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Nitric oxide release from a biodegradable cysteine-based polyphosphazene

Electronic Supplementary Information

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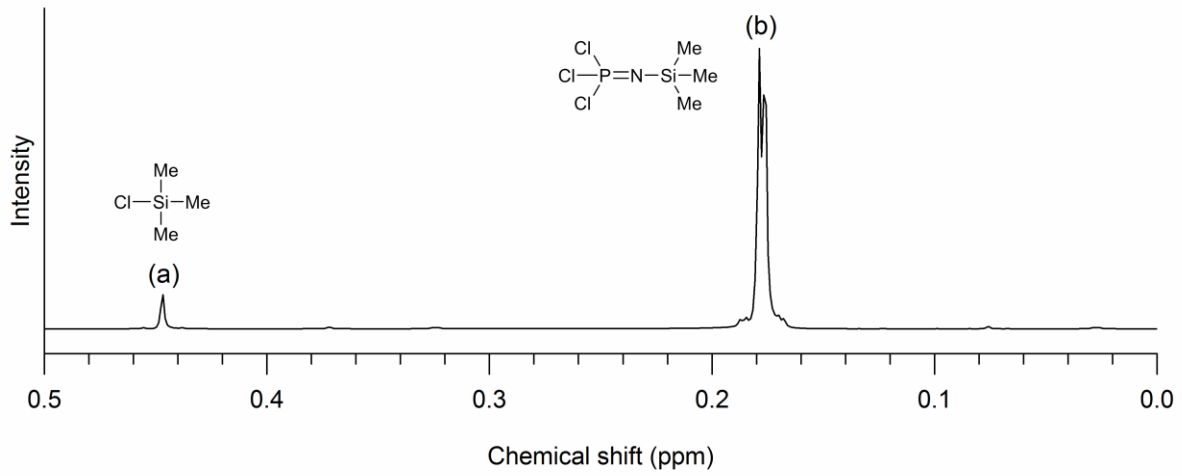

Figure S1. ^{1}H NMR of trichloro(trimethylsilyl)phosphoranimine. ^{1}H NMR δ_H/ppm (400 MHz, $CDCl_3$): (a) 0.45 (Me_3SiCl impurity, approx. 5%), (b) 0.18 (distorted doublet, $Cl_3P{=}NSiMe_3$).

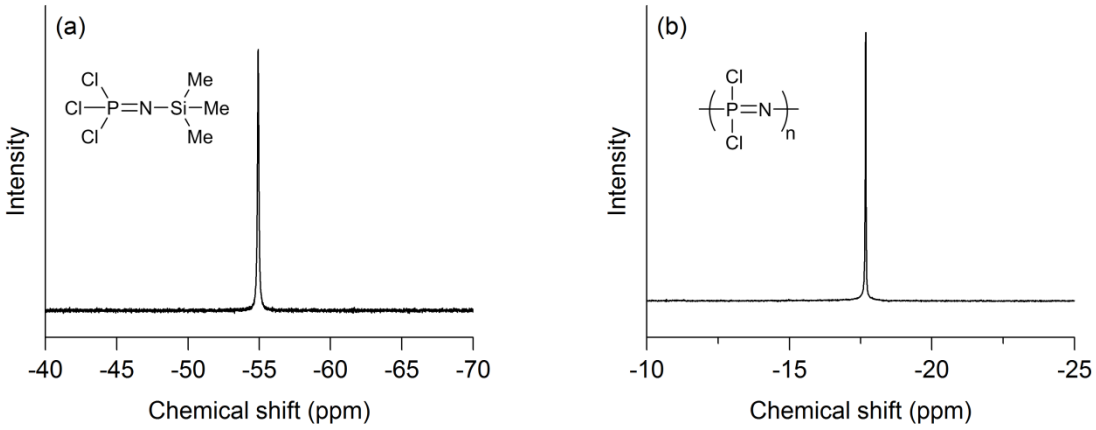

Figure S2. ^{31}P NMR of (a) trichloro(trimethylsilyl)phosphoranimine and (b) poly(dichlorophosphazene).^{31}P NMR δ_P/ppm (162 MHz, $CDCl_3$): (a) -55 ($Cl_3P{=}NSiMe_3$), (b) -18 ($-PCl_2{=}N-$). Spectra referenced to triphenylphosphine (-6 ppm, not shown).

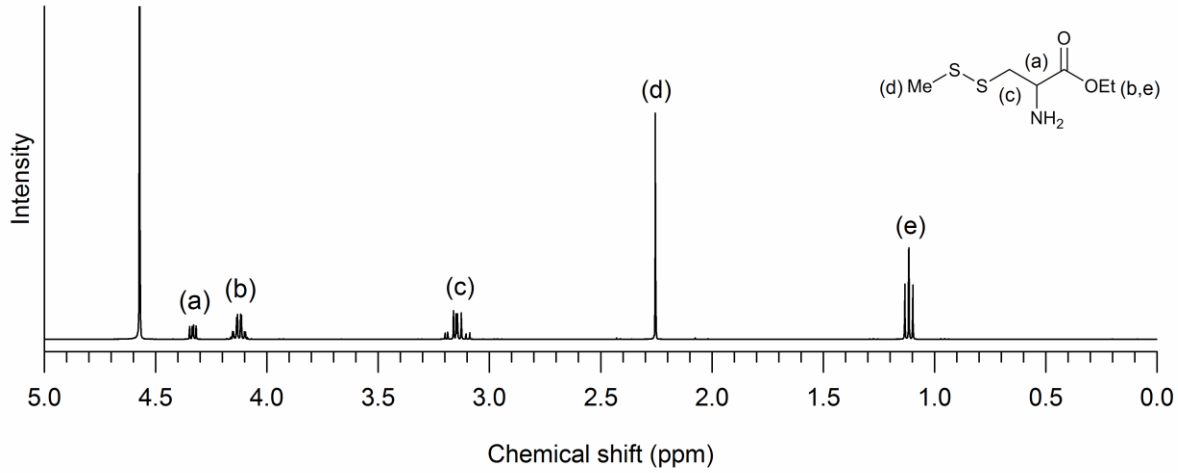

Figure S3. ^{1}H NMR of ethyl *S*-methylthiocysteinate. ^{1}H NMR δ_H/ppm (400 MHz, D_2O): (a) 4.34 (dd, -CH-), (b) 4.18 – 4.07 (m, -OCH_2-), (c) 3.20 – 3.09 (m, -$SSCH_2$-), (d) 2.25 (s, -$SSCH_3$), (e) 1.12 (t, -CH_3). Spectrum referenced to maleic acid (6.2 ppm, not shown).

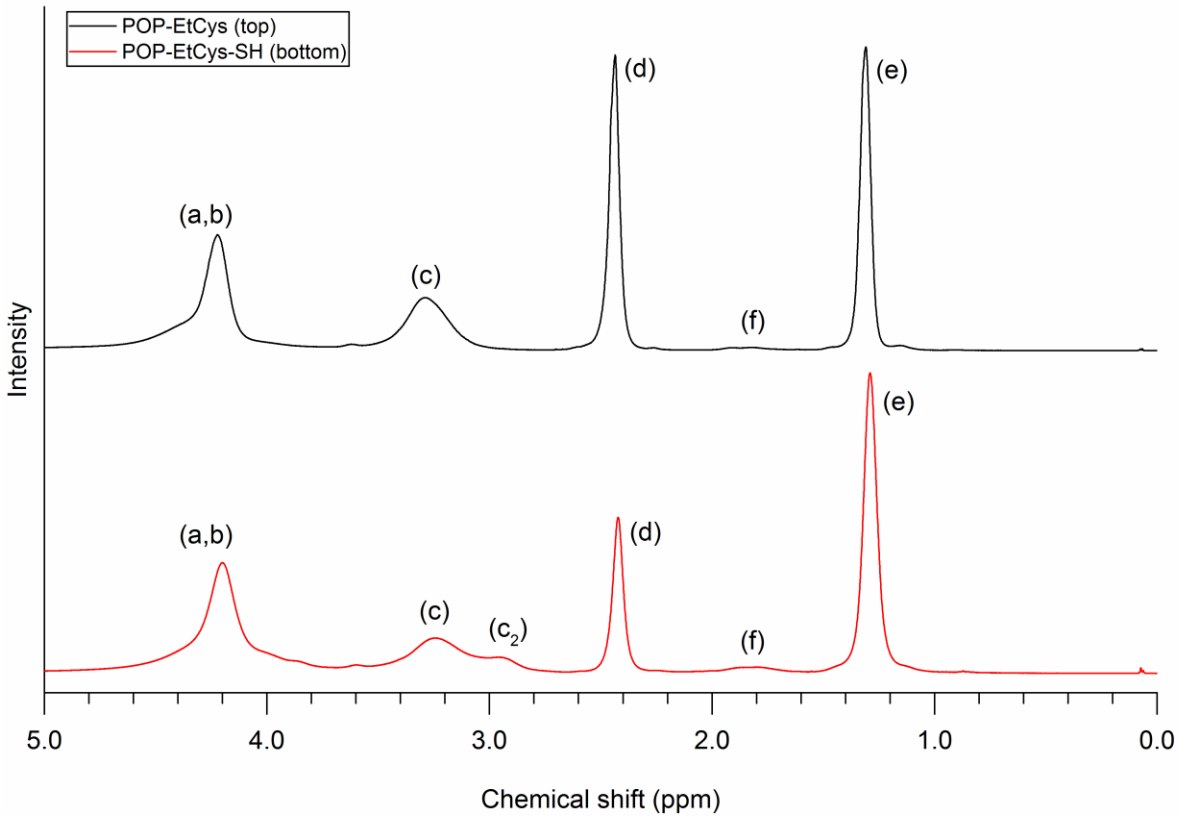

Figure S4. ^{1}H NMR of poly(bis(ethyl *S*-methylthiocysteinyl)phosphazene) (POP-EtCys) and poly(ethyl *S*-methylthiocysteinyl-*co*-ethyl cysteinyl phosphazene) (POP-EtCys-SH). ^{1}H NMR δ_H/ppm (400 MHz, $CDCl_3$): (a,b) 4.6 – 4.0 (-CH-, -OCH_2-), (c) 3.29 (-$SSCH_2$-), (c_2) 2.95 (-SCH_2-), (d) 2.43 (-$SSCH_3$), (e) 1.31 (-CH_3), (f) 1.83 (-SH). Concentration: 20 mg mL^{-1}.

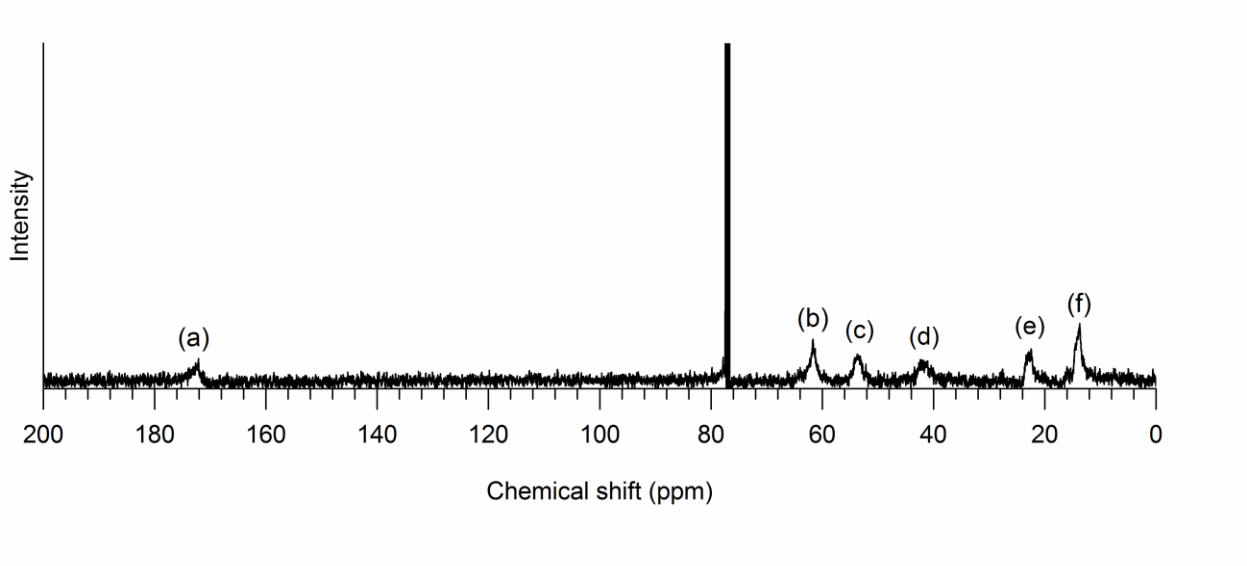

Figure S5. ^{13}C NMR of poly(ethyl *S*-methylthiocysteinyl-*co*-ethyl cysteinyl phosphazene) (POP-EtCys-SH). ^{13}C NMR δ_C/ppm (100 MHz, $CDCl_3$): (a) 173 ($-CO_2-$), (b) 61 ($-OCH_2-$), (c) 54 (-CH-), (d) 43 ($-SSCH_2-$), (e) 23 ($-SSCH_3$), (f) 14 ($-CH_3$). Concentration: 200 mg mL^{-1}.

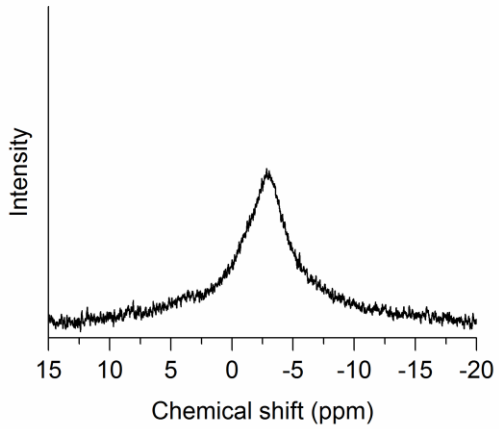

Figure S6. ^{31}P NMR of poly(ethyl *S*-methylthiocysteinyl-*co*-ethyl cysteinyl phosphazene) (POP-EtCys-SH). ^{31}P NMR δ_P/ppm (162 MHz, $CDCl_3$): -2.6. Spectrum referenced to triphenylphosphine (-6 ppm, not shown) to determine central value, then reacquired in the absence of a reference to avoid peak overlap. Concentration: 200 mg mL^{-1}.

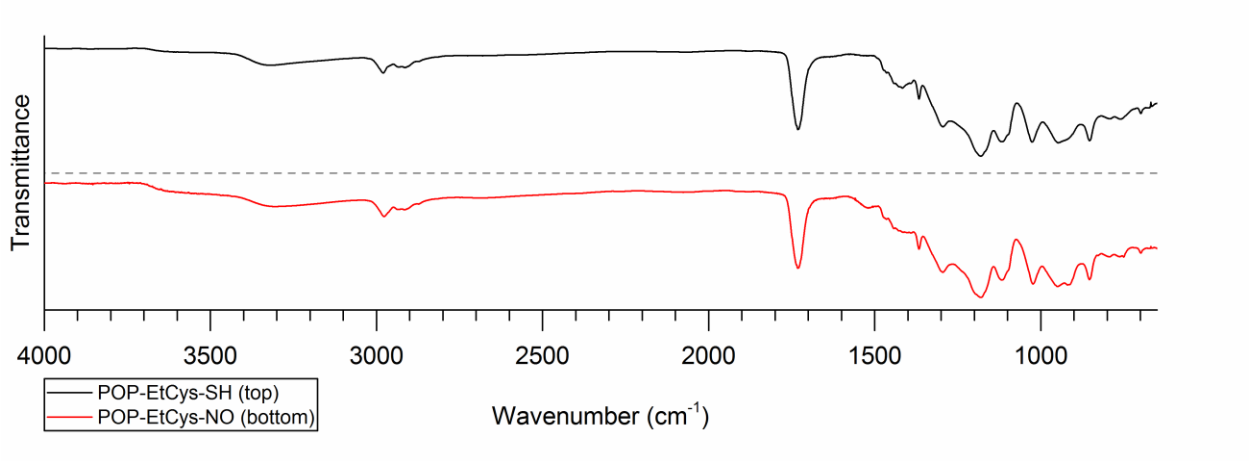

Figure S7. ATR-FTIR spectra of poly(ethyl *S*-methylthiocysteinyl-*co*-ethyl cysteinyl phosphazene) (POP-EtCys-SH) (top), and the *S*-nitrosated derivative (POP-EtCys-NO) (bottom). POP-EtCys-SH: IR ν_{max}/cm^{-1}: 3320, 2980, 2914, 1732, 1417, 1367, 1295, 1180, 1117, 1026, 948, 853, 792, 760, 698. POP-EtCys-NO: IR ν_{max}/cm^{-1}: 3300, 2977, 2915, 1732, 1520, 1367, 1296, 1180, 1117, 1024, 950, 920, 853, 794, 763, 750, 699.

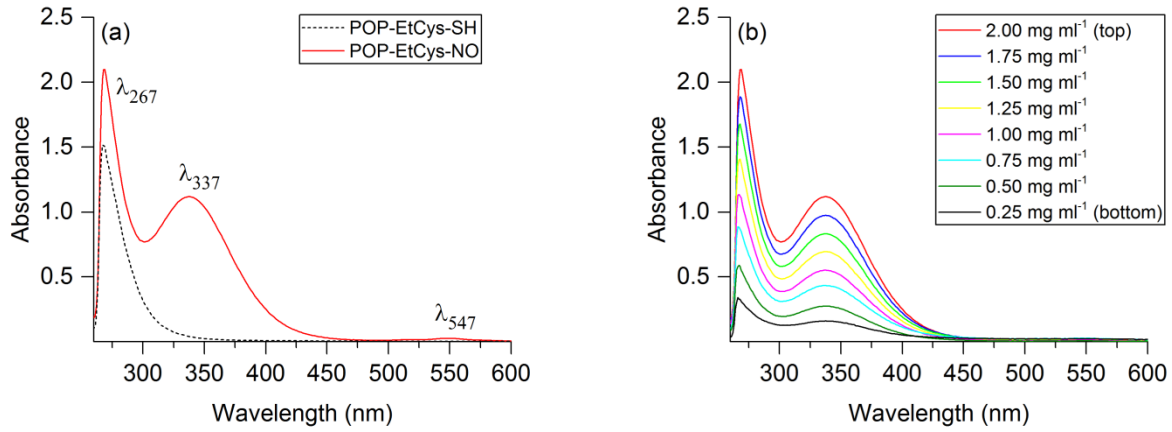

Figure S8. UV-Vis spectra of poly(ethyl *S*-methylthiocysteinyl-*co*-ethyl cysteinyl phosphazene) (POP-EtCys-SH) and the *S*-nitrosated derivative (POP-EtCys-NO) in DMF. The characteristic absorbances associated with the successful formation of primary *S*-nitrosothiols are shown in (a), while (b) illustrates the relationship between polymer concentration and the prominent absorbance at 337 nm that is often attributed to a π→π* transition.