Supplementary Information for:

Rubber-Elasticity and Electrochemical Activity of Iron(II) Tris(bipyridine) Crosslinked Poly(dimethylsiloxane) Networks

Zachary H. Williams,[a] Emily D. Burwell,[a] Ambre E. Chiomento,[a] Kyle J. Demsko,[a] Jacob T. Pawlik,[a] Shannon O. Harris,[a] Mark R. Yarolimek,[a] Megan B. Whitney,[a] Michael Hambourger,[a,*] Alexander D. Schwab[a,*]

[a] A. R. Smith Department of Chemistry, Appalachian State University, 525 Rivers Street, Boone, NC 28608

Corresponding author email addresses:

hambourgerms@appstate.edu (M.H.), schwabad@appstate.edu (A.D.S.).

Table of Contents:

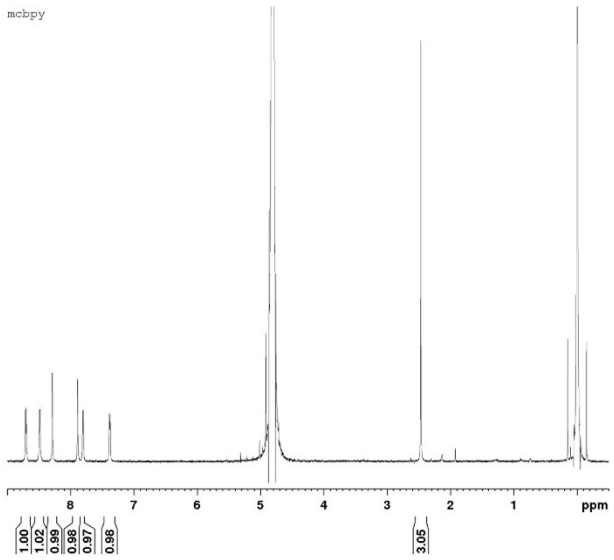

Figure S1. ^{1}H NMR spectrum of **1** in D_2O.

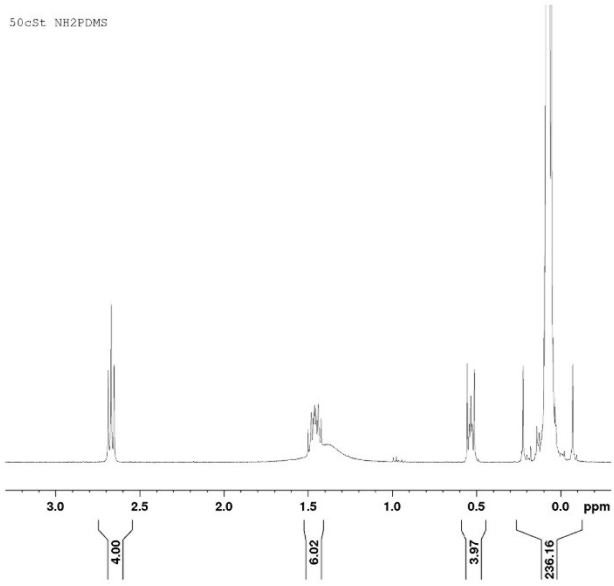

Figure S2. ^{1}H NMR spectrum of 50 cSt NH_2PDMS in $CDCl_3$.

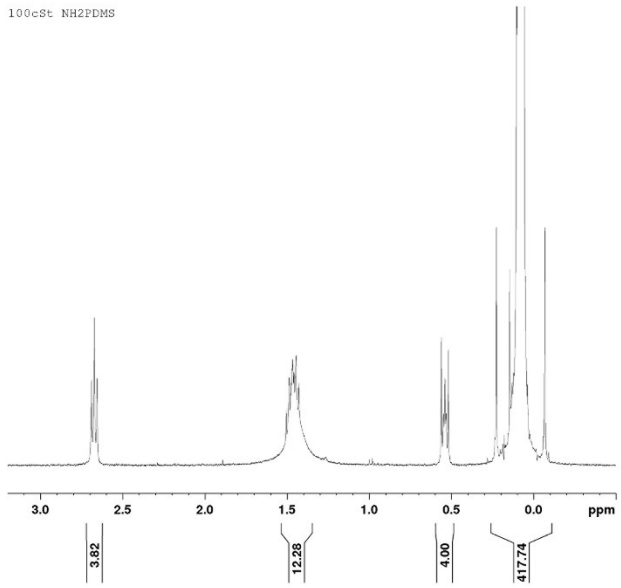

Figure S3. ^{1}H NMR of 100 cSt NH_2PDMS in $CDCl_3$.

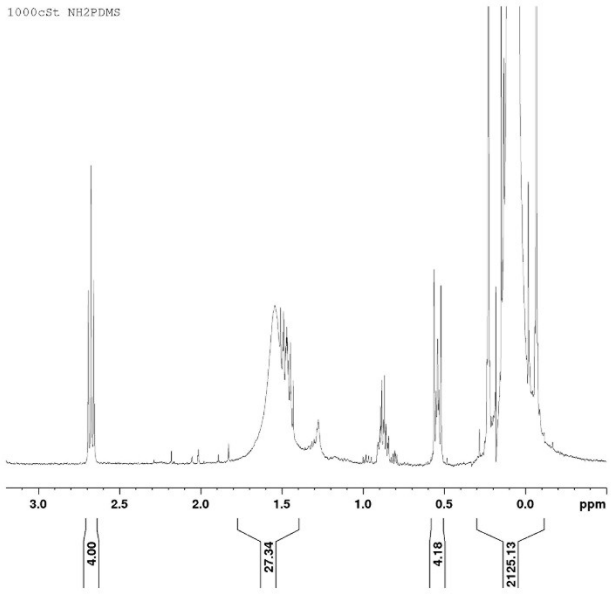

Figure S4. ^{1}H NMR of 1000 cSt NH_2PDMS in $CDCl_3$

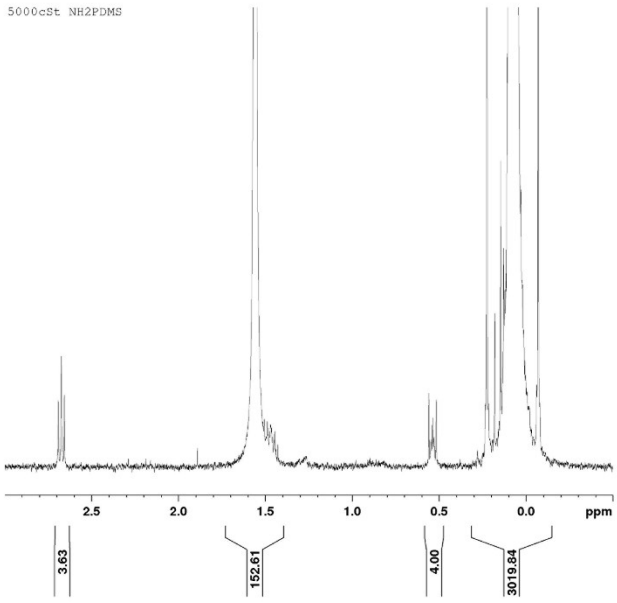

Figure S5. ^{1}H NMR of 5000 cSt NH_2PDMS in $CDCl_3$.

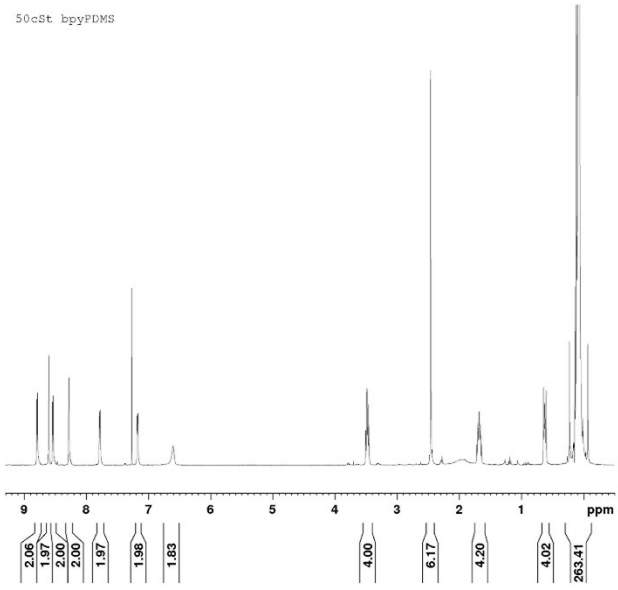

Figure S6. ^{1}H NMR of bpyPDMS made from 50cSt NH_2PDMS in $CDCl_3$.

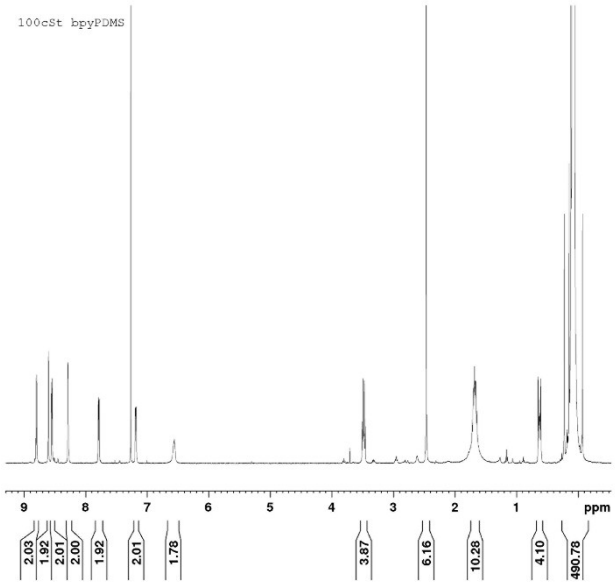

Figure S7. ^{1}H NMR of bpyPDMS made from 100 cSt NH_2PDMS in $CDCl_3$.

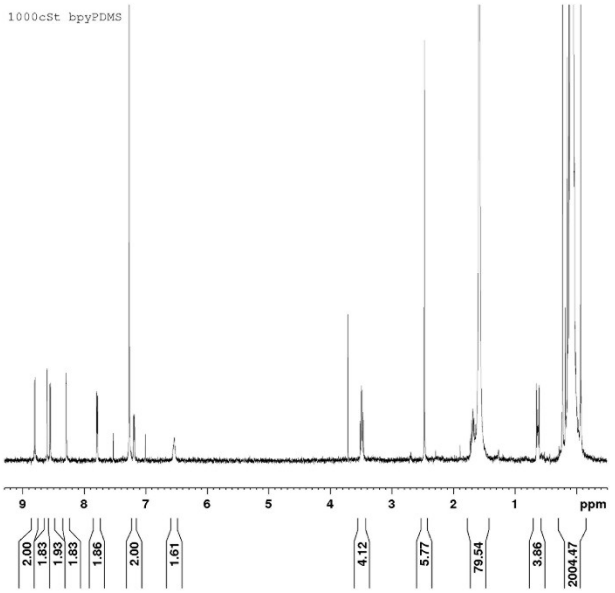

Figure S8. ^{1}H NMR of bpyPDMS made from 1000 cSt NH_2PDMS in $CDCl_3$.

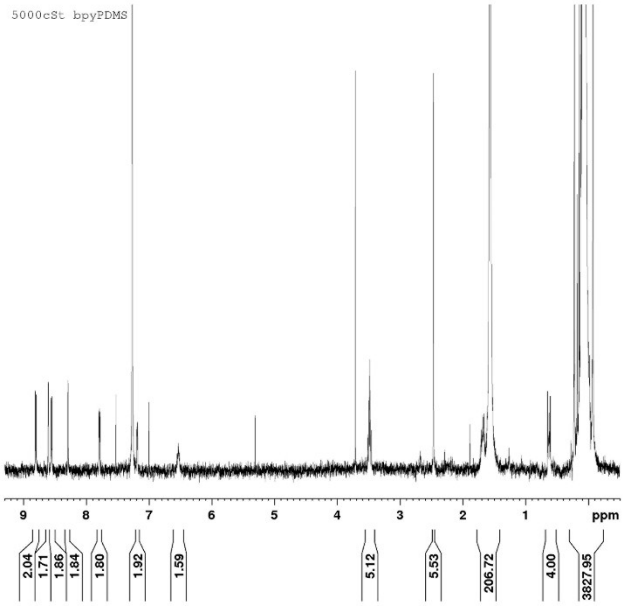

Figure S9. ^{1}H NMR of bpyPDMS made from 5000 cSt NH_2PDMS in $CDCl_3$.

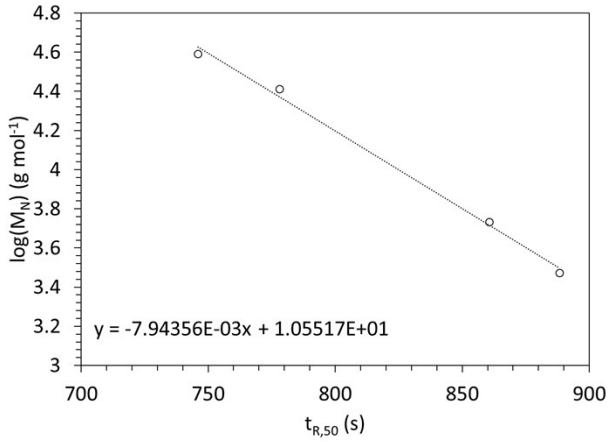

Figure S10. GPC molecular weight calibration curve made from number average molecular weight determined by ^{1}H NMR of NH_2PDMS samples and the $t_{R,50}$ retention times.

Table S1. Spectrophotometric titration data used to make Figure 4. In the table, m_i and m_f are the masses of the cuvette before and after an addition of a 0.0715% (w/w) $Fe(BF_4)_2 \cdot 6H_2O$ solution in THF (except addition 0), m_{FeBF4} is the cumulative mass of $Fe(BF_4)_2 \cdot 6H_2O$ added to the cuvette, and m_{THF} is the mass of THF in the cuvette. Concentrations of –bpy endgroups, [-bpy], and iron(II), $[Fe^{2+}]$, are calculated assuming the volume of the solution in the cuvette is equal to the volume of pure THF calculated as m_{THF}/ρ ($\rho = 0.880$ g mL^{-1}). A_{540} is the absorbance of the solution at 540 nm.

addition	m_i (g)	m_f (g)	m_{FeBF4} (µg)	m_{THF} (g)	$[Fe^{2+}]$ (µM)	[-bpy] (µM)	A_{540}
0	9.0581	11.1212	0	2.062	0	333	0.005
1	11.1219	11.1661	2.47	2.107	30.5	326	0.181
2	11.1661	11.2104	49.4	2.151	59.9	319	0.384
3	11.2104	11.2544	73.9	2.195	87.8	313	0.633
4	11.2543	11.2984	98.5	2.239	115	307	0.877
5	11.2985	11.3422	123	2.283	140	301	0.907
6	11.3421	11.3865	148	2.327	165	295	0.92
7	11.3864	11.4304	172	2.371	189	290	0.923
8	11.4299	11.4742	197	2.414	212	284	0.925

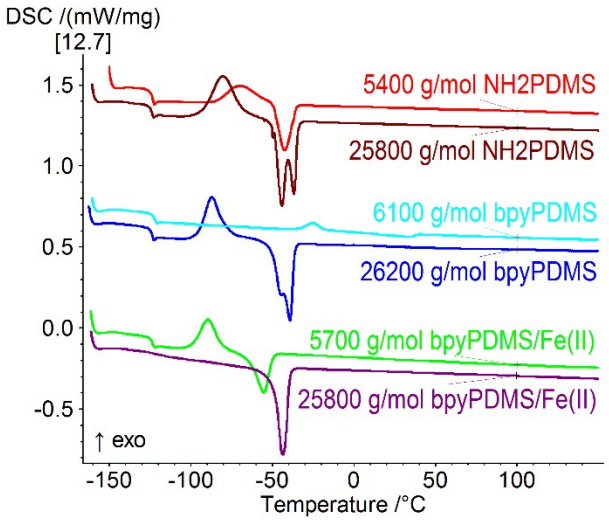

Figure S11. DSC thermograms of amine terminated PDMS (NH2PDMS), bipyridine-terminated PDMS (bpyPDMS), and bpyPDMS crosslinked with $Fe(BF_4)_2$ with –bpy:Fe^{2+} equal to 3:1 (bpyPDMS/Fe(II)). Additional thermograms are shown in Figure 5.

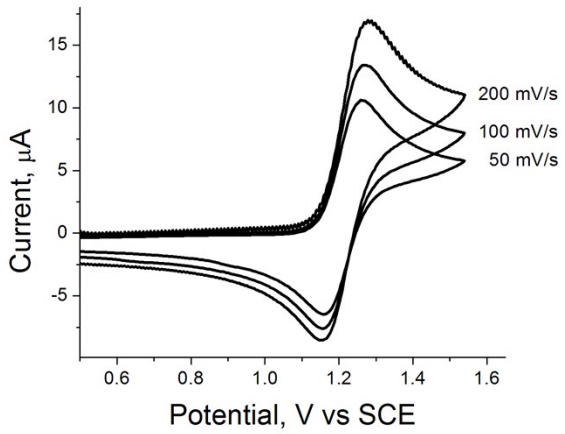

Figure S12. Cyclic voltammograms of 3300 g/mol bpyPDMS/Fe(II) drop cast on a glassy carbon working electrode, recorded at three scan rates. Voltammograms were recorded in 0.1 M $TBAPF_6$ in acetonitrile. The electrode was equilibrated by cycling fifty times from -0.3 to 1.5 V at 100 mV/s, prior to recording the voltammograms shown.

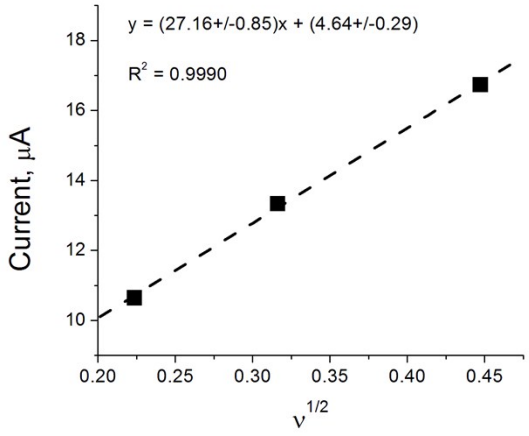

Figure S13. Anodic peak current as a function of the square root of scan rate ($\nu^{1/2}$) for the three voltammograms shown in Figure S12.