Arylsulfanyl Radical Lifetime in Nanostructured Silica:

Dramatic Effect of the Organic Monolayer Structuration

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Electronic Supplementary Information

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Example of kinetic profile: SBA₃₃-1*

EPR decay curves

SBA₁₇-1:



















































Enter		Line width		ATT
Епиу		$H_{pp1}(G)^{a}$	$H_{pp2}(G)^{b}$	ΔH_{pp}
а	SBA ₁₇ -1	12.85	13.20	0.35
b	SBA33-1	13.97	14.00	0.03
с	SBA71-1	14.17	13.64	-0.53
d	SBA239-1	14.87	14.58	-0.19
e	SBA ₁₇ -1*	13.49	13.07	-0.42
f	SBA33-1*	10.61	12.81	2.20
g	SBA ₇₁ -1*	11.67	12.67	1.00
h	SBA230-1*	11.80	14.22	2.42

Variation of EPR line width for SBA_n-1 and SBA_n-1*

^a Line width at the beginning of the irradiation. ^b Line width at the end of the irradiation (+/- 0.3G).

Spin density calculation



The arylsufanyl radicals, 1' and 2', corresponding to SBA_n-1 and SBA_n-2 have been simulated with the gaussian 09 software. The spin densities have been extracted from simulations performed following the G3(MP2)RAD procedure.¹ This method is adapted to predict reliable thermochemical data for radical species.

The percentage of spin density (Mulliken population based on the HF wave function with the GTMP2Large basis set) on the sulfur atom is 85 % for the urea spacer (SBA_n-1) and 87% for the ether spacer (SBA_n-2).

Dimerization of phenylsulfanyl radicals

The geometry of phenylsulfanyl dimer was optimized, with the gaussian 09 software, at the B3LYP/6-311+G(d,p) level of theory. A scan was also performed around the C-S-S-C torsion. It shows an energy profile with two minima (with the same energy) at +82.5° and -82.5°, a local maximum (5 kcal/mol higher than the minimum) at 180° (i.e. the phenyl rings are parallel but shifted on both sides of the S-S bond), and a global maximum (8 kcal/mol higher than the minimum) at 0° (the phenyl rings are eclipsed, but their planes make an angle of approximately 40°).

¹ Henry, D. J.; Sullivan, M. B.; Radom, L. G3-RAD and G3X-RAD: Modified Gaussian-3 (G3) and Gaussian-3X (G3X) Procedures for Radical Thermochemistry. *J. Chem. Phys.* **2003**, *118*, 4849-4860.



Classical molecular dynamics simulations of grafted silica pores

Molecular dynamics simulations were performed with the DLPOLY_4 software.² All systems were first submitted to a short (100 ps) equilibration run (20 ps in the NVE ensemble, the rest in the NVT ensemble). The NVT production runs were performed during 2 ns for the larger loading (1/11), and 0.5 ns, for the other loadings (represented by 10 different samples). The temperature was kept constant at 300K with a Nosé-Hoover³ type thermostat with a relaxation time of 0.5 ps. The time step was 1fs, except for passivated systems were 0.25 fs was used.

Long range interactions were cut-off after 14 angströms. Electrostatics interactions were handled with Ewald summations (precision 1e-6). Trajectory snapshots and system properties were recorded every ps for future analysis.

The pores were created according to the Brodka approach.⁴ The "inorganic builder" of the program VMD⁵ was used to create an amorphous silica box. This box was replicated to reach a size of 114.61318 Å on the x and y direction, while the original size (58.173357 Å) was kept in the z direction. The box was truncated in order to keep only 64 Å in x and y directions. All the atoms within 25 Å of the z axis were removed in order to create a cylindrical pore of 50 Å diameter. All silicon atoms that were bonded to less than 4 oxygens were removed from the

² Todorov, I.T.; Smith, W.; Trachenko, K.; Dove, M.T. DL_POLY_3: New Dimensions in Molecular Dynamics Simulations via Massive Parallelism. *J. Mater. Chem.* **2006**, *16*, 1911–1918.

³ Hoover, W. G. Canonical Dynamics. Equilibrium Phase-Space Distributions. *Phys. Rev. A* **1985**, *31*, 1695–1697.

⁴ Brodka, A.; Zerda, T. W. Properties of Liquid Acetone in Silica Pores: Molecular Dynamics Simulation. *J. Chem. Phys.* **1996**, *104*, 6319–6326.

⁵ Humphrey, W.; Dalke, A.; Schulten, K. VMD - Visual Molecular Dynamics. *J. Mol. Graphics* **1996**, *14*, 33–38.

surface of the pore, as well as the oxygen atoms only linked to these silicon atoms. The groups consisting of one silicon atom bonded to three non-bridging oxygens were also removed. Three hundred aryl sulfanyl radicals (CH₃-CH₂-CH₂-O-C₆H₄-S[•]) were regularly positioned on a flat surface of length equal to the perimeter of the pore and width equal to the depth of the pore. This flat surface was then rolled up to form a cylinder and the coordinates of the atoms were scaled accordingly. The radicals were then introduced inside the silica pore. Each radical was then linked to the closest silicon atom, by removing one hydrogen atom from the tail methyl group and one non-bonded oxygen atom from the silicon atom. In case the same silicon atom was close from two radicals, one radical was pushed toward the next silicon. In case all silicon atoms around one radical were already "occupied" by another radical, this chain was removed. In no case two radicals were linked to the same silicon atom. At the end, 293 arylsulfanyl radical chains were grafted to the silica pore. This produced the 1/11 loading system. As its surface was nearly fully occupied by grafted radicals, it was considered representative of this loading. Therefore, only one sample was created with this loading. To prepare the 1/44 and 1/110 loading systems, 225 and 270 out of the 300 chains were randomly removed respectively from the flat surface before folding it into a cylindrical shape. As previously, the radicals were introduced inside the pore and grafted to the nearest silicon atom. This process was repeated ten times, producing 10 different samples of these loadings, which were simulated (after equilibration) during 0.5 ns each. The results for these loadings are averaged over these ten samples.

In order to passivate the surface of the pore, trimethylsilyl groups were linked to one of the non-bridging oxygen atoms of the Si(OH)₂ groups on the surface.

The wall atoms of silicon and oxygen were kept frozen, but they interacted with the grafted chains through van der Waals and electrostatic interactions.

These classical simulations were repeated with two differents force fields (DREIDING and GAFF) in order to check that our results were independent from the choice of the parameters set.

The partial charges for the bulk silica were taken from the work of Brodka *et al.*⁴: qSi=1.283e, qO=-0.629e. An additional (united) atom type was created for the hydroxyl groups at the surface of silica: On. The partial charge of On (qOn=-0.4415e) was fixed in order to obtain system's neutrality in a non-grafted system composed of 4120 bulk O, 2279 Si and 753 On. In the grafted system, some On are replaced by the tethered radicals. Therefore, in order to insure system's neutrality in the grafted systems, the charge for the grafted Si atoms were

modified ($qSi^*=qSi+qOn-qR$), where qR is the total charge of the radical (where one H has been removed from the terminal methyl).

The partial charges for the radical, simulated with the GAFF force field, were obtained with the RESP procedure.⁶



The partial charges used with DREIDING were obtained through Gasteiger procedure.⁷



charges	DREIDING/Gasteiger	GAFF/RESP
Si	0.868663	0.870463
С	-0.1018	-0.12
Н	0.0272	0.029
С	-0.048	0.07
Н	0.0351	0.014
С	0.0257	0.095
Н	0.0747	0.042
0	-0.3512	-0.346
Car	0.0683	0.24
Car	-0.04950	-0.194
Har	0.08740	0.141
Car	-0.06330	-0.071
Har	0.08520	0.094
Car	0.01170	0.104
S	-0.0527	-0.182

To model the bond stretching, the following form was used: $U_{bond}=1/2k_r(r_{ij}-r_{ij}^0)^2$ with the following parameters:

 ⁶ Wang, J.; Wolf, R. M.; Caldwell, J. W.; Kollman, P. A.; Case, D. A. Development and Testing of a General Amber Force Field. *J. Comput. Chem.* 2004, 25, 1157–1174. Erratum in *J. Comput. Chem.* 2005, 26,114.
⁷ Gasteiger, J.; Marsili, M. Iterative Partial Equalization of Orbital Electronegativity—A Rapid Access to

Atomic Charges. *Tetrahedron* **1980**, *36*, 3219–3228.

	DREIDING ⁸		GAFF ⁹	
bonds	r ⁰ (Å)	k _r (kcal/mol/Å ²)	r ⁰ (Å)	k _r (kcal/mol/Å ²)
C-H	1.09	700	1.092	674.60
Car-H	1.02	700	1.087	688.60
C-C	1.53	700	1.535	606.20
Car-Car	1.39	1050	1.387	956.80
C-0	1.42	700	1.439	603.00
Car-O	1.35	700	1.373	744.80
Car-S	1.73	700	1.787	491.60
C-Si	1.697	700	1.697*	700*

* inexistent in GAFF, copied from DREIDING

To model the angle bending, the following form was used: $U_{angle}=1/2k_{\theta}[\cos(\theta_{ijk})-\cos(\theta_{ijk})]^{2}$ with the following parameters:

	DREIDING ⁸	GAFF ⁹				
angles	θ ⁰ (degrees)	k_{θ} (kcal/mol/rad ²)	θ^0 (degrees)	k_{θ} (kcal/mol/rad ²)		
Si-C-C	109.471	112.53	109.471*	112.53*		
Si-C-H	109.471	112.53	109.471*	112.53*		
C-C-C	109.471	112.53	110.63	126.40		
Н-С-Н	109.471	112.53	108.35	78.80		
H-C-C	109.471	112.53	110.05	92.80		
C-C-O	109.471	112.53	108.42	135.60		
H-C-O	109.471	112.53	108.70	101.80		
C-O-Car	104.51	106.70	117.60	124.80		
O-Car-Car	120.00	133.33	119.20	139.60		
Car-Car-Car	120.00	133.33	119.97	134.40		
H-Car-Car	120.00	133.33	120.01	97.00		
Car-Car-S	120.00	133.33	120.13	123.00		

* inexistent in GAFF, copied from DREIDING

To model the torsions around dihedral angles, the following form is used: $U_{dih} = A[1 + \cos(m\varphi_{ijkl} - \delta)]$ with the following parameters:

	DREIDING ⁸			GAFF ⁹
dihedrals	A (kcal/mol)	m	δ (degree)	A (kcal/mo
Si-C-C-H	0.11111	3	0.0	0.07778
Si-C-C-C	0.11111	3	0.0	0.07778
Н-С-С-Н	0.11111	3	0.0	0.07500
H-C-C-C	0.11111	3	0.0	0.08000

dihedrals	A (kcal/mol)	m	δ (degree)	A (kcal/mol)	m	δ (degree)
Si-C-C-H	0.11111	3	0.0	0.07778	3	0.0
Si-C-C-C	0.11111	3	0.0	0.07778	3	0.0
Н-С-С-Н	0.11111	3	0.0	0.07500	3	0.0
H-C-C-C	0.11111	3	0.0	0.08000	3	0.0
H-C-C-O	0.11111	3	0.0	0.12500	1	0.0
C-C-C-O	0.11111	3	0.0	0.07778	3	0.0
H-C-O-Car	0.33333	3	0.0	0.19167	3	0.0
C-C-O-Car	0.33333	3	0.0	0.19167	3	0.0
C-O-Car-Car	0.5	2	180.0	0.45000	2	180.0
O-Car-Car-Car	3.125	2	180.0	1.81250	2	180.0
O-Car-Car-H	3.125	2	180.0	1.81250	2	180.0
Car-Car-Car-Car	3.125	2	180.0	1.81250	2	180.0
H-Car-Car-Car	3.125	2	180.0	1.81250	2	180.0

⁸ Mayo, S. L.; Olafson, B. D.; Goddard III, W. A. DREIDING: A Generic Force Field for Molecular Simulations. *J. Phys. Chem.* **1990**, *94*, 8897–8909.
⁹ Wang, J.: Cieplak, P.: Kollman, P. A. How Well Does a Restrained Electrostatic Potential (RESP) Model

Perform in Calculating Conformational Energies of Organic and Biological Molecules?. J.Comput. Chem. 2000, 21, 1049–1074.

H-Car-Car-H	3.125	2	180.0	1.81250	2	180.0
Car-Car-Car-S	3.125	2	180.0	1.81250	2	180.0
H-Car-Car-S	3.125	2	180.0	1.81250	2	180.0

Improper dihedrals (Ca1...Ca2...Ca3-H, where Ca1 and Ca2 are bonded to Ca3), with the same form than proper dihedrals, were introduced to maintain the aromatic ring planar in the GAFF force field. For this purpose the following parameters were used: A=0.55 kcal/mol, m=2, =180.0°.

For the van der Waals potential, the Lennard-Jones form was used with the DREIDING force field:

U_{non-bonded}= $4\epsilon_{ij}[(\sigma_{ij}/r_{ij})^{12}-(\sigma_{ij}/r_{ij})^{6}]$, where $\sigma_{ij}=(\sigma_i+\sigma_j)/2$ and $\epsilon_{ij}=(\epsilon_i\epsilon_j)^{1/2}$. while the 12-6 form was used with the GAFF force field: $U_{non-bonded}=[A_{ij}/r_{ij}^{12}-B_{ij}/r_{ij}^{6}]$, where $A_{ij}=(\epsilon_i\epsilon_j)^{1/2}(R^m_i+R^m_j)^{12}$ and $B_{ij}=2(\epsilon_i\epsilon_j)^{1/2}(R^m_i+R^m_j)^{6}$. with the following parameters:

	DREIDING ⁸		GAFF ⁹			
	ε _i (kcal/mol)	σ _i (Å)	$\mathbf{R}^{m}_{i}(\mathbf{A})$	ε _i (kcal/mol)		
Si	0.0950	3.9511	2.135	0.310		
0	0.2150	3.1271	1.6837	0.170		
С	0.0950	3.4567	1.908	0.1094		
Car	0.0950	3.4567	1.908	0.086		
Н	0.1000	2.8509	1.487	0.0157		
Har	0.1000	2.8509	1.459	0.015		
S	0.2150	3.6883	2.000	0.250		

Non-bonded 1,4-interactions were not scaled with DREIDING force field, while with GAFF, electrostatic was scaled by a factor 0.83333 and van der Waals by a factor 0.5. The curves for the C-S-S-C dihedral angle given in the article were smoothed by applying a running average.

Snapshots of vSBA_n-2 pores calculated with GAFF force field



Snapshots of vSBA_A-2 pore calculated with GAFF FF. a) Transverse section. b) Longitudinal section. Color key: S (yellow), C (blue), H (white), O (red), Si (green).



Snapshots of vSBA_B-2 pore calculated with GAFF FF. a) Transverse section. b) Longitudinal section. Color key: S (yellow), C (blue), H (white), O (red), Si (green).



Snapshots of vSBA_C-2 pore calculated with GAFF FF. a) Transverse section. b) Longitudinal section. Color key: S (yellow), C (blue), H (white), O (red), Si (green).

Distance and dihedral angle estimated with GAFF FF

- Distance between sulfur atoms



- (CSSC) dihedral angle with d(S-S)< 5 Å



Experimental procedures for organic precursors

General procedure. All reactions were carried out in dry glassware using magnetic stirring and a positive pressure of argon. Commercially available solvents were used as purchased, without further purification. CH_2Cl_2 was distilled over CaH_2 and store under dry conditions. THF was distilled over sodium benzophenone ketyl prior to use. Dry state adsorption conditions and purification were performed on Macherey Nagel silica gel 60 Å (70-230 mesh). Analytical thin layer chromatography was performed on pre-coated silica gel plates. Visualization was accomplished by UV (254 nm) and with phosphomolybdic acid in ethanol. ¹H NMR, ¹³C NMR spectra were recorded on 300 or 400 MHz spectrometers. Chemical shifts (δ) are reported in ppm. Signals due residual protonated solvent (¹H NMR) or to the solvent (¹³C NMR) served as the internal standard: CDCl₃ (7.27 ppm and 77.0 ppm), C₆D₆ (7.15 ppm and 128.62 ppm). Multiplicity is indicated by one or more of the following: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet), br (broad). The lists of coupling constants (*J*) correspond to the order of multiplicity assignment and are reported in Hertz (Hz). APT was used for ¹³C spectra assignment. All melting points were uncorrected and were recorded in open capillary tubes using a melting point apparatus.

4-Hydroxythiophenol, diethyl 2,2'-azobis(2-methylpropionate) and 4-iodobenzoic acid are commercially available, they were used as purchased without purification. p-Nitrothiophenol,¹⁰ p-nitrothiophenyl thioacetate,¹¹ p-aminothiophenyl thioacetate,¹² (4iodophenyl)methanol¹³ were prepared according to a literature procedure.

¹⁰ Bellale, E. V.; Chaudhari, M. K.; Akamanchi, K. G. A Simple, Fast and Chemoselective Method for the Preparation of Arylthiols. *Synthesis* **2009**, 3211-3213.

¹¹ Ranu, B. C.; Dey, S. S.; Hajra, A. Highly Efficient Acylation of Alcohols, Amines and Thiols Under Solvent-Free and Catalyst-Free Conditions. *Green Chem.* **2003**, **5**, 44-46.

¹² Bellamy, F. D.; Ou, K. Selective Reduction of Aromatic Nitro Compounds with Stannous Chloride in Non Acidic and Non Aqueous Medium. *Tetrahedron Lett.* **1984**, *25*, 839-842.

¹³ Gibson, S. E.; Mainolfi, N.; Kalindjian, S. B.; Wright, P. T.; White, A. J. P. A New Class of Non-Racemic Chiral Macrocycles: A Conformational and Synthetic Study. *Chem. Eur. J.* **2005**, *11*, 69-80.

Synthesis of precursor 1:



S-4-(3-(Triethoxysily1)propy1)ureido)phenyl ethanethioate (1). To a suspension of *p*-aminothiophenyl thioacetate (**C**) (840 mg, 5.02 mmol, 1 equiv) in anhydrous THF (16 mL) under argon was added 3-(triethoxysily1)propyl isocyanate (1.4 mL, 5.53 mmol, 1.1 equiv). The resulting mixture was stirred at 50 °C for 13 days. The reaction was monitored by ¹H NMR. After completion, the mixture was evaporated and the residue was washed with pentane and then filtrated 3 times to give pure product as a pale yellow solid (1.90 g, 3.76 mmol, 91%). Mp 150 °C. ¹H NMR (400 MHz, CDCl₃) δ : 7.35 (d, *J* = 8.6 Hz, 2 H, Ar*H*), 7.28 (d, *J* = 8.6 Hz, 2 H, Ar*H*), 6.74 (br s, 1 H, N*H*), 5.12 (br s, 1 H, N*H*), 3.82 (q, *J* = 6.8 Hz, 6 H, OC*H*₂CH₃), 3.23 (q, *J* = 6.5 Hz, 2 H, HNC*H*₂), 2.41 (s, 3 H, SC*H*₃), 1.64 (quint, *J* = 7.3 Hz, 2 H, CH₂C*H*₂CH₂), 1.22 (t, *J* = 7.0 Hz, 9 H, OCH₂C*H*₃), 0.65 (t, *J* = 8.0 Hz, 2 H, SiC*H*₂). ¹³C NMR (100 MHz, DMSO-*d*₆) δ : 194.6 (S*C*=O), 154.9 (HNCONH), 142.0 (CNH), 135.2 (CH₄r), 118.2 (CSAc), 118.0 (CH₄r), 57.7 (OCH₂CH₃), 41.7 (NCH₂), 29.9 (*C*H₃), 23.2 (CH₂CH₂CH₂), 18.2 (OCH₂CH₃), 7.2 (SiCH₂). ²⁹Si CPMAS NMR (79.5 MHz) δ : -45.4. HRMS (ESI): *m/z*: calcd for [M+H]⁺ C₁₈H₃₁N₂O₅SSi: 415.1717, found: 415.1725.

Synthesis of precursor 2:



4-[(4-Hydroxyphenyl)disulfanyl]phenol (D). 4-Hydroxythiophenol (15 g, 119 mmol) was stirred vigorously in DMSO (60 mL) at 60 °C under air during one hour. The reaction was monitored by TLC. After completion, the mixture was diluted with iced water and filtrated to afford after drying pure disulfide (14.9 g, 59 mmol, 100 %). ¹H NMR (400 MHz, CDCl₃) δ : 7.33 (d, *J* = 8.5 Hz, 4H, Ar*H*), 6.77 (d, *J* = 8.8 Hz, 4H, Ar*H*), 5.61 (br s, 2H, O*H*). ¹³C NMR (100 MHz, CDCl₃) δ : 156.1 (CO), 134.0 (CS), 133.0 (C_{Ar}H), 116.1 (C_{Ar}H). HRMS (ESI): *m/z*: calcd for [M+Ag]⁺ C₁₂H₁₀O₂S₂Ag: 356.9168, found: 356.9167.

1-(Prop-2-en-1-yloxy)-4-{[4-(prop-2-en-1-yloxy)phenyl]disulfanyl}benzene (E). To a suspension of 4-[(4-hydroxyphenyl)disulfanyl]phenol (**D**) (7.6 g, 29.6 mmol, 1 equiv) in acetone (50 mL) under argon were added K₂CO₃ (24.9 g, 180 mmol, 6 equiv) and allylbromide (7.88 mL, 91 mmol, 3 equiv). The resulting mixture was stirred one night at 50 °C. The reaction was monitored by TLC. After completion, the mixture was diluted with water, and extracted three times with Et₂O. Organic extracts were washed with water, dried over MgSO₄ and concentrated. The residue was purified using silica gel column (5-10 % EtOAc in pentane) to give **E** as a yellow oil (7.98 g, 24.1 mmol, 82%). ¹H NMR (400 MHz, CDCl₃) δ: 7.38 (d, *J* = 8.8 Hz, 4H, Ar*H*), 6.84 (d, *J* = 8.8 Hz, 4H, Ar*H*), 6.04 (ddt, *J* = 17.1, 10.5, 5.3 Hz, 2H, CH=CH₂), 5.40 (dd, *J* = 17.1, 1.5 Hz, 2H, CH=CH₂), 5.29 (dd, *J* = 10.5, 1.5 Hz, 2H, CH=CH₂), 4.52 (dt, *J* = 5.3, 1.5 Hz, 4H, OCH₂). ¹³C NMR (100 MHz, CDCl₃) δ: 159.0 (C_{Ar}-O), 133.0 (CH=CH₂), 132.6 (C_{Ar}H), 128.7 (C_{Ar}-S), 118.0 (CH=CH₂), 115.5 (C_{Ar}H), 69.0 (OCH₂). HRMS (ESI): *m*/z: calcd for [M+H]⁺ C₁₈H₁₉O₂S₂: 331.0821, found: 331.0818.

4-(Prop-2-en-1-yloxy)benzenethiol (F). To a solution of **E** (8 g, 24.2 mmol, 1 equiv) in CH₂Cl₂ (60 mL) and AcOH (120 mL) under argon was added zinc powder (14.4 g, 0.6 mol, 25 equiv) previously activated by washing with HCl 10%, H₂O, EtOH and Et₂O. The mixture was stirred one hour at 60 °C. The reaction was monitored by TLC. After completion, the mixture was filtrated on Celite, washed with CH₂Cl₂ and concentrated to afford pure **F** as a yellow oil (7.24 g, 43.6 mmol, 90%). ¹H NMR (400 MHz, CDCl₃) δ : 7.25 (d, *J* = 8.8 Hz, 2H, Ar*H*), 6.81 (d, *J* = 8.8 Hz, 2H, Ar*H*), 6.03 (ddt, *J* = 17.3, 10.5, 5.3 Hz, 1H, CH=CH₂), 5.40 (dd, *J* = 17.3, 1.5 Hz, 1H, CH=CH₂), 5.28 (dd, *J* = 10.5, 1.5 Hz, 1H, CH=CH₂), 4.50 (dt, *J* = 5.3, 1.5 Hz, 2H, OCH₂), 3.36 (s, 1H, SH). ¹³C NMR (100 MHz, CDCl₃) δ : 157.6 (C_{Ar}-O),

133.2 (*C*H=CH₂), 132.5 (*C*H_{Ar}), 120.2 (*C*_{Ar}-SH), 117.9 (*C*H=*C*H₂), 115.7 (*C*H_{Ar}), 69.1 (OCH₂). HRMS (ESI): m/z: calcd for [M+H]⁺ C₉H₁₁OS: 167.0525, found: 167.0524.

S-4-(Allyloxy)phenyl 2,2-dimethylpropanethioate (G). To F (1.06 g, 6.4 mmol, 1 equiv) in CH₂Cl₂ (16 mL), under argon at -20 °C, was added pyridine (4.7 mL, 58.4 mmol, 9 equiv) and DMAP (120 mg, 1 mmol, 15 mol%). Pivaloyl chloride (1.2 mL, 9.8 mmol, 1.5 equiv) was then slowly added. The reaction was monitored by TLC. After completion, the mixture was diluted with water and the organic phase extracted with 0.1 M HCl solution, brine, dried over MgSO₄ and concentrated. The residue was purified using silica gel column (4% Et₂O in pentane) to afford **G** (1.4 g, 5.7 mmol, 89%). ¹H NMR (400 MHz, CDCl₃) δ : 7.28 (d, *J* = 8.8 Hz, 2H, Ar*H*), 6.94 (d, *J* = 8.8 Hz, 2H, Ar*H*), 6.05 (ddt, *J* = 17.3, 10.5, 5.5 Hz, 1H, CH=CH₂), 5.41 (dd, *J* = 17.3, 1.5 Hz, 1H, CH=CH₂), 5.29 (dd, *J* = 10.5, 1.2 Hz, 1H, CH=CH₂), 4.55 (dt, *J* = 5.5, 1.5 Hz, 2H, OCH₂), 1.31 (s, 9H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ : 200.3 (C=O), 159.5 (CA_r-O), 136.4 (CH_{Ar}), 132.9 (CH=CH₂), 118.9 (CA_r-S), 117.9 (CH=CH₂), 115.5 (CH_{Ar}), 68.9 (OCH₂), 46.8 (C_{Piv}), 27.4 (CH₃). HRMS (ESI): *m/z*: calcd for [M+H]⁺ C₁₄H₁₉O₂S: 251.1100, found: 251.1101.

S-4-(3-(triethoxysilyl)propoxy)phenyl 2,2-dimethylpropanethioate (2). To compound **G** (1.38 g, 5.51 mmol, 1 equiv) in THF (21 mL) under argon was added triethoxysilane (4.1 mL, 22 mmol, 4 equiv). The medium was heated to 80 °C and chloroplatinic acid (60 mg) was added and the reaction was stirred at 80 °C. After one night (RMN ¹H monitoring), the mixture was concentrated, pentane was added and the resulting solution filtrated under argon and concentrated. The oil was distilled (10^{-2} bar) first at 130 °C. The distillate was removed and the residue was distilled at 180 °C to afford almost pure product **2** as a yellow oil (670 mg, 1.6 mmol, 29%). ¹H NMR (400 MHz, CDCl₃) δ : 7.27 (d, *J* = 8.8 Hz, 2H, Ar*H*), 6.91 (d, *J* = 8.8 Hz, 2H, Ar*H*), 3.94 (t, *J* = 6.7 Hz, 2H, ArOC*H*₂), 3.83 (q, *J* = 7.0 Hz, 6H, SiOC*H*₂), 1.90 (quint, *J* = 6.8 Hz, 2H, OCH₂C*H*₂). 1.30 (s, 9H, 3x C*H*₃), 1.23 (t, *J* = 7.0 Hz, 9H, 3 x C*H*₃), 0.76 (t, *J* = 8.3 Hz, 2H, SiC*H*₂). ¹³C NMR (100 MHz, CDCl₃) δ : 201.2 (C=O), 160.0 (C_{Ar}-O), 136.4 (C_{Ar}-H), 118.4 (C_{Ar}-S), 115.3 (C_{Ar}H), 70.0 (OCH₂), 58.4 (OCH₂), 48.4 (C_{Piv}), 27.4 (CH₃), 22.7 (CH₂), 18.3 (CH₃), 6.5 (CH₂). HRMS (ESI): *m*/z: calcd for [M+NH₄]⁺ C₂₀H₃₈NO₅SSi: 432.2235, found: 432.2236.

Experimental procedures for materials

Thermogravimetric (TGA) measurements were carried out with a TGA Q500 apparatus (TA Instruments) under dynamic air atmosphere (sample flow rate 40 ml/min). SAXS experiments were performed on SAXSess-MC2 (Anton-Paar, GmbH, Austria) with a sealed copper tube as X-ray source (wavelength is 0.15417 nm (Cu K- α)) and CCD camera as detection system. The N₂ adsorption/desorption isotherms were obtained at 77 K on a Micrometrics ASAP2010. The specific surface area was determined with the Brunauer, Emmett, and Teller (BET) method and the pore size distribution was calculated from the desorption isotherms using the Barrett Joyner Halenda (BJH) method.¹⁴ Prior to adsorption, the samples were outgassed at 373 K overnight under a vacuum pressure of 2×10^{-3} mbar. All solid-state Cross Polarization Magic Angle Spinning (CPMAS) NMR spectra were obtained on a Bruker Avance-400 MHz NMR spectrometer operating at a ¹³C and ²⁹Si resonance frequency of 101.6 MHz and 79.5 MHz, respectively. ¹³C and ²⁹Si CPMAS experiments were performed with a commercial Bruker Double-bearing probe. About 100 mg of samples were placed in zirconium dioxide rotors of 4-mm outer diameter and spun at a Magic Angle Spinning rate of 10 kHz. The CP technique¹⁵ was applied with a ramped ¹H-pulse starting at 100% power and decreasing until 50% during the contact time in order to circumvent Hartmann-Hahn mismatches.^{16,17} The contact times were 2 ms for ¹³C CPMAS and 5 ms for ²⁹Si CPMAS. To improve the resolution, a dipolar decoupling GT8 pulse sequence¹⁸ was applied during the acquisition time. To obtain a good signal-to-noise ratio, 6144 scans were accumulated using a delay of 2 s in ¹³C CPMAS experiment, and 4096 scans with a delay of 5 s in ²⁹Si CPMAS experiment. The ¹³C and ²⁹Si chemical shifts were referenced to tetramethylsilane. Tetraethylorthosilicate is commercially available. Tetraethylorthosilicate was distilled before used.



SBA₁₇-1. In a typical procedure, 2 g of pluronic P-123 $(EO_{20}PO_{70}EO_{20})$ were dissolved in deionized water (14 mL) and 2

¹⁴ Rouquerol, F., Rouquerol, J., Llewellyn, P., Maurin, G. & Sing, K. S. W. Adsorption by Powders and Porous Solids: Principles, Methodology and Applications 2nd edition (Academic Press: London, 2013).

¹⁵ Schaefer, J.; Stejskal, E. O. R. Carbon-13 Nuclear Magnetic Resonance of Polymers Spinning at the Magic Angle. J. Am. Chem. Soc. **1976**, 98, 1031–1032.

¹⁶ Peersen, O. B.; Wu, X.; Kustanovich, I.; Smith, S.O. Variable-Amplitude Cross-Polarization MAS NMR. *J. Magn. Reson.* **1993**, *104*, 334–339.

¹⁷ Cook, R. L.; Langford, C. H.; Yamdagni, R.; Preston, C. M. A Modified Cross-Polarization Magic Angle Spinning ¹³C NMR Procedure for the Study of Humic Materials. *Anal. Chem.* **1996**, *68*, 3979–3986.

¹⁸ Gerbaud, G.; Ziarelli, F.; Caldarelli, S. Increasing the Robustness of Heteronuclear Decoupling in Magic-Angle Sample Spinning Solid-State NMR. *Chem. Phys. Lett.* **2003**, *377*, 1–5.

M hydrochloric acid solution (60 mL) by stirring for 3 h at 40 °C. Tetraethoxysilane (3.75 g, 18 mmol, 9 equiv) and thiol precursor 1 (850 mg, 2 mmol, 1 equiv), previously dissolved in a few millilitres of ethanol, were then added. The mixture was stirred 24 h at 40 °C, then warmed without stirring at 100 °C for 2 days, filtrated, washed twice with water, once with ethanol and finally extracted with a Soxlhet apparatus (ethanol) for one day. The wet powder was filtrated, washed twice with ethanol, acetone and diethylether. After one night at 80 °C under vacuum, a white powder was recovered. The molar composition of the synthesis mixture was as follows: (1-x) M TEOS : x M 1 :0.017 M P123 Polymer : 188 M H₂O : 5.8 M HCl, where x denotes the number of moles of presursor 1. 13 C CPMAS NMR (101.6 MHz) δ : 156.8, 130.0, 119.3, 69.7 (P123), 59.7 (CH₂O), 41.7, 22.1, 15.8 (P123), 8.3. ²⁹Si CPMAS NMR (79.5 MHz) δ: -67.6 (T³), -92.2 (Q²), -102.1 (Q³), -109.5 (Q⁴). BET Surface Area: 556 m²/g. BJH Desorption Average Pore Diameter: 4.5 nm. Elem. Anal.: 2.52% S. SAXS: d = 11.2 nm (shouldering).



SBA₃₃-1. The material was prepared by following the previous procedure from tetraethoxysilane (4.05 g, 19.48 mmol, 19 equiv) and thiol precursor 1 (425 mg, 1.025 mmol, 1 equiv). ¹³C CPMAS NMR (101.6 MHz) δ: 156.7, 130.7, 119.5, 69.6 (P123), 58.8 (CH₂O), 41.2, 22.5, 15.7 (P123), 8.5. ²⁹Si CPMAS NMR (79.5 MHz) δ: -67.8 (T³), -92.8 (Q²), -102.4 (Q³), -111.1 (Q⁴). BET

Surface Area: 421 m²/g. BJH Desorption Average Pore Diameter: 6.5 nm. Elem. Anal.: 1.42% S. SAXS: d = 12.1 nm (shouldering).



SBA₇₁-1. The material was prepared by following the previous procedure from tetraethoxysilane (4.5 mL, 20 mmol, 39 equiv) and thiol precursor 1 (213 mg, 0.513 mmol, 1 equiv). ¹³C CPMAS

NMR (101.6 MHz) δ: 156.8, 128.2, 118.2, 69.4 (P123), 57.3 (CH₂O), 41.9, 21.9, 15.0 (P123), 8.2. ²⁹Si CPMAS NMR (79.5 MHz) δ: -66.5 (T³), -92.0 (Q²), -101.3 (Q³), -110.6 (Q⁴). BET Surface Area: 617 m²/g. BJH Desorption Average Pore Diameter: 6.9 nm. Elem. Anal.: 0.71% S. SAXS: d = 10.2 nm.



SBA239-1. The material was prepared by following the previous procedure from tetraethoxysilane (4.5 mL, 20 mmol, 39 equiv) and thiol precursor 1 (213 mg, 0.513 mmol, 1 equiv). ¹³C CPMAS

NMR (101.6 MHz) δ: 156.6, 131.6, 120.4, 69.6 (P123), 58.7 (CH₂), 41.9, 21.9, 15.2 (P123),

8.4. ²⁹Si CPMAS NMR (79.5 MHz) δ : -66.0 (T³), -92.0 (Q²), -101.2 (Q³), -110.0 (Q⁴). BET Surface Area: 807 m²/g. BJH Desorption Average Pore Diameter: 6.1 nm. Elem. Anal.: 0.22% S. SAXS: d = 10.1 nm, a = 8.8 nm.

SBA₂₁-2. In a typical procedure, 1 g of pluronic P-123 (EO₂₀PO₇₀EO₂₀) was dissolved in deionized water (7 mL) and 2 M hydrochloric acid solution (30 mL) by stirring for 3 h at 40 °C. Tetraethoxysilane (1.92 g, 9.23 mmol, 9 equiv) and thiol precursor **2** (425 mg, 1.02 mmol, 1 equiv) were then added. The mixture was stirred 24 h at 40 °C, then warmed without stirring at 100 °C for 2 days, filtrated, washed twice with water, once with ethanol and finally extracted with a Soxlhet apparatus (ethanol) for one day. The wet powder was filtrated, washed twice with ethanol, acetone and diethylether. After one night at 80 °C under vacuum, a white powder was recovered. The molar composition of the synthesis mixture was as follows: (1-x) M TEOS : x M **2** : 0.017 M P123 Polymer : 188 M H₂O : 5.8 M HCl, where x denotes the number of moles of precursor **2**. ¹³C CPMAS NMR (101.6 MHz) δ : 158.9, 135.6, 114.5, 69.1 (P123), 59.2, 45.9, 26.7 (P123), 21.9, 15.5 (P123), 8.4. ²⁹Si CPMAS NMR (79.5 MHz) δ : -56.6(T²), -65.4(T³), -91.9 (Q²), -101.4 (Q³), -110.2 (Q⁴). BET Surface Area: 370 m²/g. BJH Desorption Average Pore Diameter: 6.2 nm. Elem. Anal.: 2.17% S. SAXS: 11.7 nm (shouldering).

SBA₃₇-2. The material was prepared by following the previous procedure from tetraethoxysilane (2.03 g, 9.75 mmol, 19 equiv) and organic precursor 2 (213 mg, 0.513 mmol, 1 equiv). ¹³C CPMAS NMR (101.6 MHz) δ : 159.7, 135.5, 126.7, 114.7, 69.7 (P123), 59.3, 46.4, 25.9 (P123), 21.8, 15.5 (P123), 6.9. ²⁹Si CPMAS NMR (79.5 MHz) δ : -56.4 (T²), -64.5 (T³), -91.7 (Q²), -101.0 (Q³), -109.8 (Q⁴). BET Surface Area: 479 m²/g. BJH Desorption Average Pore Diameter: 4.4 nm. Elem. Anal.: 1.31% S. SAXS: No signal.

Si OH

SBA₇₃-2. The material was prepared by following the previous procedure from tetraethoxysilane (2.04 g, 9.77 mmol, 39 equiv) and organic precursor 2 (104 mg, 0.251 mmol, 1 equiv). ¹³C CPMAS NMR

 $(101.6 \text{ MHz}) \delta$: 158.1, 135.4, 114.3, 75.1, 69.3 (P123), 58.4, 25.5 (P123), 21.2, 15.2 (P123), 5.8. ²⁹Si CPMAS NMR (79.5 MHz) δ : -56.9 (T²), -64.7 (T³), -92.2 (Q²), -101.4 (Q³), -110.0 (Q⁴). BET Surface Area: 628 m²/g. BJH Desorption Average Pore Diameter: 5.6 nm. Elem. Anal.: 0.70% S. SAXS: d = 11.3 nm.

General procedure for mesoporous silicas passivation. To non-passivated silica (1 g) in suspension in toluene (75 mL) were added triethylamine (5.5 mL) and trimethylsilylchloride (4.1 mL). The medium was heated one night at 70 °C and then one hour at 100 °C before being filtrated and washed once with toluene and once with ethanol. The recovered powder was stirred in ethanol during 4 h and then filtrated, washed twice with ethanol and twice with diethylether. After one night under vacuum at 80 °C, an orange/brown powder was recovered.

Experimental Procedures for EPR Analysis

EPR experiments were performed with commercially available HPLC grade solvents and reactants, which were used as received. EPR experiments were performed on an ELEXSYS Bruker instrument and the Bruker BVT 3000 set-up was utilized to control the temperature. The photolysis instrument (ORIEL version 66901 with an energy supplier version 68911) is equipped with a 300X UXL306 arc Xe lamp (200–800 nm) with an optical fiber (1 m, version 77620). Irradiation was also performed with a Rayonet apparatus (RPR-200, 16 UV lamps RPR-300) and Hamamatsu LC8 01A light source with a 360-370 nm filter. EPR spectra were simulated using WinSim 2002 software.

In a 4 mm quartz-glass tube, 35 mg of functionalized silica were degassed with three freezepump-thaw cycles with a 10^{-5} mbar vacuum pump. EPR spectra for direct observation of sulfur centered radicals experiments were recorded with the parameters: modulation amplitude = 1 G, receiver gain = 90 dB, modulation frequency = 100 kHz, power = 20 mW, sweep width = 200 G, conversion time = 24 ms, sweep time = 25 s, number of scans = 2.





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HS-

Ŋ_NO₂







S24













S-4-(3-(3-(Triethoxysilyl)propyl)ureido)phenyl ethanethioate (1): ¹H NMR





S-4-(3-(3-(Triethoxysilyl)propyl)ureido)phenyl ethanethioate (1): 13C NMR (APT)

4-[(4-Hydroxyphenyl)disulfanyl]phenol (D) : ¹H NMR



4-[(4-Hydroxyphenyl)disulfanyl]phenol (D) : ¹³C NMR (APT)



1-(Prop-2-en-1-yloxy)-4-{[4-(prop-2-en-1-yloxy)phenyl]disulfanyl}benzene (E): ¹H NMR







1-(Prop-2-en-1-yloxy)-4-{[4-(prop-2-en-1-yloxy)phenyl]disulfanyl}benzene (E): ¹³C NMR (APT)





4-(Prop-2-en-1-yloxy)benzenethiol (F): ¹H NMR







4-(Prop-2-en-1-yloxy)benzenethiol (F): ¹³C NMR (APT)





S-4-(Allyloxy)phenyl 2,2-dimethylpropanethioate (G): ¹H NMR





S-4-(Allyloxy)phenyl 2,2-dimethylpropanethioate (G): ¹³C NMR (APT)



S-4-(3-(triethoxysilyl)propoxy)phenyl 2,2-dimethylpropanethioate (2): ¹H NMR



S37

S-4-(3-(triethoxysilyl)propoxy)phenyl 2,2-dimethylpropanethioate (2): ¹³C NMR (APT)



TEM pictures

Silicas for TEM measurements were embedded in epoxy resin. Samples were prepared using ultramichrotomy techniques and then deposited on copper grids. TEM measurements were carried out at 120kV with a JEOL 1200 EXII microscope.

SBA17-1



SBA₃₃-1







Small Angle X-Ray Scattering (SAXS): SBA₁₇-1, SBA₃₃-1, SBA₇₁-1, SBA₂₃₉-1



Small Angle X-Ray Scattering (SAXS): SBA₂₁-2, SBA₃₇-2, SBA₇₃-2



Nitrogen adsorption/desorption analysis: SBA17-1



Nitrogen adsorption/desorption analysis: SBA₃₃-1



Nitrogen adsorption/desorption analysis: SBA71-1



Nitrogen adsorption/desorption analysis: SBA239-1



Nitrogen adsorption/desorption analysis: SBA₂₁-2



Nitrogen adsorption/desorption analysis: SBA₃₇-2



Nitrogen adsorption/desorption analysis: SBA73-2



¹³C CP-MAS solid state NMR of SBA₁₇-1:



²⁹Si CP-MAS solid state NMR of SBA₁₇-1:



¹³C CP-MAS solid state NMR of SBA₃₃-1:



¹³C CP-MAS solid state NMR of SBA₇₁-1:



²⁹Si CP-MAS solid state NMR of SBA₇₁-1:



¹³C CP-MAS solid state NMR of SBA₂₃₉-1:



²⁹Si CP-MAS solid state NMR of SBA₂₃₉-1:



¹³C CP-MAS solid state NMR of SBA₂₁-2:



²⁹Si CP-MAS solid state NMR of SBA₂₁-2:



¹³C CP-MAS solid state NMR of SBA₃₇-2:



²⁹Si CP-MAS solid state NMR of SBA₃₇-2:



²⁹Si CP-MAS solid state NMR of SBA₇₃-2:





ATG for SBA₂₁-2, SBA₃₇-2, SBA₇₃-2.

