Correlating Surface-Functionalization of Mesoporous Silica with Adsorption and Release of Pharmaceutical Guest Species

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SUPPORTING INFORMATION

Table S1. Quantities of amino organosilica and C_{60} fullerene species incorporated into mesoporous SBA-15 silica materials calculated from mass percent C as determined by elemental analysis, thermogravimetric analysis (TGA) and solid-state ^{29}Si single-pulse MAS NMR measurements.

Sample	mmoles of organosilica per gram of sample		
	Calculated by %C	Calculated by TGA	Calculated by ^{29}Si-NMR
SBA-15-APS	1.63	1.01	1.10
SBA-15-ABS	1.69	1.14	1.39
SBA-15-APhS	1.26	0.97	0.94

Sample	mmoles of C_{60} per gram of sample	
	Calculated by %C	Calculated by TGA
SBA-15-APS-C_{60}H	0.17	0.26
SBA-15-ABS-C_{60}H	0.24	0.31
SBA-15-APhS-C_{60}H	0.06	0.01

Table S2. Fitting parameters obtained by mathematical fitting of the cumulative release profiles of methylprednisolone from non-functionalized and functionalized mesoporous SBA-15 silica materials using first-order kinetic and Korsmeyer-Peppas drug release models. Beside the kinetic parameter values, the standard error is included.

| Sample		First-order kinetic release model: $F(t) = F_o \cdot (1-e^{-k \cdot t})$			Korsmeyer-Peppas model: $f(t) = K \cdot t^n$		
		Y-axis intercept $Ln(F_o)$	Rate coefficient $[min^{-1}]$	R^2	Constant, K_{K-P}	Release exponent, n	R^2
SBA-15	pH 7.4	0.62±0.001	0.0080±0.0001	0.999	4.3±0.9	0.44±0.07	0.901
SBA-15-APS		1.44±0.05	0.0201±0.001	0.982	4.2±0.5	0.46±0.02	0.985
SBA-15-ABS		0.26±0.004	0.0034±0.001	0.990	1.7±0.2	0.54±0.02	0.990
SBA-15-APS-C_{60}H		0.55±0.02	0.0072±0.0005	0.970	4.3±0.4	0.43±0.03	0.985
SBA-15-ABS-C_{60}H		0.19±0.002	0.0045±0.0001	0.998	0.6±0.1	0.73±0.03	0.992
SBA-15-APS-C_{60}H	pH 4.6	0.29±0.002	0.0060±0.0001	0.998	1.2±0.1	0.53±0.02	0.993
SBA-15-ABS-C_{60}H		0.24±0.005	0.0090±0.0003	0.989	0.7±0.1	0.62±0.03	0.991
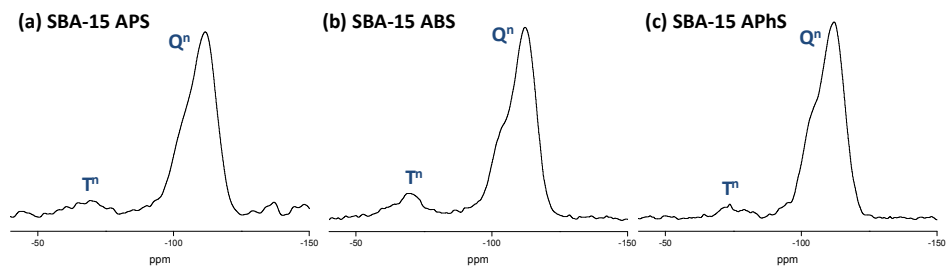
Figure S1. Solid-state 1D single-pulse ^{29}Si MAS NMR spectra of (a) SBA-15-APS, (b) SBA-15-ABS, and (c) SBA-15-APhS materials. Signals in a 1D single-pulse ^{29}Si NMR spectrum arise from chemically distinct ^{29}Si species and are resolved based on chemical shift, while their integrated areas reflect the quantities of each ^{29}Si species. Three distinct signals are observed at -110 and -102 ppm which are assigned to Q^4 and Q^3 ^{29}Si species, while the signals at ca. -65 ppm correspond to T^1, T^2, and T^3 ^{29}Si associated with amino organosilica species. The quantities of amino organosilica loadings are ascertained by comparing the integrated areas of signals from T and Q species reveal organosilica loadings (Table S1).
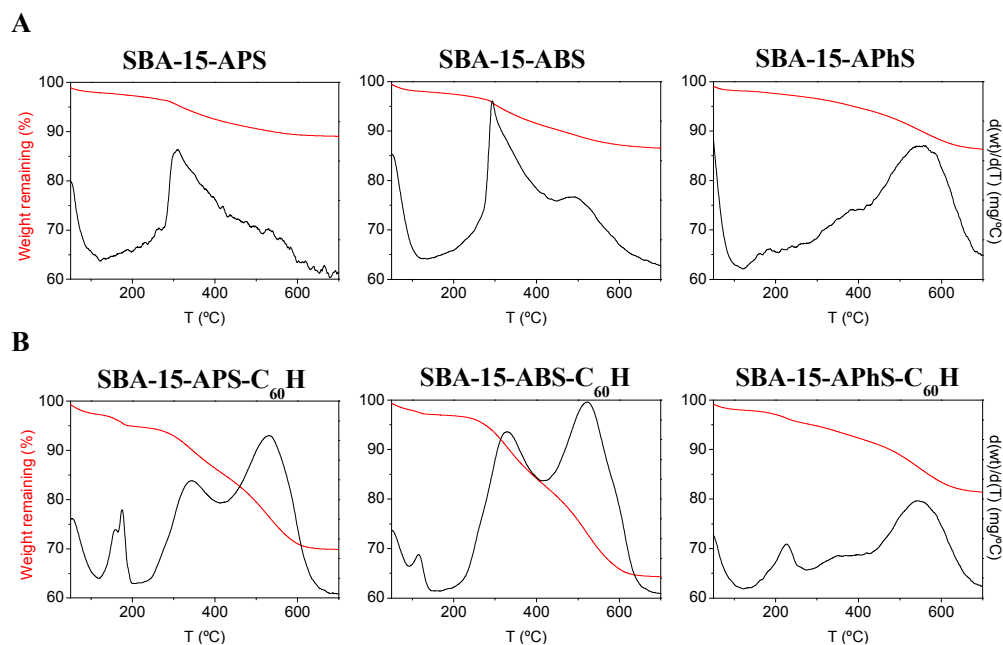
Figure S2. Thermogravimetric analyses plots of (A) SBA-15-NH$_2$ materials (B) SBA-15-NH-C$_{60}$H materials. The TGA plots of SBA-15-NH$_2$ materials (A) show mass losses between temperatures of 120 ºC and 700 ºC that are solely attributable to the decomposition of the organic moieties of amino organosilica species, and thus enable organosilica loadings to be quantified (Table S1). Additional mass losses are observed in the TGA plots of SBA-15-NH-C$_{60}$H materials (B) at temperatures of approximately 500 ºC, which are associated to the decomposition of fullerene C$_{60}$ species. A comparison of mass losses between appropriate SBA-15-NH and SBA-15-NH-C$_{60}$H materials allows incorporated C$_{60}$ species to be quantified (Table S1). In all TGA plots, mass losses between temperatures of 40 ºC and 120 ºC are attributed to the removal of adsorbed water.
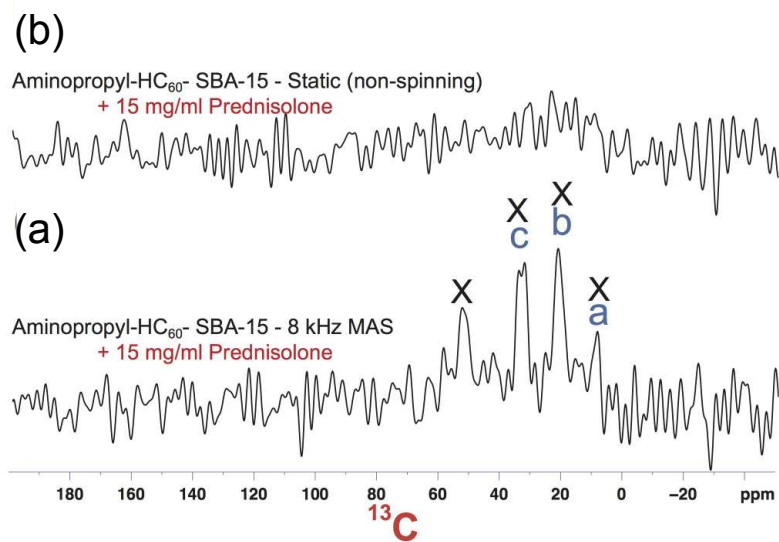
Figure S3. Solid-state 1D ^{13}C CP-MAS spectra of mesoporous SBA-15 silica functionalized with HC$_{60}$-aminopropyl groups with 15 mg mL^{-1} loadings of methylprednisolone guest species taken under (a) 8 kHz MAS and (b) static (non-spinning) conditions mg mL^{-1}. The spectra were all acquired at room temperature with a 2 ms CP contact time.
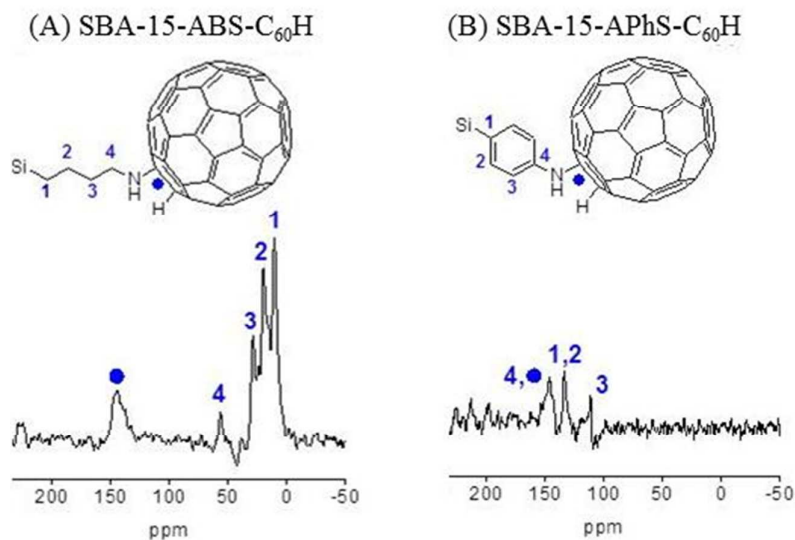
Figure S4. Solid-state 1D ^{13}C{^{1}H} CP-MAS NMR spectra of (A) SBA-15-ABS-C$_{60}$H and (B) SBA-15-APhS-C$_{60}$H materials. In A, ^{13}C signals at 11, 21, 29 and 57 ppm are assignable to ^{13}C species *1*, *2*, *3* and *4* of the aliphatic aminobutyl chains, while signals at *ca.* 145 ppm are attributable to the aromatic ^{13}C species of the C$_{60}$ fullerene moieties. In B, the ^{13}C signals at 134 ppm are assignable to the aromatic ^{13}C groups *1* and *2*, while signals at 112 and 146 ppm are associated with ^{13}C species *3* and *4*, of the aminophenyl moieties of grafted aminophenyl organosilica species. Additionally, in B, the ^{13}C signals at *ca.* 145 ppm are associated with associated with the HC$_{60}$ moieties and overlap with signals associated with species *4* of the aminophenyl moieties. Both spectra were acquired at room temperature under MAS conditions of 6 kHz with CP contact times of 1 ms.
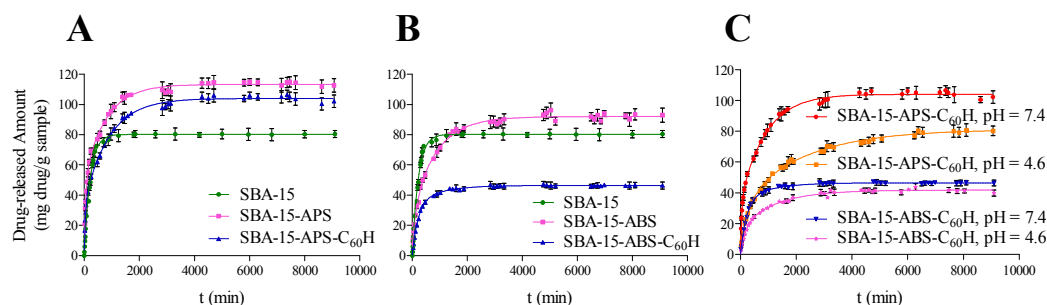
Figure S5. The cumulative profiles of methylprednisolone released into simulated body fluid (pH=7.4, 37 °C) as a percent of the methylprednisolone adsorption capacity for a given material are plotted versus time for (A) SBA-15-APS (pink, squares) and SBA-15-APS-C_{60}H (blue, triangles) materials, and (B) SBA-15-ABS (pink, squares) and SBA-15-ABS-C_{60}H (blue, triangles). In (C), the extents of methylprednisolone released for SBA-15-APS-C_{60}H materials into simulated body fluids at pH 7.4 (red, circles) and pH 4.6 (orange, squares), and from SBA-15-ABS-C_{60}H into simulated body fluids at pH 7.4 (blue, triangles) and pH 4.6 (pink, stars) are plotted versus time. Simulated body fluid under approximately neutral conditions (pH 7.4) was a PBS buffered solution, while simulated body fluid under acidic conditions (pH 4.6) was an acetate buffered solution.

References

The complete author list of reference 34:

Uritu, C.M et al.; Varganici, C.D; Ursu, L; Coroaba, A; Nicolescu, A; Dascalu, A.I; Peptanariu, D; Stan, D; Constantinescu, C.A; Simion, V; Calin, M; Maier, S.S; Pinteala, M; Barboiu, M.