Supporting Information

Functionalized Mesoporous Silica *via* an Aminosilane Surfactant Ion Exchange Reaction: Controlled Scaffold Design and Nitric Oxide Release

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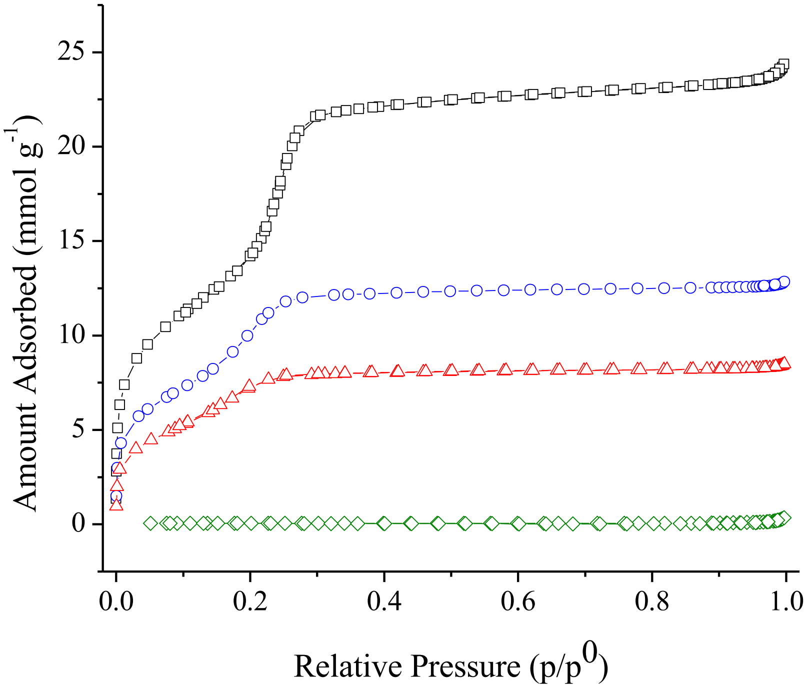

Figure S1. Nitrogen sorption isotherms for 1100 nm AEAP3-modified MSNs at reaction AEAP3 concentrations of 0 (black, square), 1.4 (blue, circle), 2.9 (red,triangle), and 11.5 mM (green, diamond). Data for the 5.7 mM AEAP3-based synthesis was omitted for clarity, as the isotherm overlapped with that for the 11.5 mM synthesis.

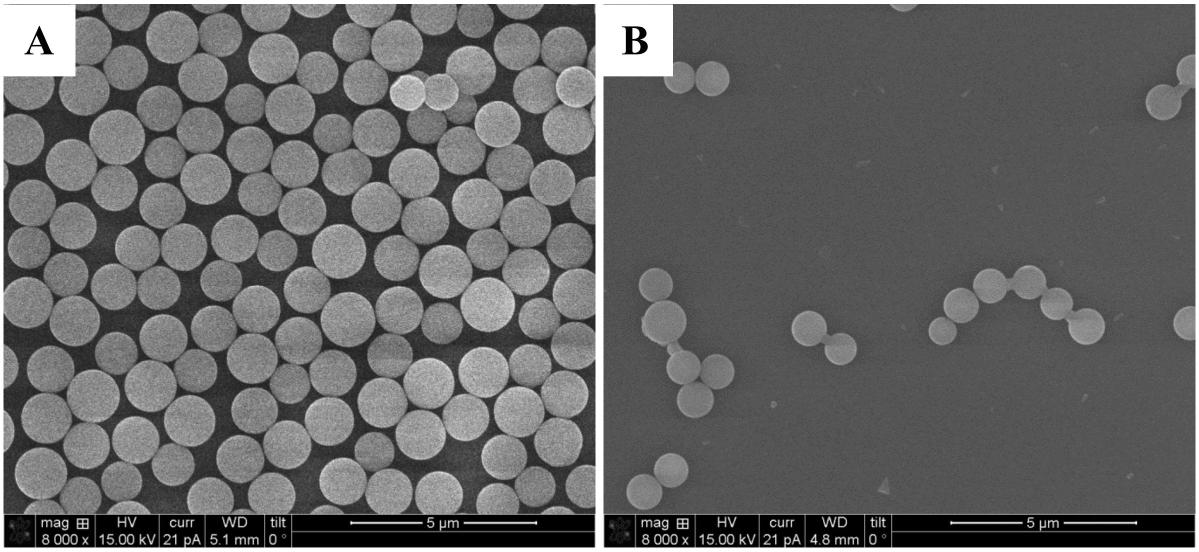

Figure S2. Scanning electron micrographs of 1100 nm AEAP3-modified particles with reactant AEAP3 concentrations of (A) 11.47 mM and (B) 14.34 mM. While the particles in (A) exhibited smooth morphology, undesirable particle agglomeration occurred at higher AEAP3 concentrations.

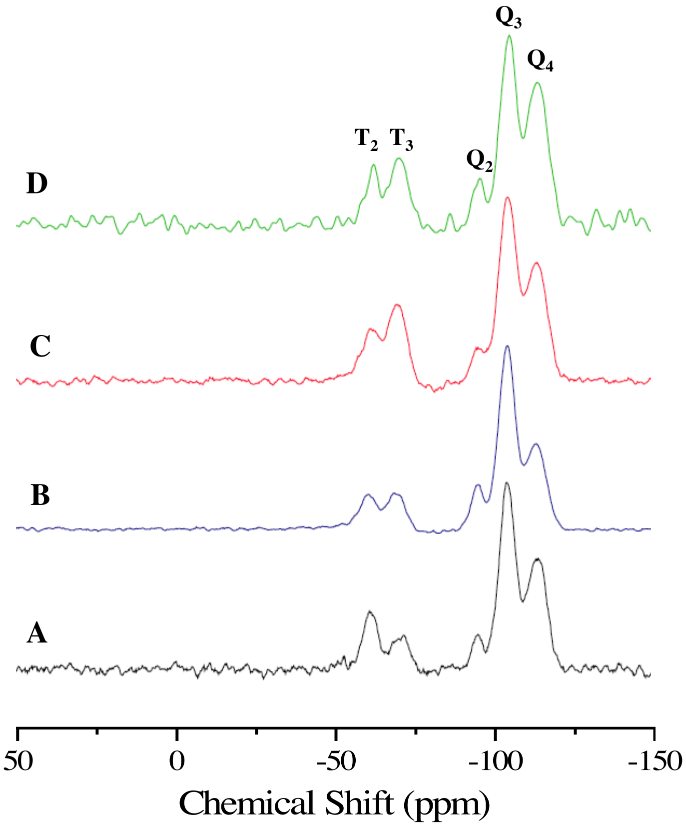

Figure S3. Solid-state CP/MAS ^{29}Si NMR spectra of (A) 1100; (B) 450; (C) 150; and (D) 30 nm AEAP3-modified

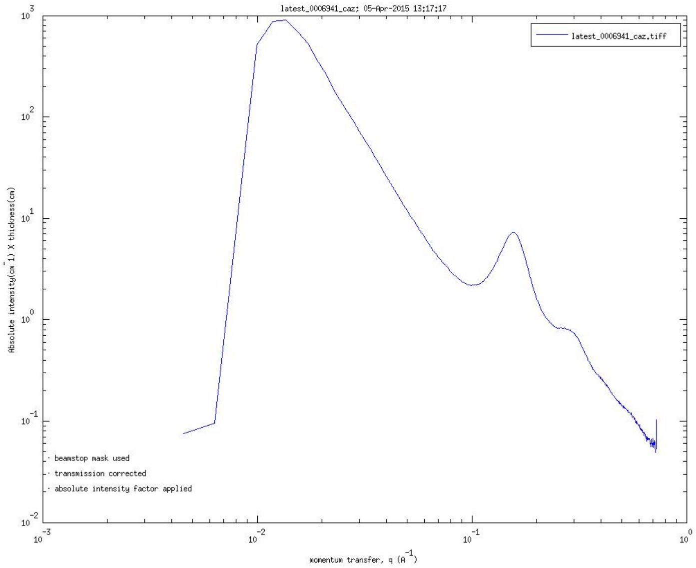

Figure S4. Raw X-ray scattering profile for unmodified 30 nm MSNs. The absence of low-angle (i.e., <0.1 Å^{-1}) waves corresponding to scattering from individual particles should be noted.

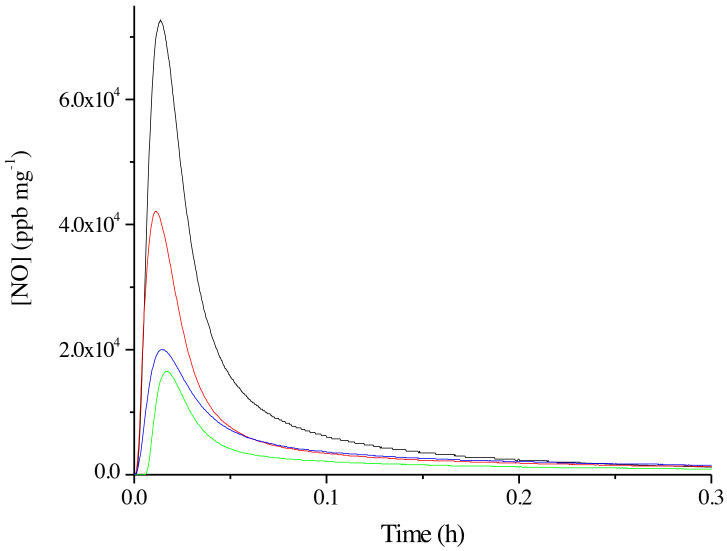

Figure S5. Real-time NO-release profiles for 30 nm MAP3/NO (black), AHAP3/NO (red), AEAP3/NO (green), and DET3/NO (blue) particles after ~20 min in PBS (pH 7.4) at 37 °C.

Table S1. Characterization of AEAP3-modified 1100 nm mesoporous silica particles as a function of reaction aminosilane concentration.[a]

[AEAP3] (mM)	$t_{1/2}$ (min)[b]	t_d (h)[c]	$[NO]_t$ (µmol mg^{-1})[d]
1.43	14.2±1.6	7.2±1.2	0.56±0.09
2.87	15.8±4.2	7.5±0.3	0.69±0.04
5.73	16.8±4.1	9.0±0.5	1.02±0.04
11.47	25.6±5.0	11.1±0.7	1.41±0.19

[a] Error bars represent standard deviation for n≥3 separate syntheses. [b] Half-life of NO release. [c] NO-release duration; time required for NO concentrations to reach ≤10 ppb mg^{-1}. [d] Total NO release.

Table S2. Elemental analysis of 150 nm APTES, BTMS, and MPTMS particles.

Silane Modification	Carbon wt%	Hydrogen wt%	Nitrogen wt%
APTES	13.21	4.08	4.49
BTMS	23.16	4.79	0.16
MPTMS	25.58	4.84	0.88

Sample calculation of *N*-diazeniumdiolate formation efficiency for AEAP3 MSNs:

For 1100 nm AEAP3 MSNs, a nitrogen content of 4.87% was measured by elemental analysis.

$$4.87\% = \frac{0.0487\ mg\ nitrogen}{1\ mg\ scaffold}$$

$$\frac{0.0487\ mg\ nitrogen}{1\ mg\ scaffold} * \frac{1\ g\ nitrogen}{1000\ mg\ nitrogen} * \frac{1}{14.007\frac{g}{mol}\ nitrogen} * \frac{10^6\ \mu mol}{1\ mol} = \frac{3.48\ \mu mol\ nitrogen}{mg}$$

$$\frac{3.48\ \mu mol\ nitrogen}{mg} * \frac{1\ mol\ secondary\ amine}{2\ mol\ amine} = \frac{1.74\ \mu mol\ secondary\ amine}{mg}$$

Upon *N*-diazeniumdiolate formation, two moles of NO react with one mole of secondary amine. The theoretical maximum NO storage is thus:

$$\frac{1.74\ \mu mol\ secondary\ amine}{mg} * \frac{2\ mol\ NO}{1\ mol\ secondary\ amine} = \frac{3.48\ \mu mol\ NO}{mg}$$

Compare to the actual NO storage as measured by chemiluminescence (1.41 µmol/mg):

$$\frac{1.41\ \mu mol\ NO/mg}{3.48\ \mu mol\ NO/mg} * 100 = 40.7\%$$