

Supporting Information

Nitric Oxide-Releasing Xerogels Synthesized from *N*-Diazeniumdiolate-Modified Silane Precursors

Wesley L. Storm and Mark H. Schoenfisch*

University of North Carolina at Chapel Hill, CB 3290, Chapel Hill, NC 27599

Table S1. Stability of *N*-diazeniumdiolate-modified xerogels in different storage conditions.

Table S2. Fragmentation/leaching from 5, 10, 15 mol% AEAP, MAP, and EAiB.

Table S3. Elemental analysis of pre-diazeniumdiolated xerogels.

Table S4. Nitric oxide release predicted by elemental analysis.

Figure S1. Nitric oxide release from *N*-diazeniumdiolate-modified silane precursors before and after ~6 months of storage.

Figure S2. Nitric oxide release from precursor sols before and after reaction.

Figure S3. Initial 12 h of NO release from 15 mol% MAP/NO-PTMOS, EAiB/NO-PTMOS, and AEAP/NO-PTMOS xerogels.

Figure S4. Cytotoxicity of leaching solutions from 15 mol% AEAP/NO-PTMOS, MAP/NO-PTMOS, and EAiB/NO-PTMOS.

Table S1. Nitric oxide release totals from 15 mol% AEAP/PT xerogels when stored in different atmospheric conditions and temperatures for 10 d. The control xerogel was analyzed immediately after drying. Each film was analyzed in 30 mL PBS (pH 7.4, 37 °C)

Storage conditions	Temperature	NO Total ($\mu\text{mol cm}^{-2}$)
Control	Control	2.1
Vacuum sealed	-20 °C	2.0
Vacuum sealed	23 °C	2.2
Ambient	23 °C	0.8

Table S2. Total amount of silicon liberated from each xerogel system after 14 d. Xerogels were stored in 10 mM PBS (pH 7.4, 37 °C) and transferred to new solutions at 4 or 7 d. Cumulative Si concentrations are the integrated totals from each time point as determined via ICP-OES.

Aminosilane	mol %	Cumulative Si concentration (ppm)	% Fragmentation
AEAP	5	1.08 ± 0.19	0.82 ± 0.14
AEAP	10	2.28 ± 0.41	1.73 ± 0.31
AEAP	15	3.03 ± 0.15	2.30 ± 0.11
MAP	5	1.70 ± 0.33	1.50 ± 0.29
MAP	10	4.09 ± 0.34	3.60 ± 0.30
MAP	15	5.46 ± 0.60	4.81 ± 0.53
EAIb	5	1.57 ± 0.87	1.39 ± 0.76
EAIb	10	3.69 ± 1.87	3.25 ± 1.65
EAIb	15	3.40 ± 1.22	3.00 ± 1.08

Table S3. Carbon, hydrogen, and nitrogen content of pre-diazeniumdiolated xerogels as determined via elemental combustion analysis.

Xerogel	%C	%H	%N
5% MAP/PTMOS	36.11 ± 1.01	7.42 ± 0.03	1.19 ± 0.24
10% MAP/PTMOS	35.24 ± 0.18	7.02 ± 0.14	2.80 ± 0.17
15% MAP/PTMOS	33.84 ± 0.32	6.85 ± 0.08	4.26 ± 0.58
15% AEAP/PTMOS	32.63 ± 0.27	6.67 ± 0.09	5.91 ± 0.33
15% EAiB/PTMOS	33.96 ± 3.73	6.55 ± 0.13	4.06 ± 0.09

Table S4. Comparison of NO release totals measured directly using chemiluminescence with NO release totals predicted by elemental analysis.

Xerogel (15 mol%)	predicted $\mu\text{mol NO mg}^{-1}$	experimental $\mu\text{mol NO mg}^{-1}$	% error
MAP/PTMOS	1.35	1.03	35.0
AEAP/PTMOS	1.21	1.00	17.5
EAiB/PTMOS	1.45	1.22	18.9

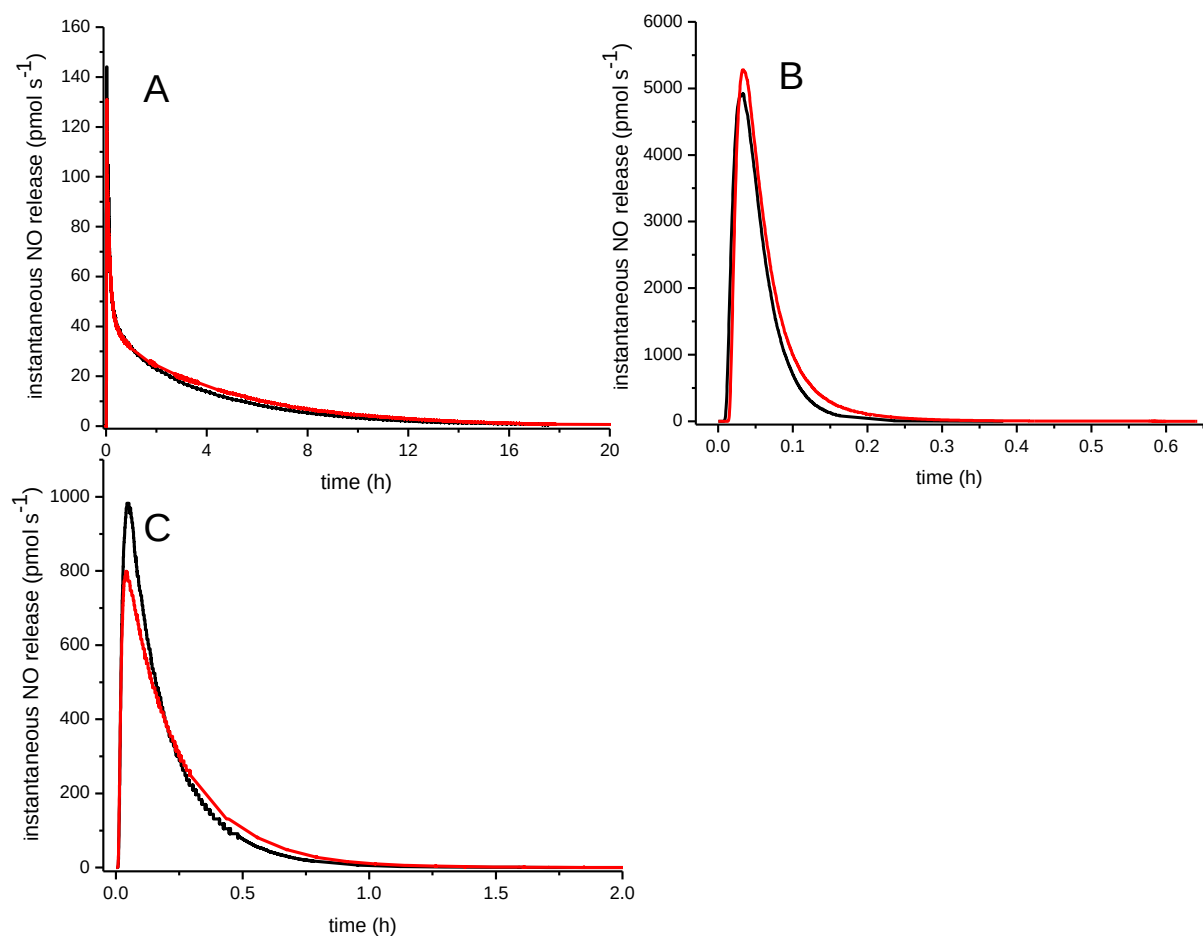


Figure S1. Nitric oxide release from (A) AEAP/NO, (B) MAP/NO and (C) EAiB/NO either immediately after synthesis (red line) or vacuum sealed at -20 °C for approximately 6 months (black line). Diazeniumdiolated precursors were diluted 1:10 in 1 M NaOH and 10 μ L of the resulting solution was added to 30 mL PBS (pH 7.4, 37 °C) and analyzed using a chemiluminescent NOA.

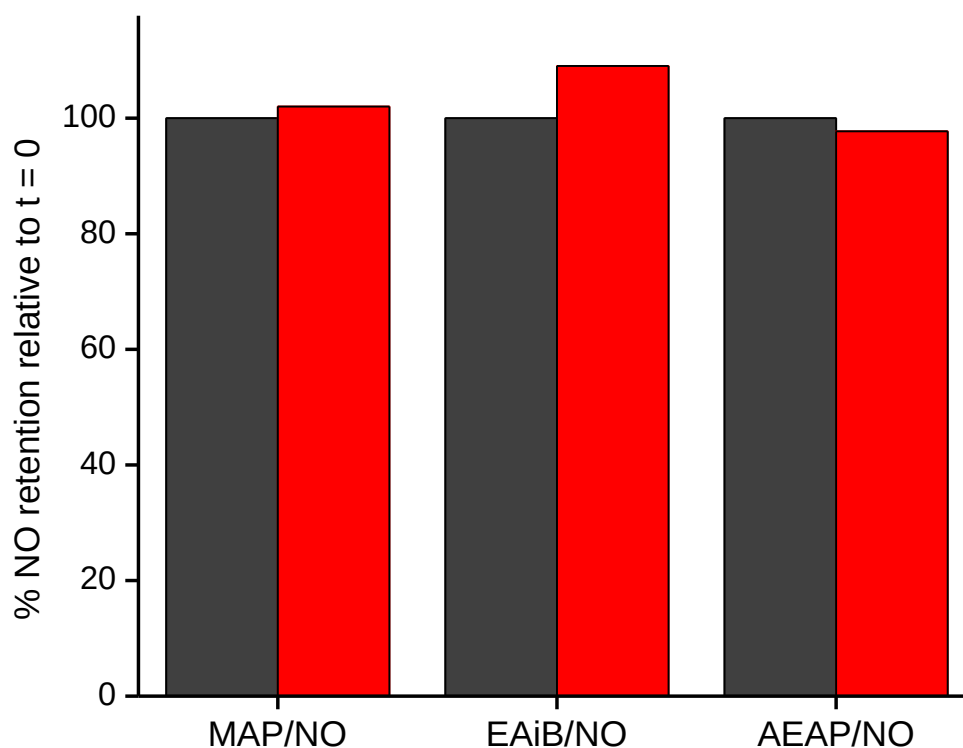


Figure S2. Total NO release from MAP/NO, EAiB/NO, and AEAP/NO sols at the beginning (dark grey bar) and end (red bar) of the reaction. Measurements were made with chemiluminescence after injecting 20 μ L of the sol directly into 30 mL PBS (pH 7.4, 37 $^{\circ}$ C). Data is normalized to the “0” reaction time, which was analyzed immediately after addition of each *N*-diazoniumdiolate NO donor.

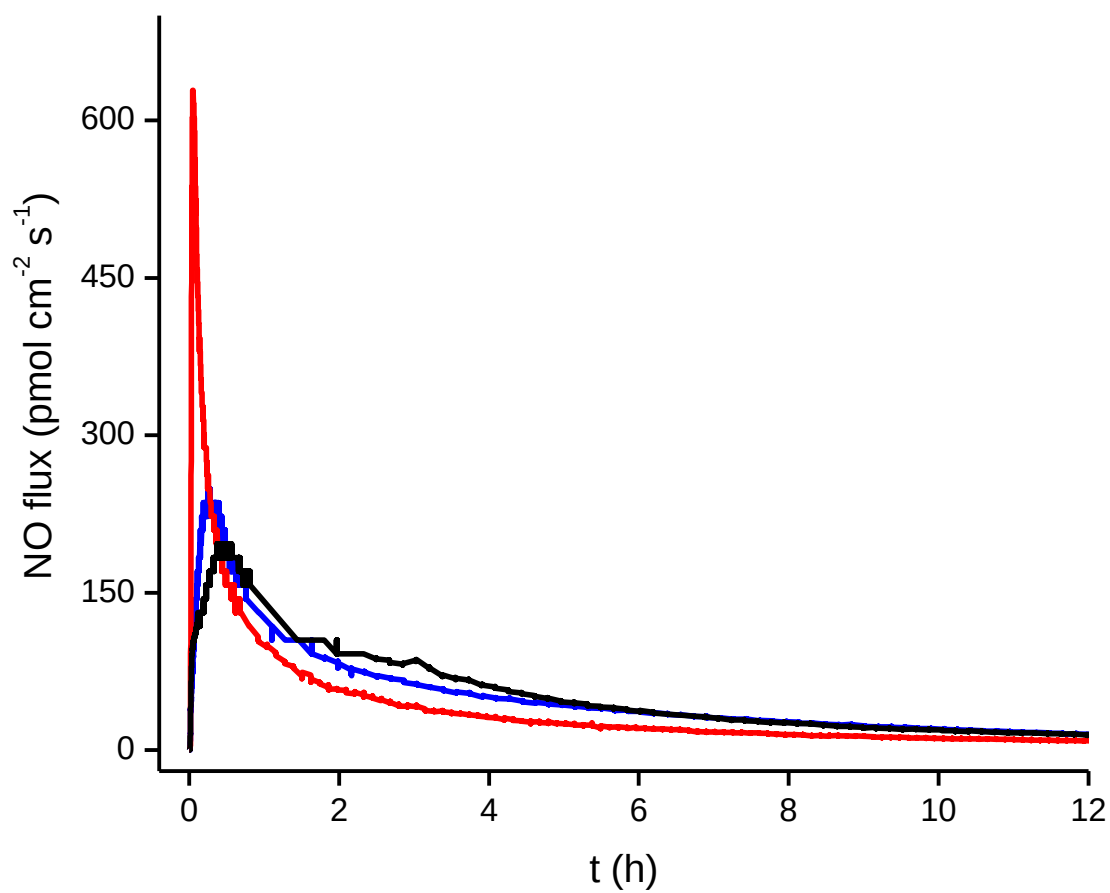


Figure S3. The initial 12 h of NO release from 15 mol% MAP/NO-PTMOS (red), EAIb/NO-PTMOS (black) and AEAP/NO-PTMOS (blue). Release measured using chemiluminescence in 30 mL PBS (pH 7.4) at 37 °C.

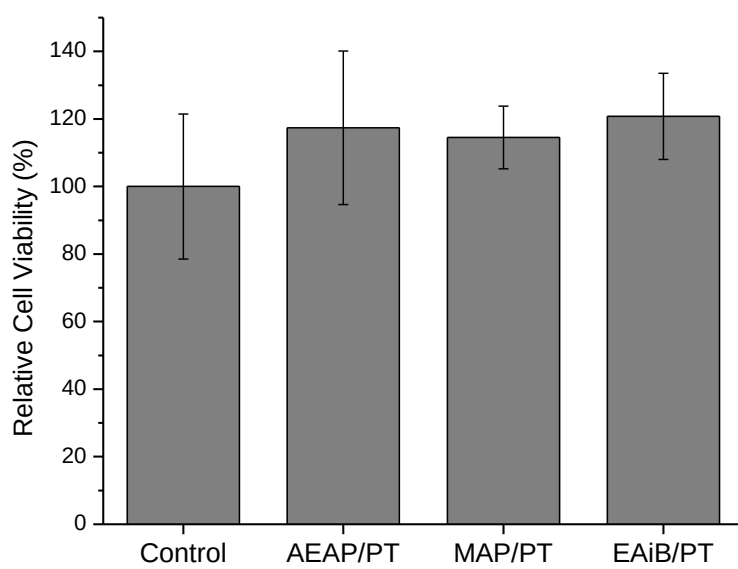


Figure S4. Cytotoxicity of AEAP/PT, MAP/PT, and EAiB/PT leachate solutions against L929 fibroblast cells.