SUPPORTING INFORMATION

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Innovative cavitand-based sol-gel coatings for the environmental monitoring of benzene and chlorobenzenes *via* solid-phase microextraction

Analytical and spectral characterizations of the developed coating like ^{1}H-NMR, ESI, ^{29}Si and ^{13}C solid state NMR spectra and scanning electron micrographies are provided in this section in order to better support the characterization of the developed materials. A detailed description of the GC-MS experimental conditions used in this work are provided in Table S-1.

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Table S-1. GC-MS analysis	
BTEX	
GC oven temperature program	40°C for 5 min, 10°C min^{-1} to 170°C, 170°C for 2 min.
Time scheduled selected-ion monitoring[a]	Delay time: 1 min hexane: *m/z* 43, 57 and 86 from 1.0 to 4.3 min; heptane and cyclohexane: *m/z* 41, 56, 71, 84 and 100 from 4.3 to 5.1 min; octane: *m/z* 43, 85 and 114 from 5.1 to 6.0 min; nonane: *m/z* 43, 57 and 99 from 6.0 to 7.1 min; benzene: *m/z* 77 and 78 from 7.1 to 9.0 min; toluene: *m/z* 91 and 92 for from 9.0 to 11.50 min; ethylbenzene, *m*-, *p*-xylene and *p*-xylene-d_{10}: *m/z* 91, 98, 105, 106 and 116 from 11.50 to 15.0 min *o*-xylene: *m/z* 91, 105 and 106 from 15.0 to 20.0 min. Dwell time: 100 ms
Chlorobenzenes	
GC oven temperature program	65°C, 10°C min^{-1} to 200°C
Time scheduled selected-ion monitoring[a]	Delay time: 1min benzene and toluene: *m/z* 77, 78, 91 and 92 from 1 to 2.5 min; chlorobenzene: *m/z* 77, 112 and 114 from 2.5 to 3.1 min; 2-chlorotoluene: *m/z* 91 and 126 from 3.1 to 4.3 min; 1,2-dichlorobenzene: *m/z* 111, 146 and 148 from 4.3 to 5.4 min; for 1,2,4-trichlorobenzene: *m/z* 145, 180 and 182 from 5.4 to 13.5 min. Dwell time: 100 ms

[a]For all the analyses, the corresponding ion ratios were used to confirm the identification of the analytes.

Table S-2. ^{1}H-NMR and ESI-MS characterization of Cavitands 1-3		
	^{1}H-NMR (300 MHz, $CDCl_3$):	**ESI-MS**
Cavitand 1	δ= 8.16 (s, 4H, Ar*H*), 7.78 (m, 8H, AA' part of an AA'BB' system), 7.47 (m, 8H, BB' part of an AA'BB' system), 7.21 (s, 4H, Ar*H*), 5.83 (m, 4H, C*H*=CH_2) 5.57 (t, 4H, C*H*Ar_2, J=7.7 Hz), 4.98 (m, 8H, CH=C*H*$_2$), 2.27 (m, 8H, Ar_2CHCH_2), 1.34 (m, 48H, CH_2)	*m/z* (%): 1547 [M+H$^+$, 100].
Cavitand 2 and Cavitand 3	δ= 8.12 (s, 4H, Ar*H*), 7.77 (m, 8H, AA' part of an AA'BB' system), 7.45 (m, 8H, BB' part of an AA'BB' system), 7.18 (s, 4H, Ar*H*), 5.53 (t, 4H, ArC*H*, J=7.7 Hz), 5.41 (bm, 2H, C*H*=CH_2), 3.80 (m, 18H, Si-O-C*H*$_2$), 2.24 (m, 8H, -C*H*$_2$CHAr_2), 1.99 (m, 8H), 1.40 (m, 52H, C*H*$_2$), 1.22 (t, 27H, Si-O-CH_2C*H*$_3$ + 3H, C*H*$_3$)	*m/z* (%): **(3)** 1875 [M+H$^+$, 50], 1898 [M+Na$^+$, 30], **(2)** 2040 [M+H$^+$, 85], 2062 [M+Na$^+$, 50]

Table S-3. LOD values obtained with the QxCav fiber in soil

	LOD ($ngKg^{-1}$)*
	QxCav
Benzene	13.93
Toluene	8.68
Chlorobenzene	2.34
2-Chlorotoluene	2.72
1,2-Dichlorobenzene	0.95
1,2,4-Trichlorobenzene	0.53

*Incubation temperature: 45°C, incubation time: 5 min, stirring: 500 rpm. Extraction temperature: 45°C, extraction time: 20 min, stirring: 250 rpm, soil sample: 3g in 12 ml of water

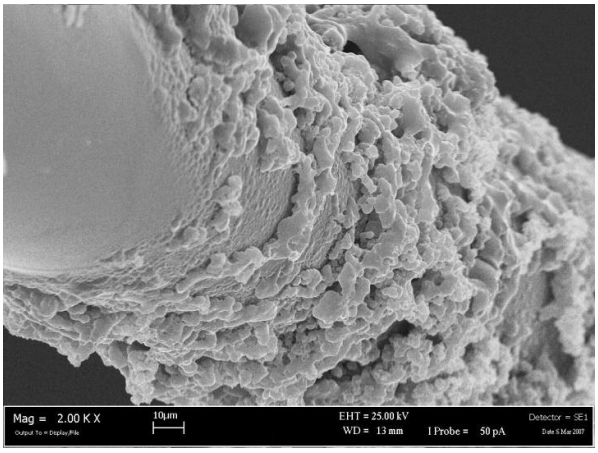

Figure S-1. Scanning electron micrography of QxCav-based coating using acetone as solvent

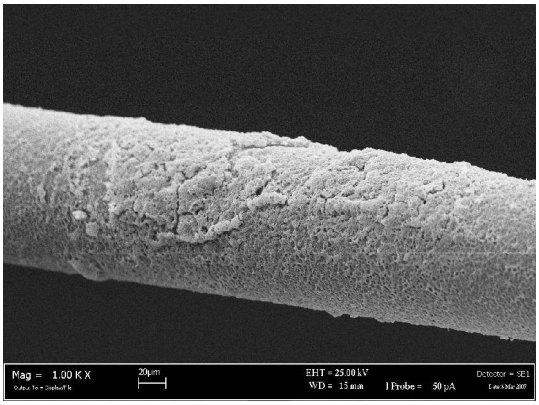

Figure S-2. Scanning electron micrography of QxCav-based coating using CH_2Cl_2 as solvent

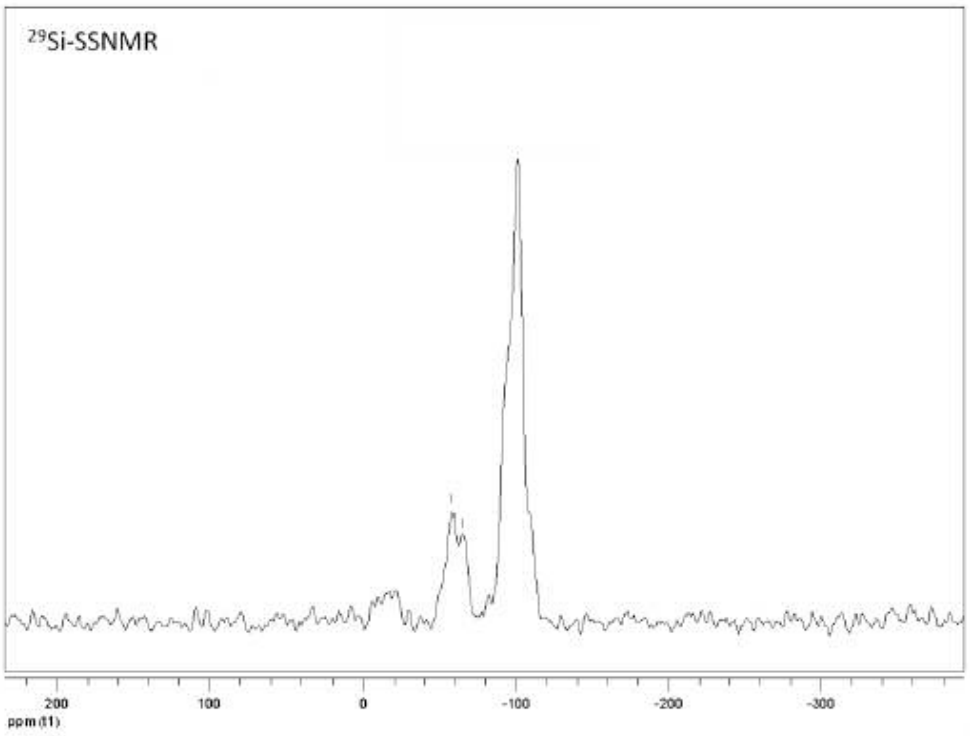

Figure S-3. ^{29}Si solid state NMR of the gel without plasticizer

The ^{29}Si spectrum in cross polarization conditions of the dried gel is constituted by three partially superimposed peaks: Q^2 (≈-92 ppm), assigned to silicon atoms bonded to two hydroxyl groups, Q^3 (≈-101 ppm), assigned to silicon atoms with one hydroxyl group and Q^4 (≈-111 ppm), assigned to silicon atoms without hydroxyl groups. Additional signals appeared in the region between -70 and -55 ppm (T^2 and T^3) belonging to silicon atoms bonded to the organic receptor.

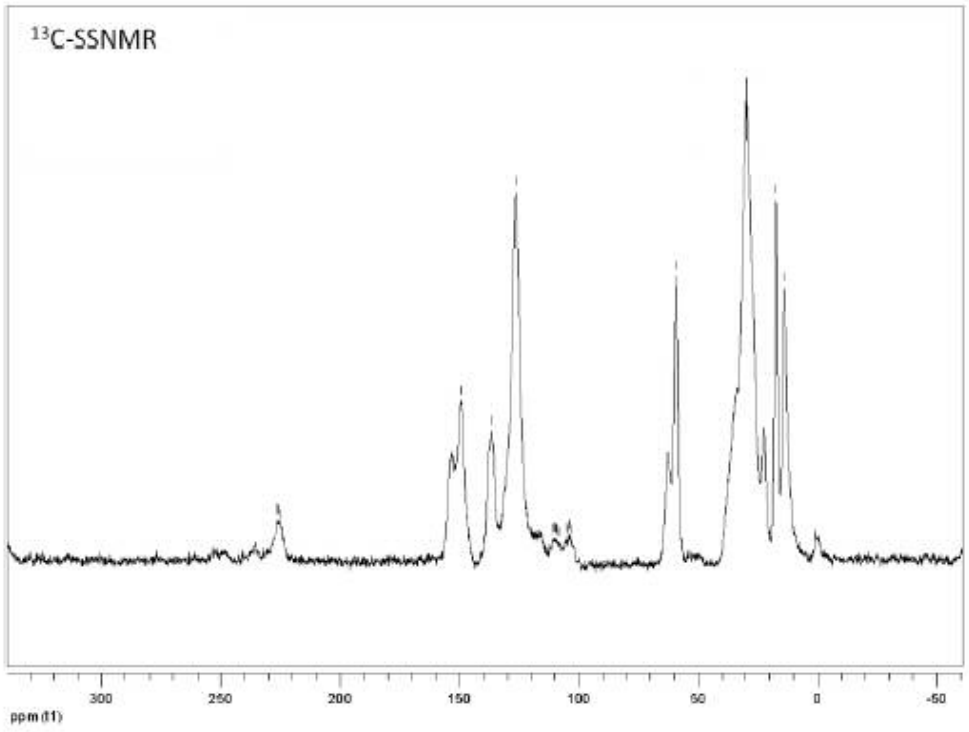

Figure S-4. ^{13}C solid state NMR of the gel without plasticizer

^{13}C-SSNMR: δ = cluster at ~150 ppm (resorcinarene aromatic carbons); multiplet centered at ~ 137 ppm (quinoxaline aromatic carbons); multiplet centered at ~ 125 ppm (resorcinarene aromatic carbons); multiplet centered at ~ 60 ppm (Si-O-CH_2); multiplet at 20-40 ppm (lower rim aliphatic chains carbons); 17.4 ppm (Si-O-CH_2-$\underline{CH_3}$), 12.7 ppm (terminal CH_3 of alkyl chains).