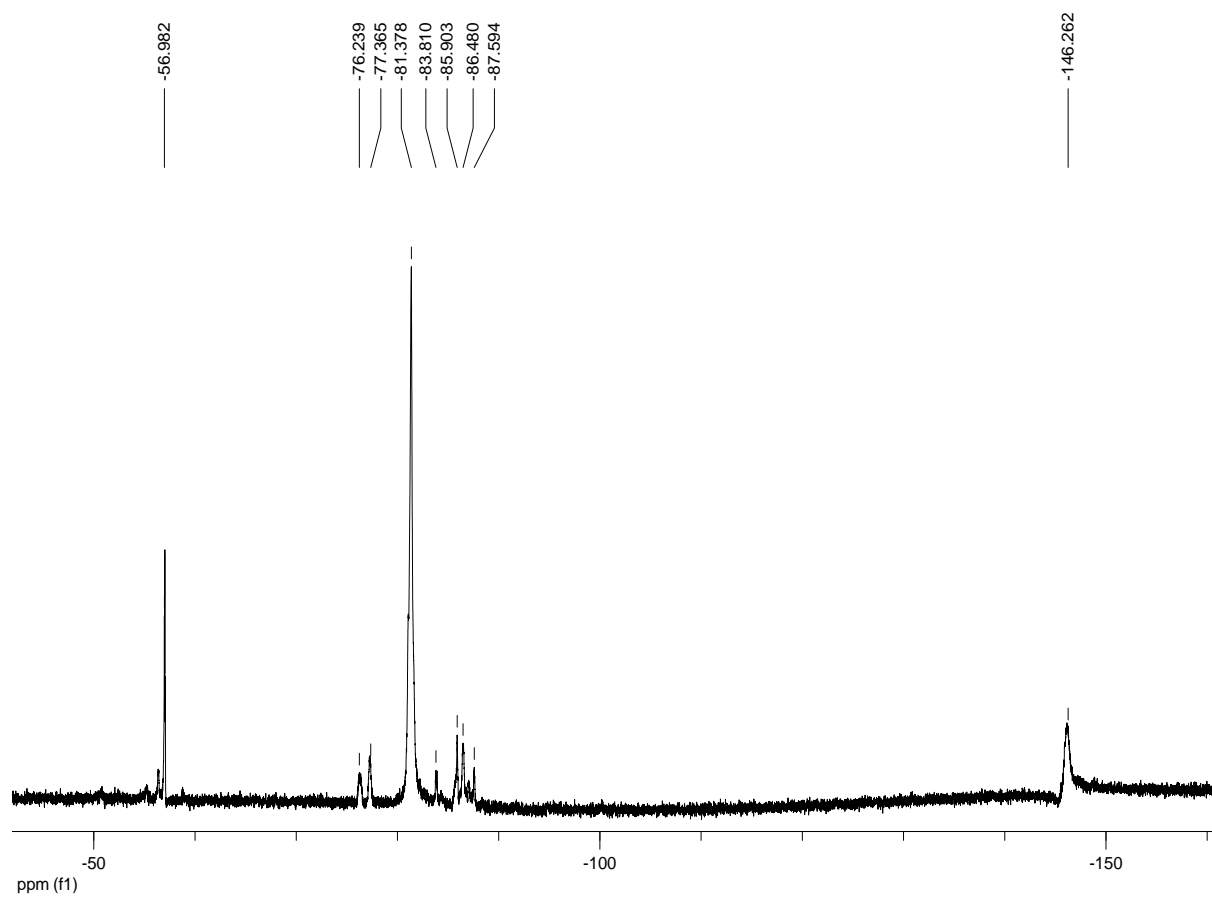
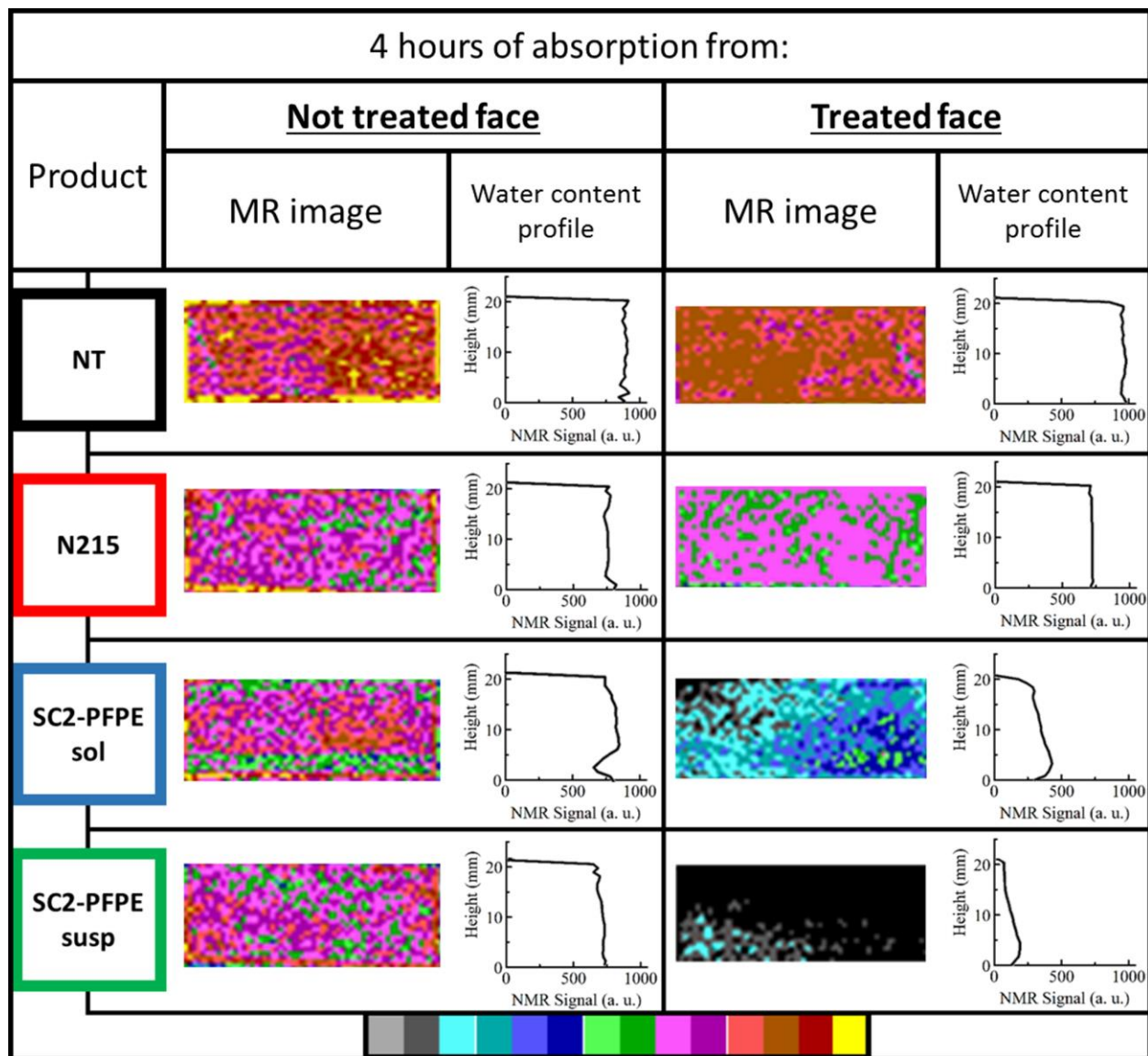**Figure S6**. ^{19}F-NMR spectrum of SC2-PFPE in CD$_3$OD/D$_2$O (95/5 w/w).

Figure S7. MRI images of the internal slices with corresponding signal profiles (obtained on the entire sample) of the same Lecce stone samples reported in Figures 2 and 4, after 4 hours of water capillary absorption from the untreated (left) and the treated (right) face.
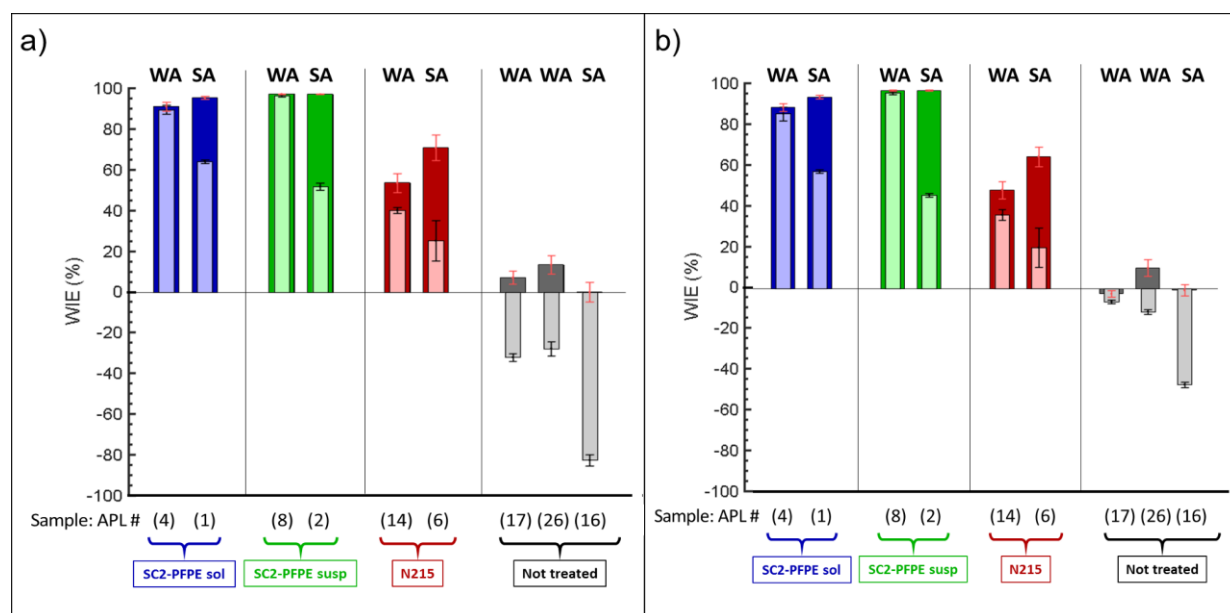
Figure S8. Water Inhibition Efficacy (*WIE*) of SC2-PFPE and N215 after different ageing conditions and at different time of water capillary absorption (wca): a) 30 minutes; b) 60 minutes. Dark colors for *WIE* measured just after treatment and light colors for *WIE* measured at 3 years after treatment. WA = Weak Ageing corresponding to 3 wet-dry cycles with wca up to 1 hour for each cycle. SA = Strong Ageing corresponding to 1 WA plus 2 wet-dry cycles with wca up to 7 days for MRI analysis followed by 2 wet-dry cycles with water saturation under vacuum and 4 wet-dry cycles with wca up to 1 hour. After vacuum saturation the specimens were left wet for 5 days before drying them. After the last wet-dry cycle, all the samples were conditioned in the dark under laboratory conditions for about 2 years.

Additional References

(1) UNI-EN 15803-2010, Conservation of Cultural Property – Test Methods. Determination of Water Vapor Permeability, 2010.

(2) Piacenti, F.; Carbonell, R. G.; Camaiti, M.; Henon, F. E.; Luppichini, E. Protective Materials for Stone - Effects on Stone Permeability and Gas Transport. In *Proceedings of International Colloquium on "Methods of Evaluating Products for the Conservation of Porous Building Materials in Monuments"* Rome 19-21 June 1995, pp 389-402.

(3) Camaiti, M. Personal communication.