Electronic Supplementary Information

SiO_2 aerogels modified by perfluoro acid amides: a precisely controlled hydrophobicity

S. A. Lermontov,*[a,b] N. A. Sipyagina,[a,b] A. N. Malkova,[a,b] A. V. Yarkov,[a] S. G. Vasil'ev,[c] N.P. Simonenko,[d] A. E. Baranchikov,[b,d] V. K. Ivanov[d,e]

[a] *Institute of Physiologically Active Compounds of the Russian Academy of Sciences, 1 Severnij pr., Chernogolovka, 142432, Russia. E-mail: lermontov52@yandex.ru; Fax: +74965249508; Tel: +74965242587.*
[b] *Moscow State University, Department of Chemistry, 1 Leninskie gory, Moscow, 119991, Russia.*
[c] *Institute of Problems of Chemical Physics of the Russian Academy of Sciences, Academician Semenov avenue 1, Chernogolovka, 142432.*
[d] *Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, 31 Leninsky av., Moscow, 119991, Russia.*
[e] *National Research Tomsk State University, 36 Lenin av., Tomsk , 634050, Russia.*

S1. The characterization of **M1**–**M5** monomers used for the synthesis of SiO_2 aerogels modified by fluorinated acid amides:

M1

The ^{1}H NMR spectrum ($CDCl_3$), δ_H (ppm): 0.5 m (2H, Si-C**H$_2$**), 1.55 m (2H, CH_2-C**H$_2$**-CH_2), 3.15 m (2H, C**H$_2$**-NH), 3.4 s (9H, C**H$_3$**-O), 7.75 broad s (1H, N**H**).

The ^{13}C NMR spectrum ($CDCl_3$), δ_C (ppm): 6.2 (Si-**C**H_2), 21.7 (CH_2-**C**H_2-CH_2), 42 (**C**H_2-NH), 50 (**C**H_3-O), 115.9 quartet ($^1J_{CF}$ 287 Hz **C**F_3), 157.4 quartet ($^2J_{CF}$ 37 Hz **C**=O).

The ^{19}F NMR spectrum ($CDCl_3$), δ_F (ppm): -76.5 s.

Mass-spectrum m/z: 243 $(M\text{-}CH_3OH)^+$, 178 $(M\text{-}C(0)CF_3)^+$, 121 $(Si(OCH_3)_3)^+$, 91 $(Si(OCH_3)_2+H)^+$.

M2

The ^{1}H NMR spectrum ($CDCl_3$), δ_H (ppm): 0.3 m (2H, Si-C**H$_2$**), 1.35 m (2H, CH_2-C**H$_2$**-CH_2), 3.0 m (2H, C**H$_2$**-NH), 3.2 s (9H, C**H$_3$**-O), 7.9 broad s (1H, N**H**).

The ^{13}C NMR spectrum ($CDCl_3$), δ_C (ppm): 5.7 (Si-**C**H_2), 21.5 (CH_2-**C**H_2-CH_2), 41.9 (**C**H_2-NH), 49.4 ((**C**H_3-O)$_3$), 106.6 tq ($^1J_{CF}$ 265 Hz; $^2J_{CF}$ 39 Hz **C**F_2), 117.7 qt ($^1J_{CF}$ 286 Hz; $^2J_{CF}$ 35 Hz **C**F_3), 157.4 t ($^2J_{CF}$ 26 Hz **C**=O).

The ^{19}F NMR spectrum ($CDCl_3$), δ_F (ppm): -84.4 s (3F, C**F$_3$**), -124.3 s (2F, C**F$_2$**).

Mass-spectrum m/z: 293 $(M\text{-}CH_3OH)^+$, 206 $(M\text{-}C_2F_5)^+$, 178 $(M\text{-}C(0)C_2F_5)^+$, 121 $(Si(OCH_3)_3)^+$, 91 $(Si(OCH_3)_2+H)^+$.

M3

The ^{1}H NMR spectrum ($CDCl_3$), δ_H (ppm): 0.49 m (2H, Si-C**H$_2$**), 1.53 m (2H, CH_2-C**H$_2$**-CH_2), 3.19 m (2H, C**H$_2$**-NH), 3.4 s (9H, C**H$_3$**-O), 7.45 and 7.52 two broad s (1H, N**H**).

The ^{13}C NMR spectrum ($CDCl_3$), δ_C (ppm): 7.4 and 6.1 (Si-**C**H_2), 22.0 and 22.1 (CH_2-**C**H_2-CH_2), 41.95 and 41.98 (**C**H_2-NH), 49.8 and 49.9 (**C**H_3-O), 53.1 (CF-O**C**H_3), 105.5 dq ($^1J_{CF}$ 245 Hz; $^2J_{CF}$ 35 Hz **C**F), 119.2 qd ($^1J_{CF}$ 286 Hz; $^2J_{CF}$ 35 Hz **C**F_3), 160.3 and 160.4 two d ($^2J_{CF}$ 32 Hz **C**=O).

The bifurcation of some signals of NMR ^{1}H and ^{13}C spectra is explained by E-/Z- isomerism of the amide group.

The ^{19}F NMR spectrum ($CDCl_3$), δ_F (ppm): -82 s (3F, C**F$_3$**), -136.9 s (1F, C**F**).

Mass-spectrum m/z: 305 $(M\text{-}CH_3OH)^+$, 178 $(M\text{-}C(0)CF(OCH_3)CF_3)^+$, 132 $(CF_3CF(OCH_3)+H)^+$, 121 $(Si(OCH_3)_3)^+$, 91 $(Si(OCH_3)_2+H)^+$.

M4

The ^1H NMR spectrum ($CDCl_3$), δ_H (ppm): 0.6 m (2H, Si-C**H$_2$**), 1.65 m (2H, CH_2-C**H$_2$**-CH_2), 3.3 m (2H, C**H$_2$**-NH), 3.5 s (9H, C**H$_3$**-O), 7.6 broad s (1H, N**H**).

The ^{13}C NMR spectrum ($CDCl_3$), δ_C (ppm): 6.2 (Si-**C**H_2), 21.7 (CH_2-**C**H_2-CH_2), 42.2 (**C**H_2-NH), 50.2 ((**C**H_3-O)$_3$), 109 tt ($^1J_{CF}$ 268 Hz; $^2J_{CF}$ 32 Hz C(O)-**C**F_2), 117 qt ($^1J_{CF}$ 288 Hz; $^2J_{CF}$ 33 Hz **C**F_3), 106-114 m (**C**F_2-**C**F_2- **C**F_2- **C**F_2), 157.7 t ($^2J_{CF}$ 26 Hz **C**=O).

The ^{19}F NMR spectrum ($CDCl_3$), δ_F (ppm): - 81.7 t (3F, $^2J_{CF}$ 10 Hz C**F$_3$**), -120.4 t (2F, $^2J_{CF}$ 13 Hz C(O)-C**F$_2$**), -122.3 s (2F, C**F$_2$**), -123.1 s (2F, C**F$_2$**), -123.4 s (2F, C**F$_2$**), -126.8 s (2F, C**F$_2$**).

Mass-spectrum m/z: 493 $(M\text{-}CH_3OH)^+$, 376 $((CH_3O)_2Si\text{-}CH_2CH_2CH_2NHC(0)C_4F_8+H)^+$, 178 $(M\text{-}C(0)C_8F_{17})^+$, 121 $(Si(OCH_3)_3)^+$, 91 $(Si(OCH_3)_2+H)^+$.

M5

The ^1H NMR spectrum ($CDCl_3$), δ_H (ppm): 0.65 m (2H, Si-C**H$_2$**), 1.7 m (2H, CH_2-C**H$_2$**-CH_2), 3.4 m (2H, C**H$_2$**-NH), 3.6 s (9H, C**H$_3$**-O), 7.4 and 7.5 two broad s (1H, N**H**).

The ^{13}C NMR spectrum ($CDCl_3$), δ_C (ppm): 6.3 and 7.5 (Si-**C**H_2), 21.8 and 22 (CH_2-**C**H_2-CH_2), 42.2 and 42.4 (**C**H_2-NH), 50.2 and 50.5 ((**C**H_3-O)$_3$), 109 tt ($^1J_{CF}$ 268 Hz; $^2J_{CF}$ 40 Hz **C**F_2), 117 qt ($^1J_{CF}$ 288 Hz; $^2J_{CF}$ 33 Hz **C**F_3), 106-114 m (**C**F_2-**C**F_2- **C**F_2- **C**F_2), 157.7 and 157.9 two t ($^2J_{CF}$ 26 Hz **C**=O).

The ^{19}F NMR spectrum ($CDCl_3$), δ_F (ppm): - 81.1 and – 81.3 two t (3F, $^2J_{CF}$ 10 Hz C**F$_3$**), -120.1 and -120.2 two t (2F, $^2J_{CF}$ 13 Hz C(O)-C**F$_2$**), -121.8 m (2F, C**F$_2$**), -122.0 m (2F, C**F$_2$**), -122.2 m (2F, C**F$_2$**), -122.8 m (2F, C**F$_2$**), -123.0 m (2F, C**F$_2$**), -126.4 m (2
F, C**F$_2$**).

The bifurcation of some signals of NMR ^1H, ^{13}C and ^{19}F spectra is explained by E-/Z- isomerism of the amide group.

Mass-spectrum m/z: 491 $(M\text{-}CH_2Si(OCH_3)_2+H)^+$, 206 $(M\text{-}C_8F_{17})^+$, 178 $(M\text{-}C(0)C_8F_{17})^+$, 121 $(Si(OCH_3)_3)^+$, 91 $(Si(OCH_3)_2+H)^+$.

Table S1 Elemental analysis data (wt.%) on modified silica aerogels.

Sample name	**Si content**	**F content**	**N content**
A1 CO_2	32.76	7.31	1.45
A2 CO_2	31.40	8.94	1.75
A5 CO_2	24.65	26.70	1.51

S2. The Solid state ^{19}F NMR spectra of **A2 CO_2**, **A3 CO_2** and **A5 CO_2**:

A2 CO_2

The ^{19}F NMR spectrum ($CFCl_3$), δ_F (ppm): - 87 s (C**F$_3$**), -126 s (C**F$_2$**).

A3 CO_2

The ^{19}F NMR spectrum ($CFCl_3$), δ_F (ppm): - 85.4 s (C**F$_3$**), -140.2 s (C**F**).

A5 CO_2

The ^{19}F NMR spectrum ($CFCl_3$), δ_F (ppm): - 83 broad m (C(O)-C**F$_2$**- C**F$_2$**), -123 broad m (C**F$_3$**-C**F$_2$**- C**F$_2$**-C**F$_2$**- C**F$_2$**-C**F$_2$**).

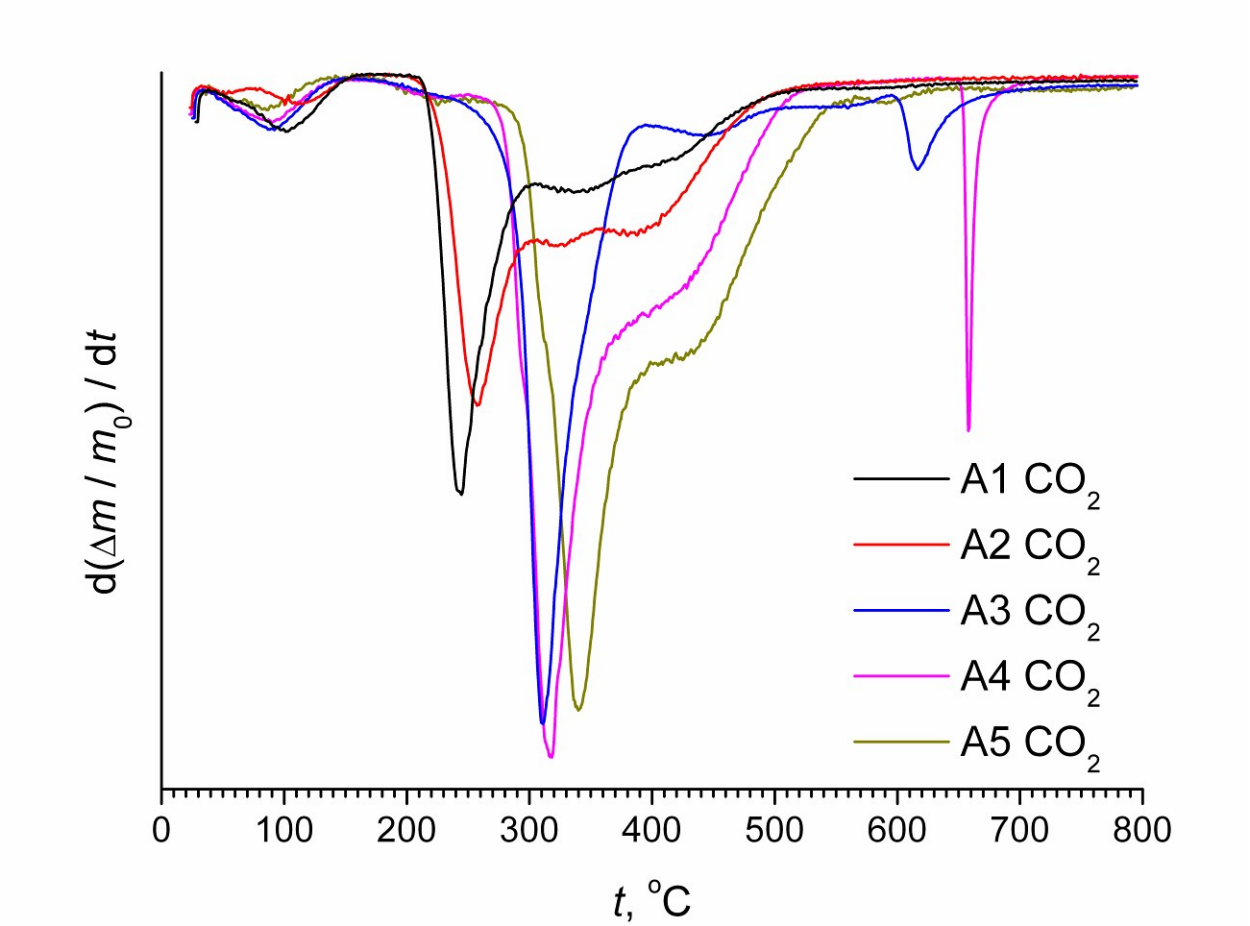


Fig. S1 Differential thermogravimetric curves of SiO_2 aerogels **A1** – **A5** modified by perfluoro acid amides supercritically dried in CO_2.

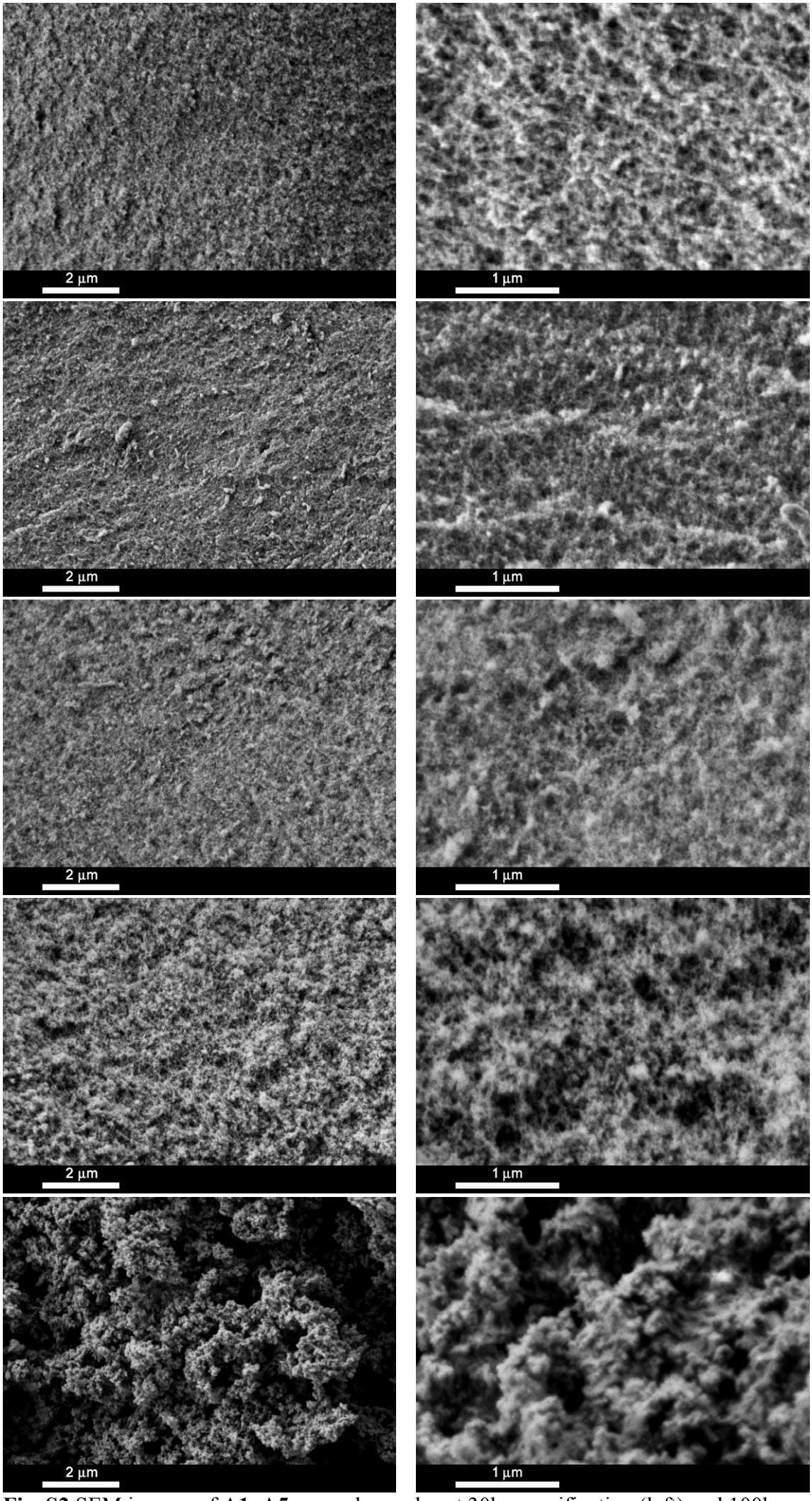


Fig. S2 SEM images of **A1**–**A5** aerogel samples at 30k magnification (left) and 100k magnification (right).

A1 IPA **A3 IPA** **A5 IPA**

Fig. S3 Images obtained using digital camera showing the appearance of a sessile water drop on the surface of aerogel samples.

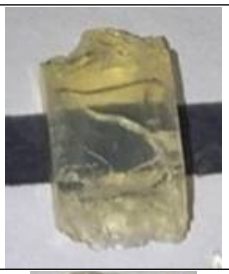
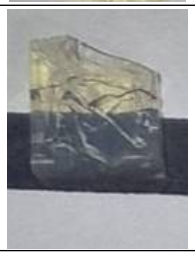
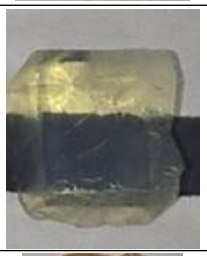
Series	SCD solvent			
	IPA	**CO_2**	**MTBE**	**HFIP**
A1				
A2				
A3				
A4				
A5				

Fig S4 Appearance of SiO_2-based aerogels modified by perfluoro acid amides.

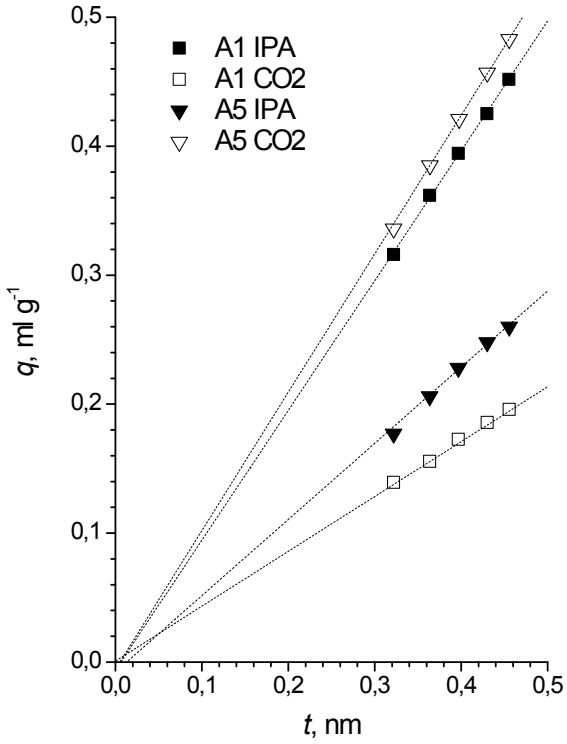


Fig. S5. *t*-plots at low statistical thickness region of SiO_2 aerogels modified by trifluoroacetamide or perfluorononanamide and supercritically dried in isopropanol and CO_2 (notation is the same as in Fig. 2).