Supplementary Informations

Direct pseudomorphic transformation of silica from rice husk into organo-functionalized MCM-41

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To reduce the cost of silica-based materials, an agricultural waste, rice husk (RH), was transformed into higher valuable products such as MCM-41 and organo-functionalized MCM-41 in the frame of circular economy. RH is the biomass waste containing the highest amount of silica (214 g kg^{-1}). Direct calcination of RH led to silica with low surface area (10 m^2 g^{-1}), which could not be transformed into MCM-41. After optimization, silica of 310 m^2 g^{-1} was produced by washing RH with HCl 0.1 mol L^{-1} at 25 °C and calcination at 600 °C. Such silica was successfully transformed in one-step synthesis at 115 °C for 24 h into highly ordered MCM-41 (800 m^2 g^{-1}) and organo-functionalized MCM-41 (510 – 720 m^2 g^{-1}) including aminopropyl and amide derivatives of amino acids (Leucine, Serine and Tyrosine). The corresponding organo-triethoxysilanes alone or in mixture were directly added in the synthesis with silica from RH, octadecyltrimethylammonium and NaOH solution. Surfactant removal was successfully performed with EtOH/NH_4NO_3 solution at 60 °C. The mesopore diameter of the materials were homogeneous and varied from 3.8 to 4.2 nm depending on the organic functions. Thanks to the use of the concept of pseudomorphic transformation, the particle size of the materials ranged from 1 to 100 μm. As proof of concept, the 50-100 μm fraction (30% of the volume) was successfully used to fill columns to run size exclusion chromatography for protein separation. The largest protein, Bovine Serum Albumine (BSA) was excluded from all materials as its kinetic diameter (d = 7.2 nm) was larger than the mesopore diameter. The smallest proteins: carbonic anhydrase (d = 4.2 nm), myoglobin (d = 3.8 nm) and lysozyme (d = 3.4 nm) were retained by the materials. Their retention factor increased as the kinetic diameter decreased, as the mesopore diameter decreased and as the hydrophobicity of the materials increased. The best separation of proteins was obtained with MCM-41 functionalized with both Leucine and Serine amide derivatives.

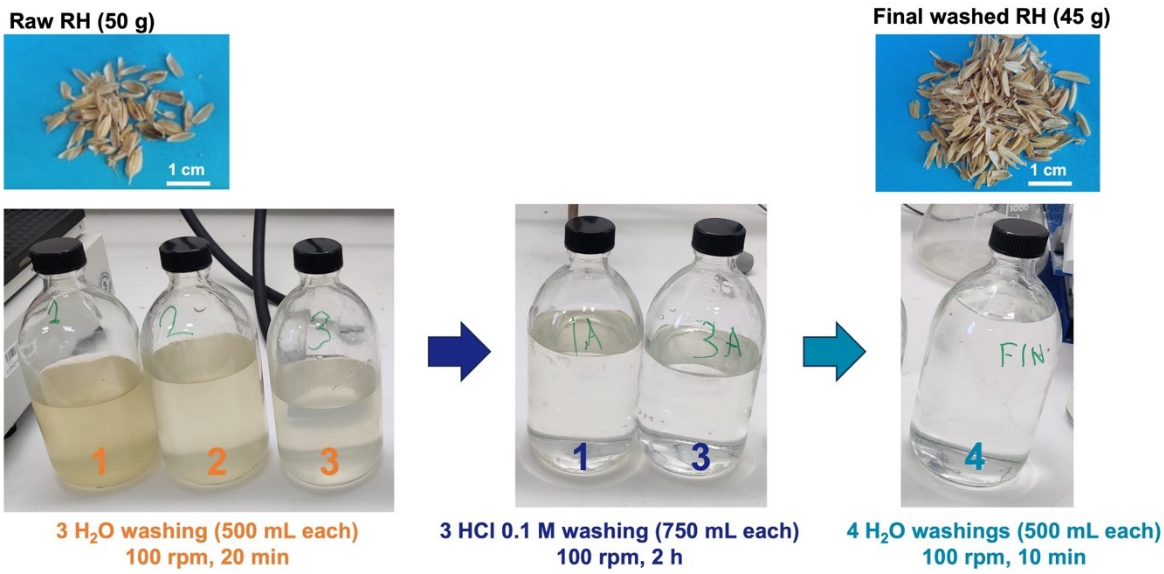

Fig. S1 Pictures of raw and final washed RH and of the supernatant solutions after the different washings: first three H_2O washings, first and third HCl 0.1 mol L^{-1} washings at 25 °C, final H_2O washing (4th H_2O washing).

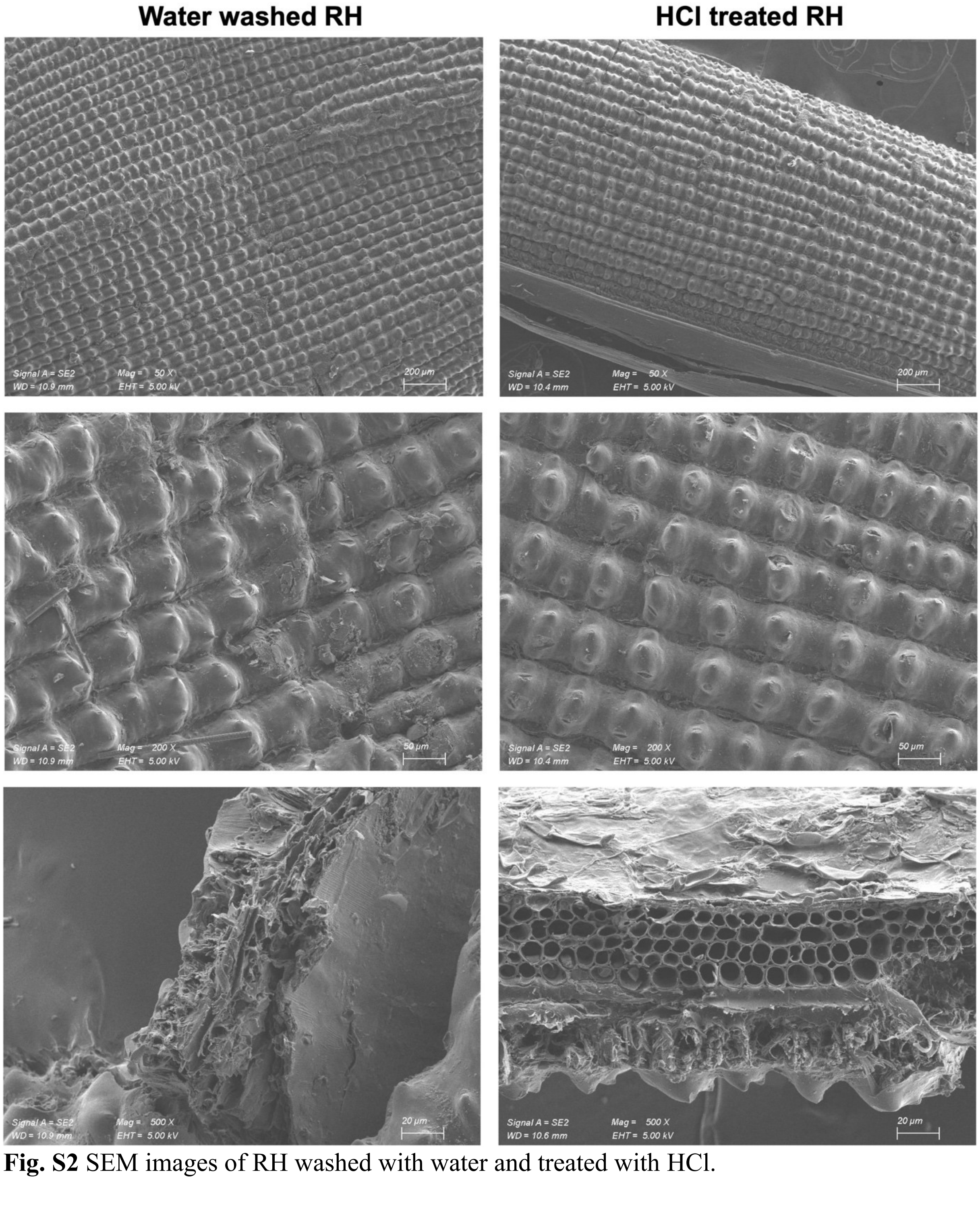

Fig. S2 SEM images of RH washed with water and treated with HCl.

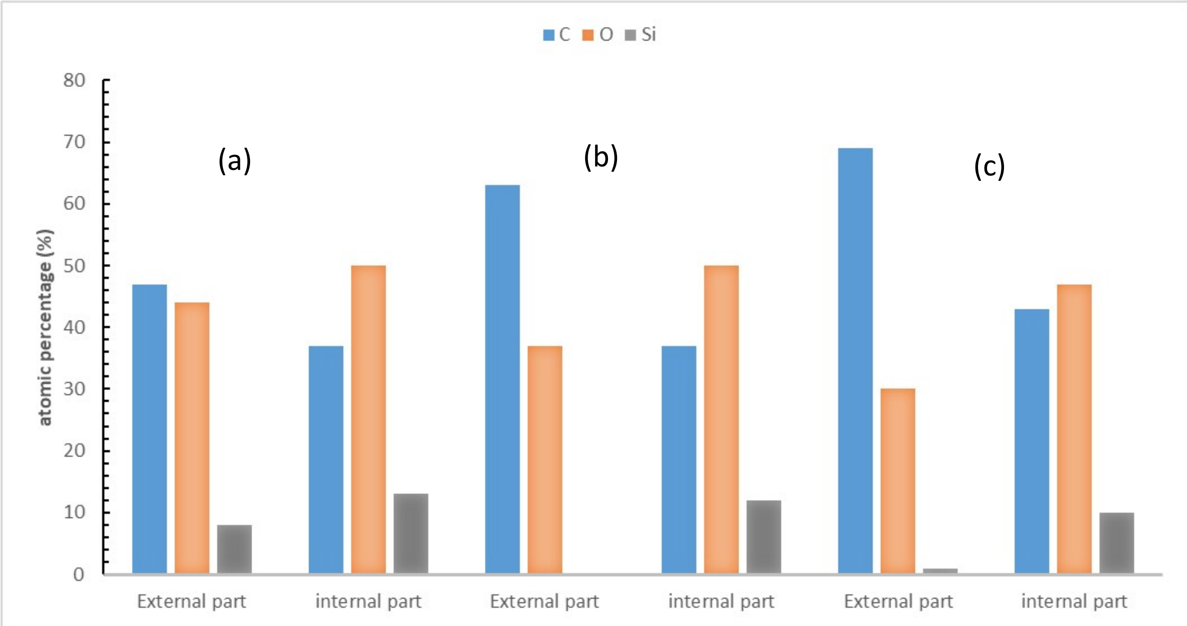

Fig. S3 EDS analysis (atomic percentage) of the internal and external parts of (a) raw rice husk, (b) rice husk washed with water and (b) HCl treated rice husk (HCl 0.1 mol L^{-1}, shaking) followed by water washing. Carbon content should not be taken into account as carbon stick was used to maintain particles on EDS supports.

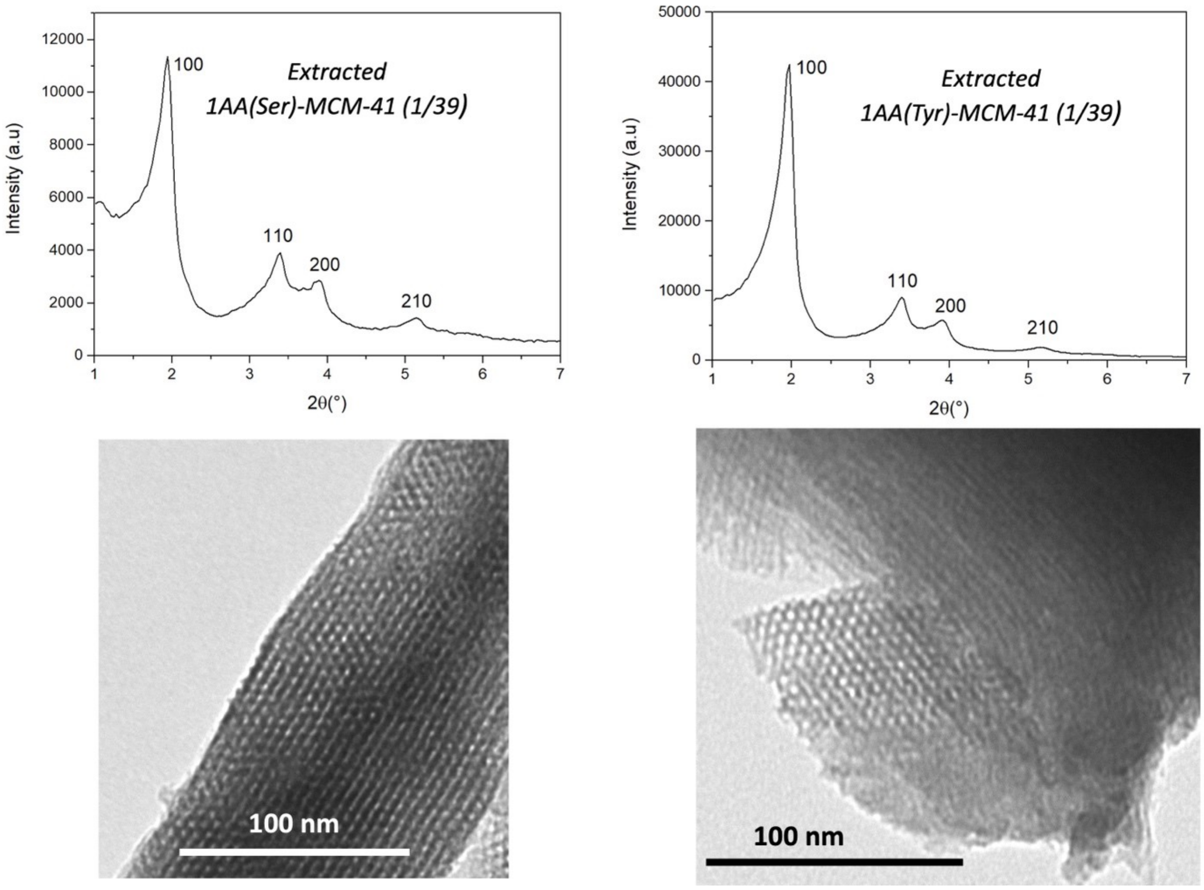

Fig. S4 XRD patterns and TEM of extracted AA-functionalized MCM-41 with (left) 1 AA (Ser) and (right) 1 AA (Tyr) for the molar ratio organosilane/SiO_2 = 1/39.

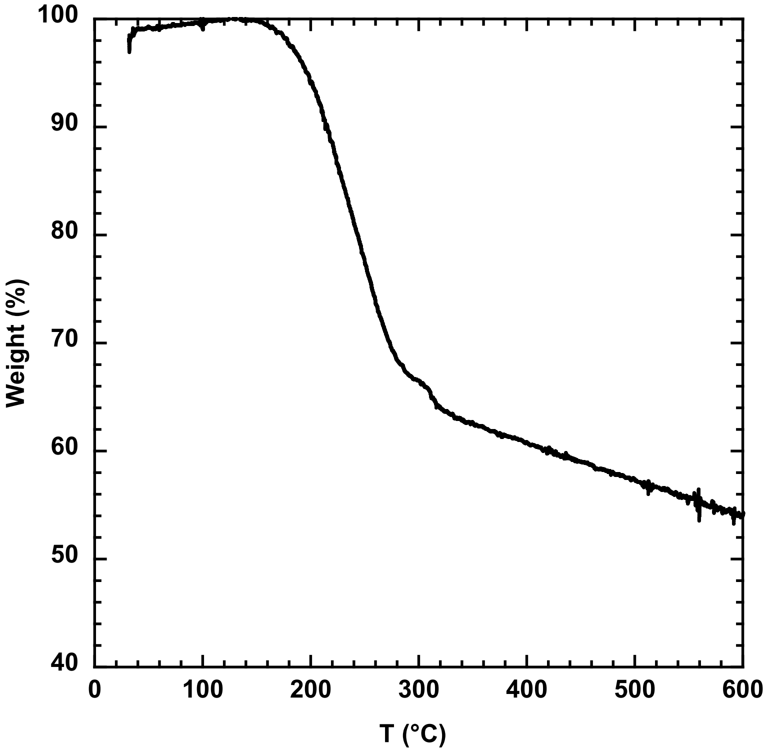

Fig. S5 TGA curve of as-synthesized MCM-41 obtained by pseudomorphic transformation of silica from RH.

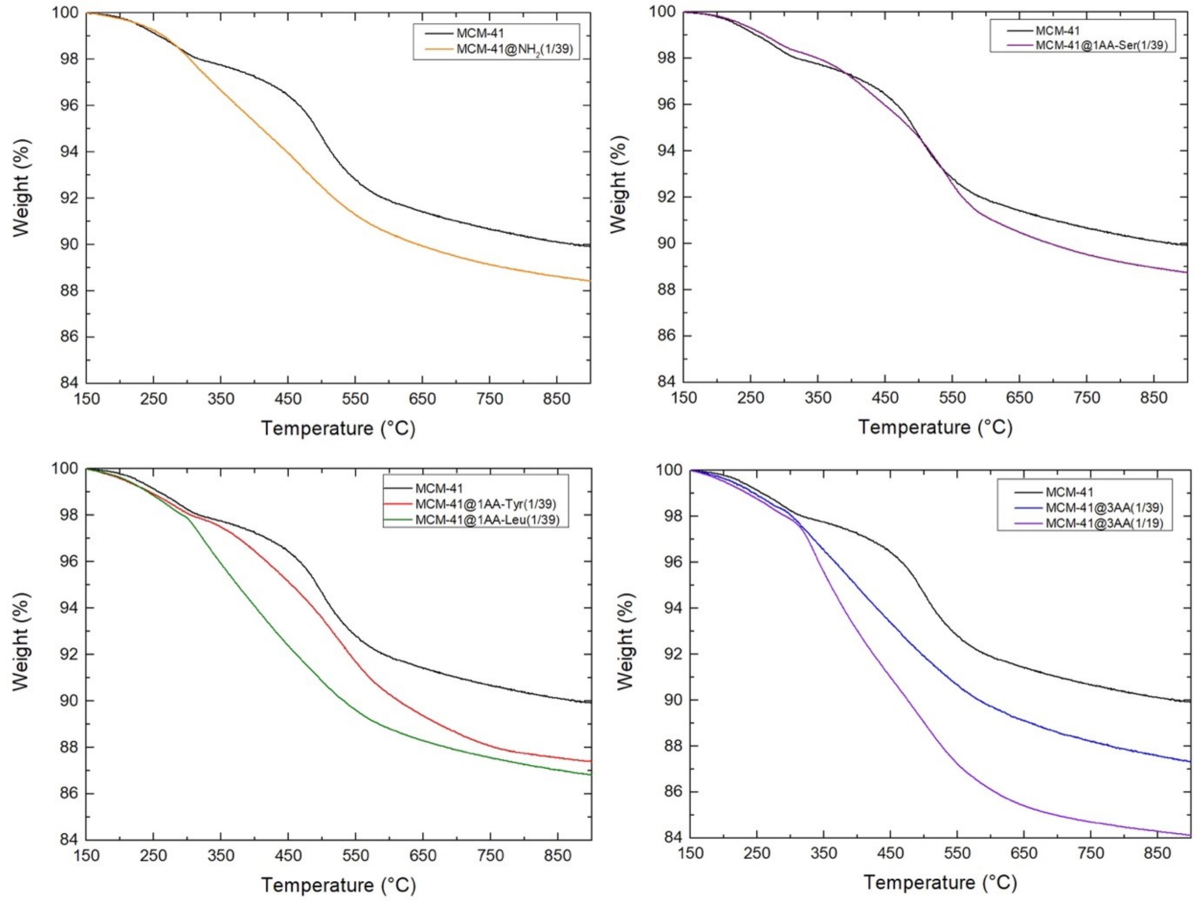

Fig. S6 Normalized ATG curves of surfactant extracted MCM-41 and organo-functionalized MCM-41 materials with aminopropyl (NH_2) or AA groups (1 AA or a mixture of 3 AA in ratio 1/3, 1/3, 1/3) for molar ratio organosilane/SiO_2 = 1/19 or 1/39.

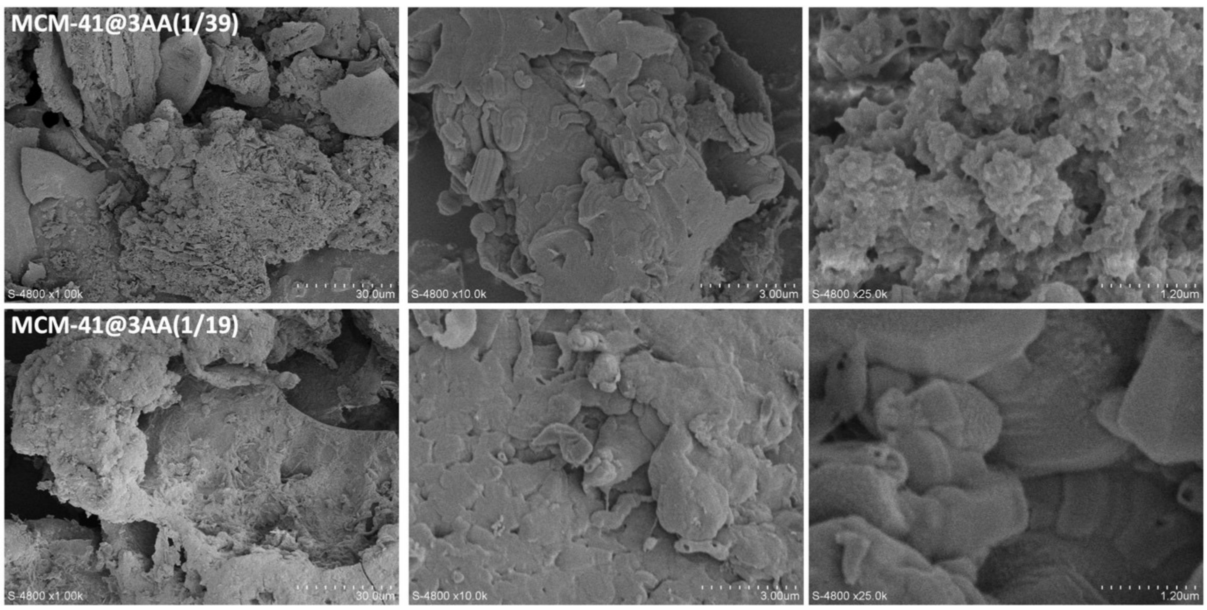

Fig. S7 SEM images of extracted AA-functionalized MCM-41 prepared with the mixtures of 3 AA (Leu, Ser, Tyr).

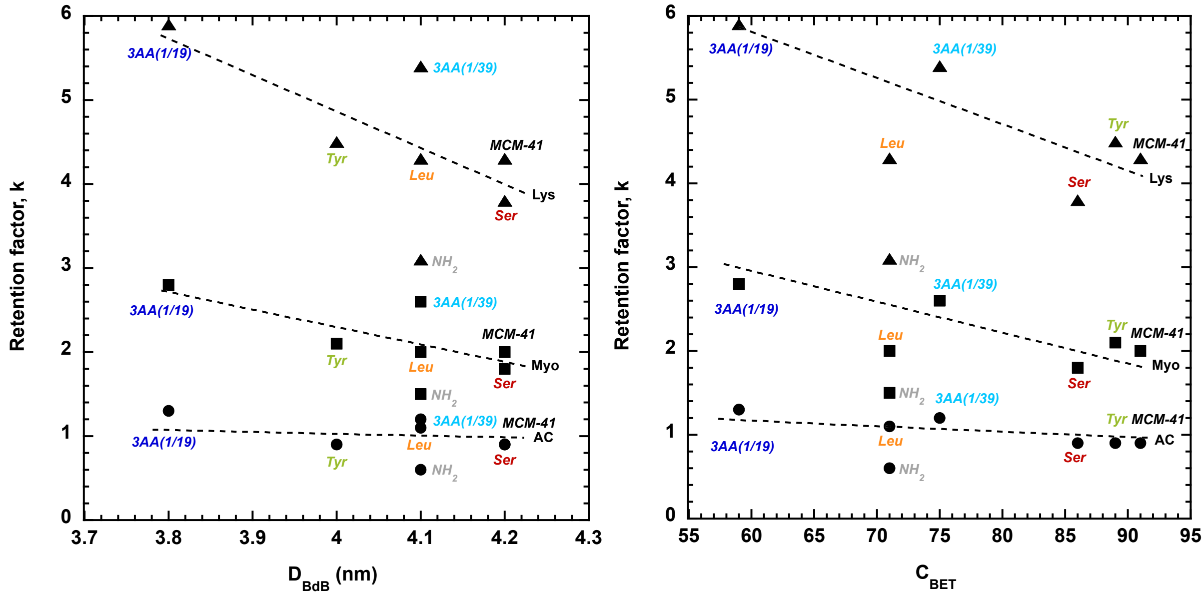

Fig. S8 Retention factors of proteins (circle) Carbonic Anhydrase (AC), (square) Myoglobin, (triangle) Lysozyme, as a function of (left) material mesopore diameter (D_{BdB}) and (right) material surface hydrophobicity (C_{BET}).

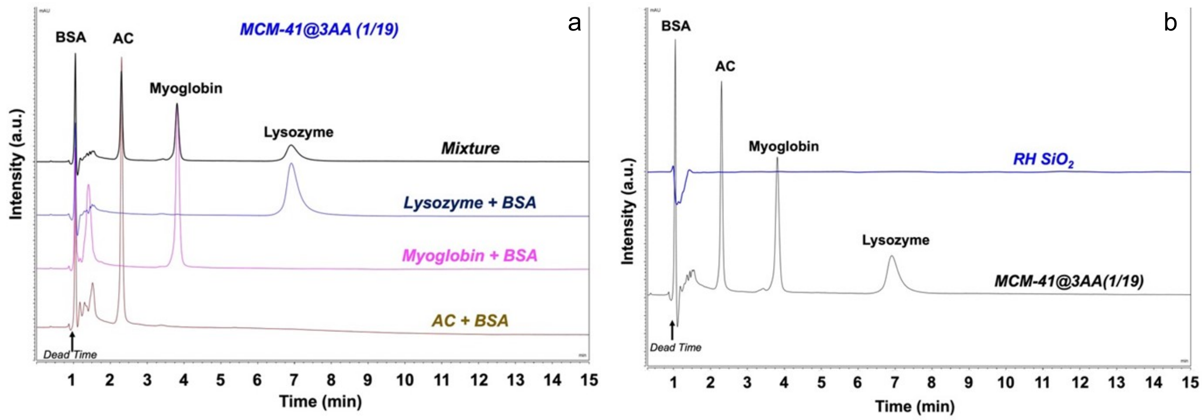

Fig. S9 Comparison of proteins separations with MCM-41@3AA(1/19) (a) for the mixture of the four proteins and for each protein mixed with BSA and (b) with a column filled with silica from RH for the mixture of the four proteins. Conditions: particles 50-100 μm, mobile phase H_2O/ACN 98/2 (v/v), flow rate 1 mL min^{-1}.

Table S1. Weight of reactants in the synthesis and yields in as-synthesized and surfactant extracted materials obtained by pseudomorphic transformation of 1 g of silica fom RH: MCM-41 and organo-functionalized MCM-41 materials with aminopropyl (NH_2) or AA groups (1 AA or a mixture of 3 AA in ratio 1/3, 1/3, 1/3) for molar ratios organosilane/SiO_2 = 1/19 or 1/39.

Materials	SiO_2 g	R-$SiO_{1.5}$[a] g	$C_{18}TMA^+$ g	Mass in synthesis g	as-synth. g	surfact. extracted g
MCM-41	1	0	0.52	1.52	1.14	0.70
MCM-41@NH2(1/39)	1	0.047	0.52	1.57	1.42	0.91
MCM-41@1AA(Tyr)(1/39)	1	0.135	0.52	1.65	1.38	0.90
MCM-41@1AA(Leu)(1/39)	1	0.114	0.52	1.63	1.41	0.89
MCM-41@1AA(Ser)(1/39)	1	0.103	0.52	1.62	1.36	0.85
MCM-41@3AA(1/39)	1	0.117	0.52	1.64	1.36	0.88
MCM-41@3AA(1/19)	1	0.240	0.52	1.76	1.58	0.89

[a]The molar weights of Si-Tyr-NH_2, Si-Ser-NH_2, Si-Leu-NH_2 are 427.57, 351.48, 377.56 g/mol, respectively, and therefore for R-$SiO_{1.5}$ incorporated in the materials: 316.31, 240.22, 266.32 g/mol.

Table S2. Elemental analysis and TGA of extracted materials: MCM-41 and organo-functionalized MCM-41 materials with aminopropyl (NH_2) or AA groups (1 AA or a mixture of 3 AA in ratio 1/3, 1/3, 1/3) for molar ratios organosilane/SiO_2 = 1/19 or 1/39.

	Elemental Analysis			**TGA**	
Materials	%C	%H	%N	Weight loss 150-900 °C %	SiO_2 weight at 900 °C %
MCM-41	5.15	2.27	1.71	9.56	84.96
MCM-41@NH_2(1/39)	5.05	2.34	1.89	11.13	84.97
MCM-41@1AA-Tyr(1/39)	6.42	2.23	1.94	11.79	81.68
MCM-41@1AA-Leu(1/39)	6.15	2.33	2.00	12.79	84.04
MCM-41@1AA-Ser(1/39)	5.24	2.32	1.74	11.10	87.24
MCM-41@3AA(1/39)	5.08	2.08	2.16	12.14	83.29
MCM-41@3AA(1/19)	7.05	2.34	2.31	15.59	82.51

Table S3. Retention factor *k* of proteins and selectivity α for the different MCM-41 type materials

Materials	***k* AC**	***k* Myoglobine**	***k* Lysozyme**	$\alpha_1 = k_{Lys}/k_{AC}$	$\alpha_2 = k_{Lys}/k_{Myo}$
MCM-41@3AA(1/19)	1.3	2.8	5.9	4.538	2.195
MCM-41@3AA(1/39)	1.2	2.6	5.4	4.500	2.077
MCM-41@1AA-Tyr(1/39)	0.9	2.1	4.5	5.000	2.143
MCM-41@1AA-Leu(1/39)	1.1	2.0	4.3	3.909	2.150
MCM-41@1AA-Ser(1/39)	0.9	1.8	3.8	4.220	2.110
MCM-41	0.9	2.0	4.3	4.480	2.195
MCM-41@NH_2(1/39)	0.6	1.5	3.1	5.167	2.067