Supporting Information

Inorganic/Organic Hybrid Silica Nanoparticles as a Nitric Oxide Delivery Scaffold

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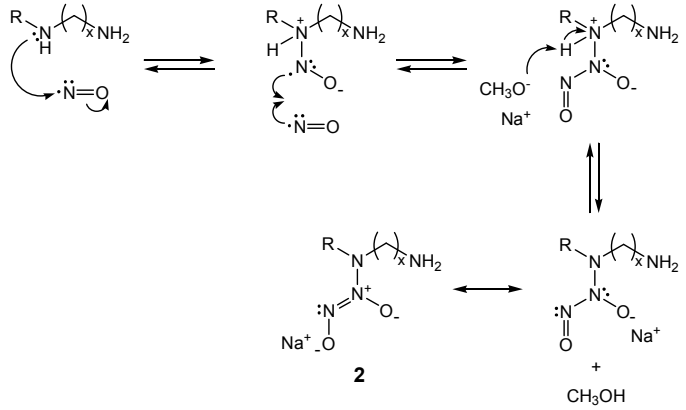
Scheme S1. Mechanism of *N*-diazeniumdiolate formation on the secondary amine nitrogen of a polyamine-based alkoxysilane precursor under basic (NaOMe) conditions (Adapted from Drago et al.[a])[b,c]



[a]Drago, R. S.; Karstetter, B. R. *J. Am. Chem. Soc.* **1961**, *83*, 1819-1822; Ragsdale, R. O.; Karstetter, B. R.; Drago, R. S. *Inorg. Chem.* **1965**, *4*, 420-422. [b]R is an alkyltrimethoxysilane group. [c]One equivalent secondary amine nitrogen (nucleophile) reacts with two equivalents of NO (Steps 1 and 2). The strong base, NaOMe promotes the deprotonation from the secondary nitrogen (Step 3), shifting the reaction equilibrium toward *N*-diazeniumdiolate formation. The anionic structure of the NO adduct is stabilized with a sodium countercation.

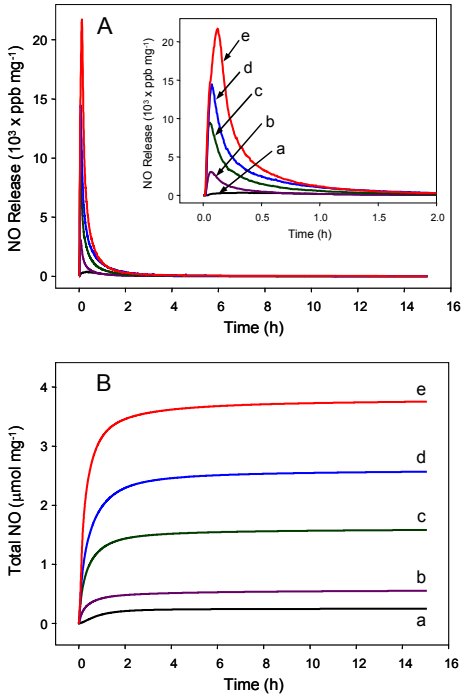


Figure S2. Real-time NO release profiles (A) and total NO release amount (B) for *N*-diazeniumdiolate-modified silica particles with different concentrations of AHAP3 precursors: (a) 10, (b) 10, (c) 25, (d) 35, and (e) 45 mol% (balance TEOS). While (a) was synthesized via a "post-formation" method, (b) – (e) were prepared via a "pre-formation" strategy. Inset plot (A') represents the expansion of graph (A) from 0 to 2 h.