

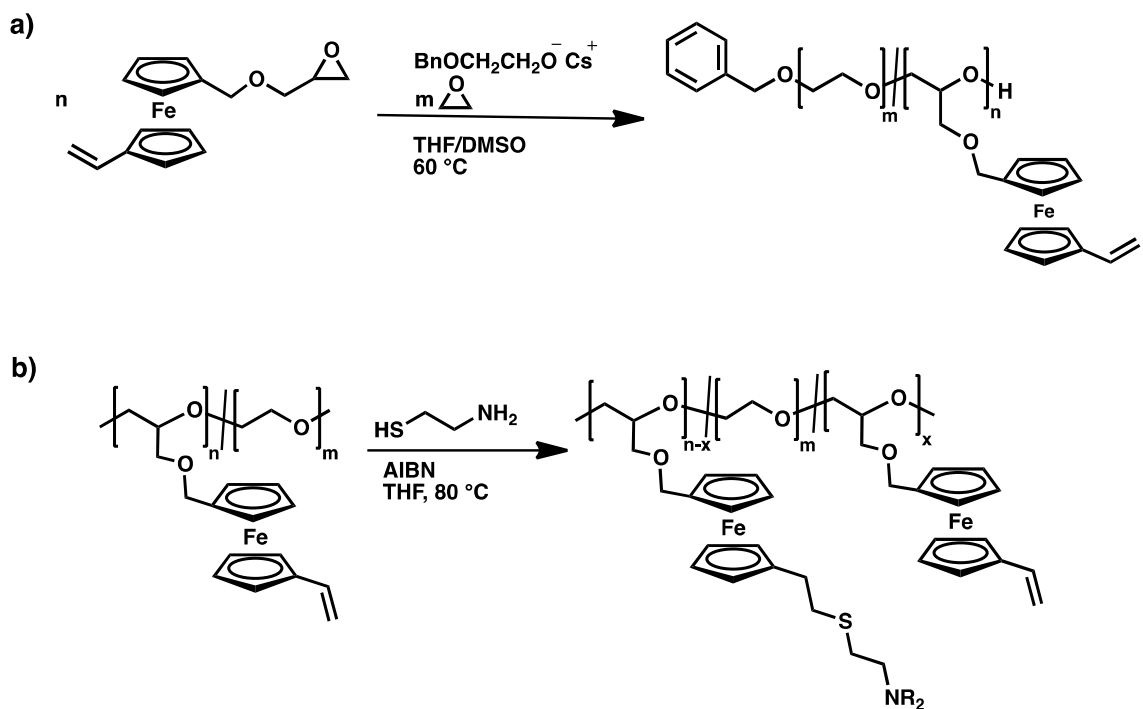
Supporting Information

Triple-Stimuli Responsive Ferrocene-Containing PEGs in Water and on Surface

*Arda Alkan, Christian Steinmetz, Katharina Landfester, and Frederik R. Wurm**

Max Planck Institute for Polymer Research (MPIP), Ackermannweg 10, 55128 Mainz,
Germany

Contact address: wurm@mpip-mainz.mpg.de, phone: 0049 6131 379 581, fax: 0049 6131 370
330.



Scheme S1. Synthetic strategy of P[VfcGE₁-*ran*-CAfcGE₉-*co*-EO₂₀₆]. a) Anionic ring-opening copolymerization of EO and VfcGE. b) Thiol-ene addition of cysteamine with available vinyl groups in P[VfcGE₁₀-*co*-EO₂₀₆].

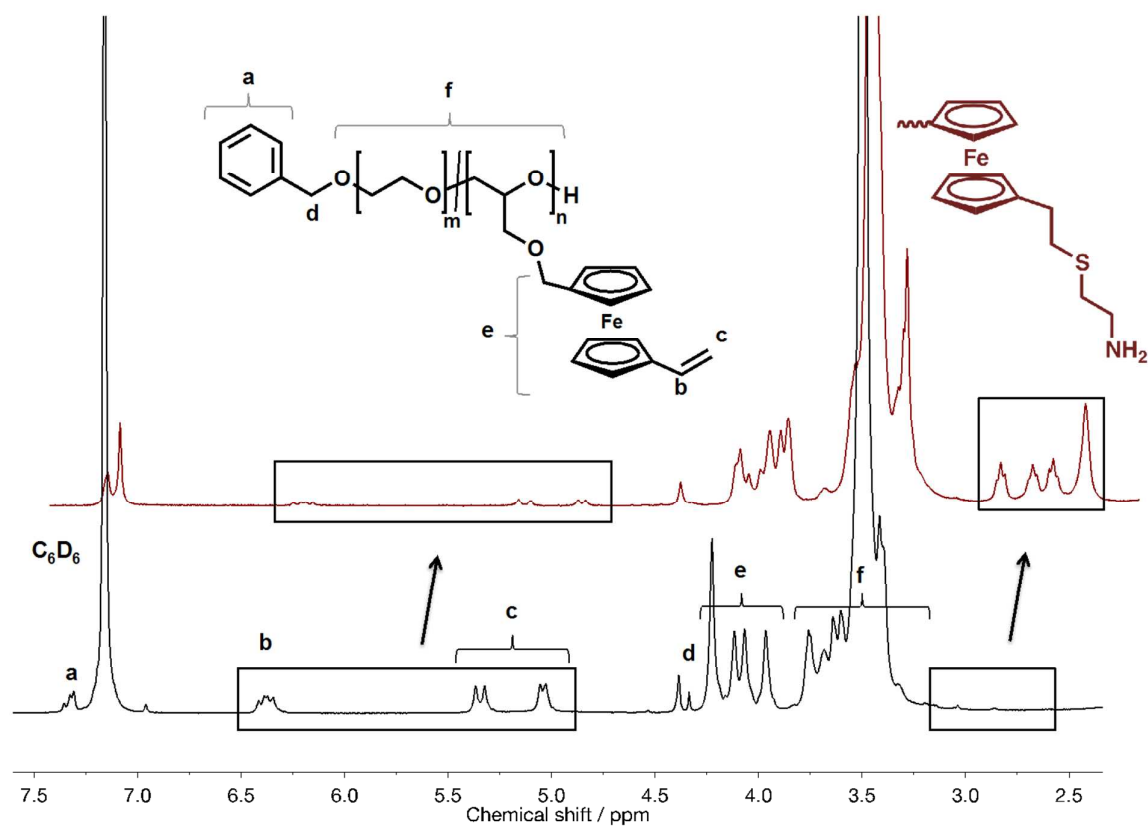


Figure S1. Functionalization of P[VFcGE₁₀-*co*-EO₂₀₆] copolymer with cysteamine followed by ^1H NMR (C_6D_6 , 400 MHz, 298 K).

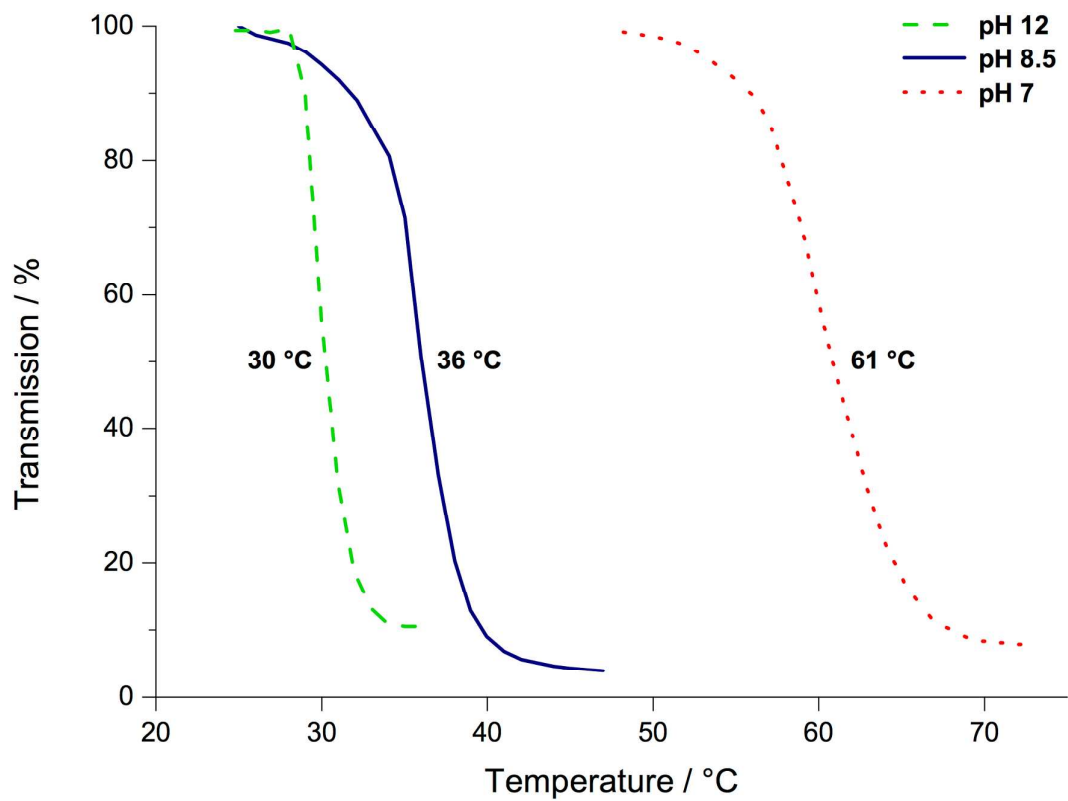
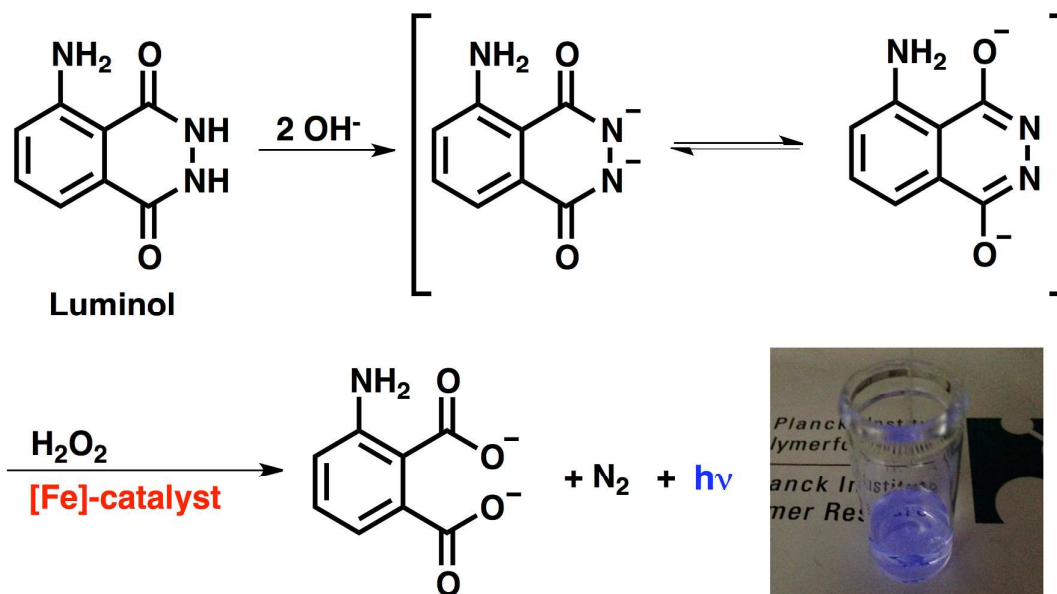


Figure S2. Turbidity measurements (heating curves) of P[VfcGE₁-*ran*-CAfcGE₉-*co*-EO₂₀₆] copolymer ($\lambda=500$ nm; heat rate=1 °C/min) at three different pH values (pH 12.0, 8.5 and 7.0).



Scheme S2. The chemiluminescence of luminol under basic conditions using hydrogen peroxide as oxidizing agent and iron (Fe) as catalyst. The photo shows the color of the chemiluminescence of the polymer solution below the T_c .

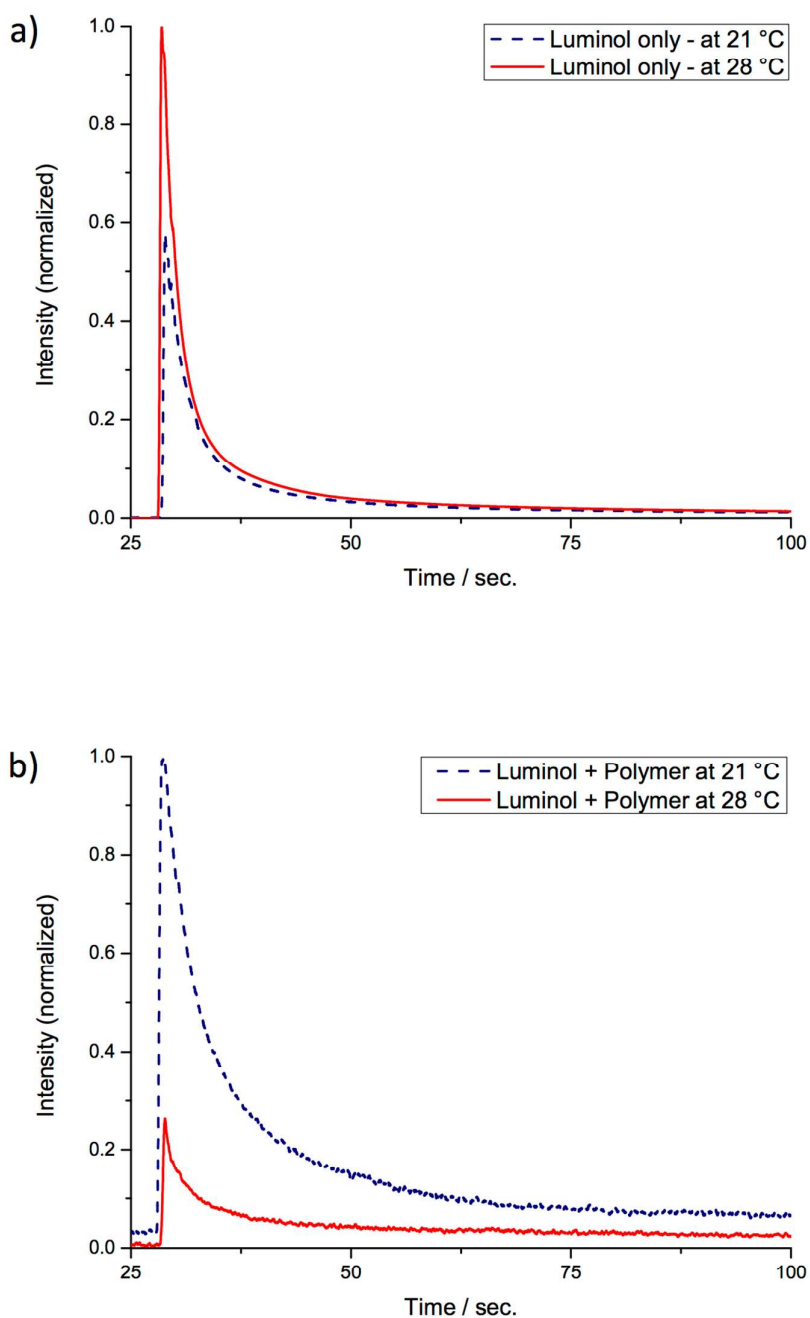
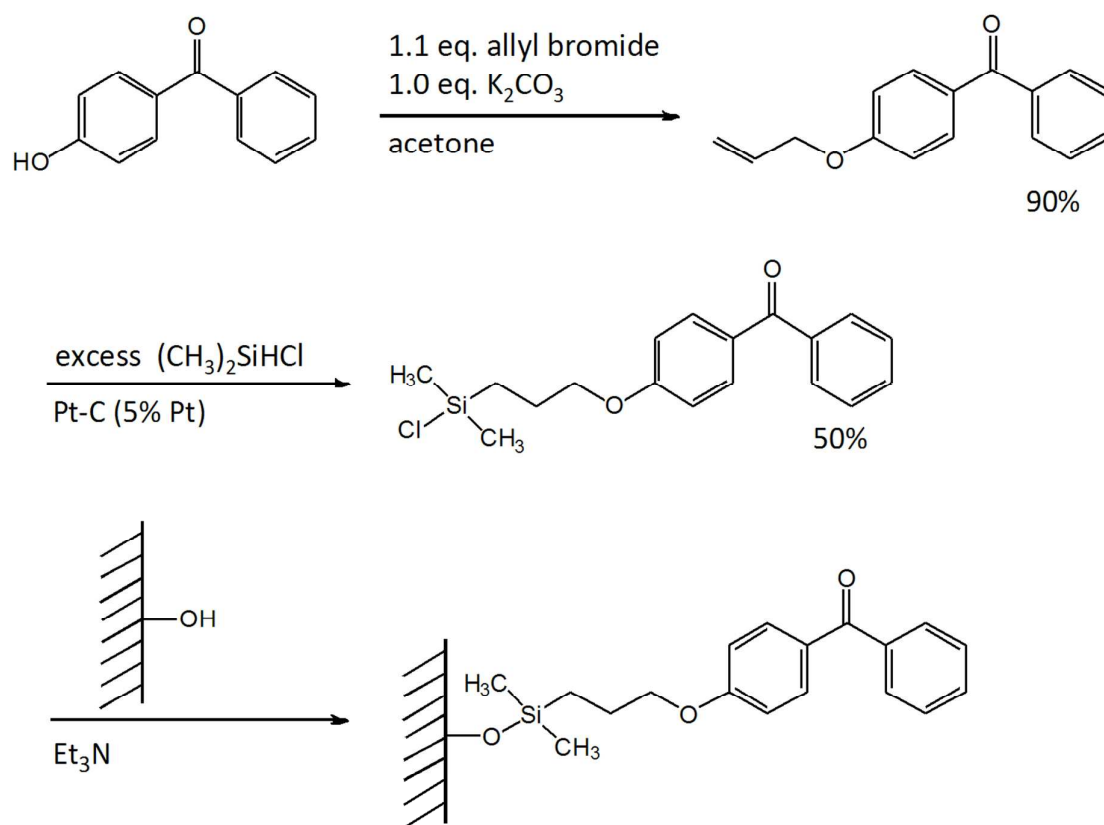


Figure S3. Comparing the chemiluminescence of luminol with and without P[VfcGE₁-*ran*-CAfcGE₁₃-*co*-EO₇₅] as catalyst. a) Chemiluminescence of luminol after the addition of hydrogen peroxide at 21 °C and 28 °C. b) Chemiluminescence of luminol after the addition hydrogen peroxide in the presence of the functionalized copolymer at 21 °C (below T_c) and 28 °C (above T_c).



Scheme S3. Synthesis of 4-(3'-chlorodimethylsilyl(propoxybenzophenone) and functionalization of glass surfaces.

The thicknesses of the polymer films (Figure S4) were analyzed by scratching the polymer film off the surface with a cannula. The vertical scratch, which is seen in the middle of the pictures (Figure S5), enables the thickness measurement of the polymer film.

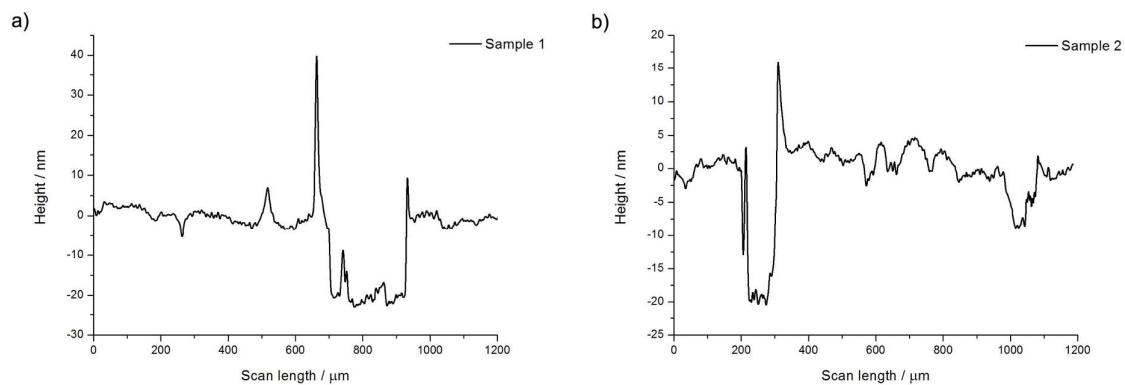


Figure S4. Height profiles of polymer modified glass surfaces: a) Sample 1 and b) Sample 2.

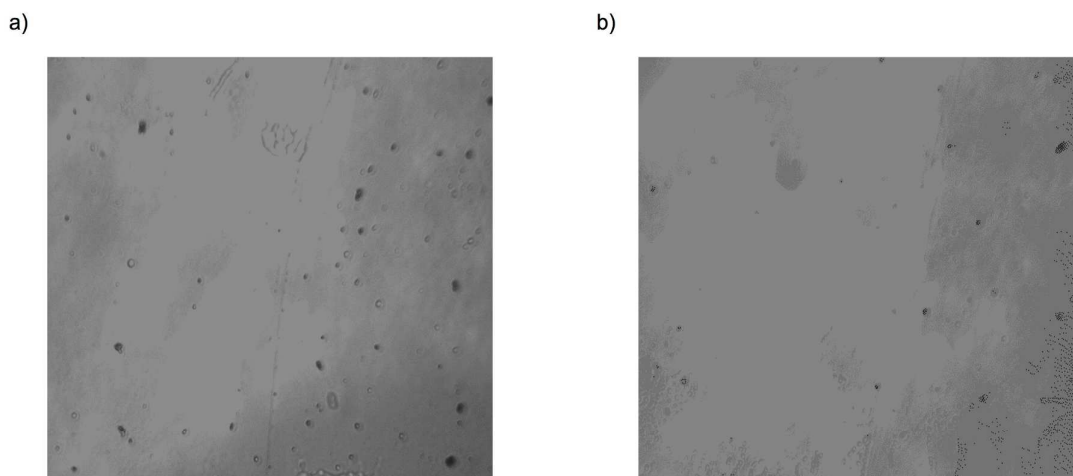


Figure S5. Topographic pictures of polymer modified glass surfaces: a) Sample 1 and b) Sample 2.

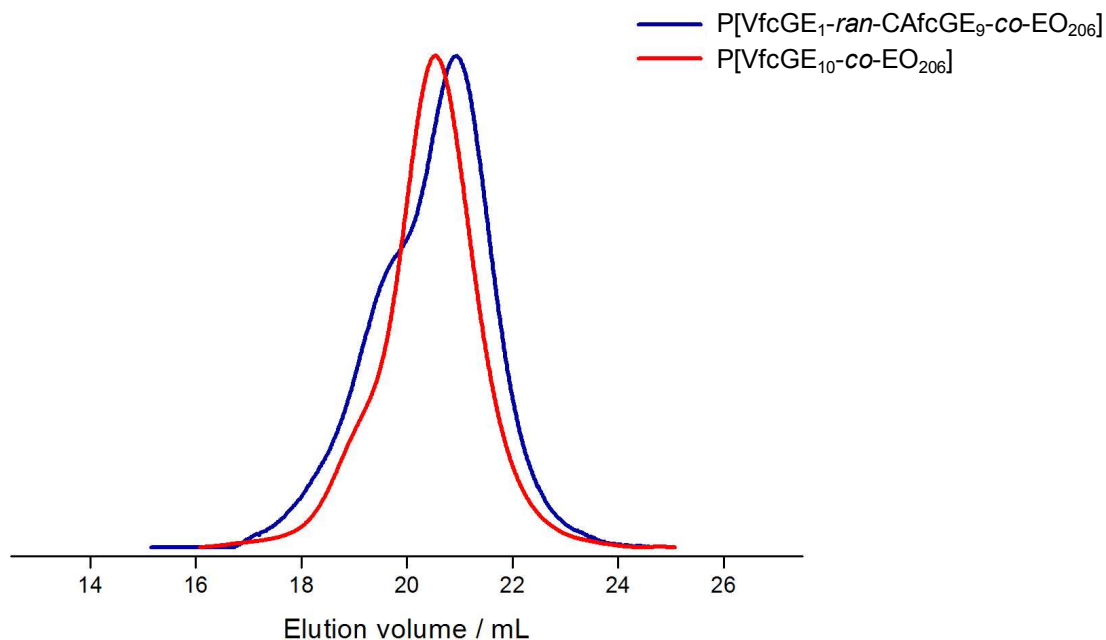


Figure S6. SEC traces of P[VFcGE₁₀-co-EO₂₀₆] (red) and after functionalization with cysteamine P[VFcGE₁-ran-CAfcGE₉-co-EO₂₀₆] (blue) (DMF, RI detection, 1 mL min⁻¹).

Table S1. Polymer Characterization.

no.	sum	VfcGE ^a / %	M_n^a / g/mol	M_n^b / g/mol	\bar{D}	T_c / °C (@pH 7)
1	BnOCH ₂ O-P[VFcGE ₁₀ -co-EO ₂₀₆]	4.8	12300	2200	1.09	37
1'	P[VFcGE ₁ -ran-CAVfcGE ₉ -co-EO ₂₀₆]	-	13000	-	-	61
2	BnOCH ₂ O-P[VFcGE ₁₄ -co-EO ₇₅]	15.4	7500	1800	1.14	-
2'	P[VFcGE ₁ -ran-CAVfcGE ₁₃ -co-EO ₇₅]	-	8500	-	-	-
3	Ph(CH ₂ O) ₂ -P[VFcGE ₇ -co-EO ₁₁₅]	5.5	7200	3000	1.07	33
3'	P[VFcGE ₁ -ran-CAVfcGE ₆ -co-EO ₁₁₅]	-	7700	-	-	63

a) Determined from ¹H NMR; b) Determined via SEC in DMF vs. PEG.

Table S2. Temperature Dependent Contact Angle Measurements of Sample 1 and 2 and References 1 and 2.

Temperature / °C		10	20	30	40	50	60	70
Sample 1	$\theta / ^\circ$	54.0	54.7	51.4	53.7	58.4	69.1	75.6
	$\Delta\theta / ^\circ$	2.6	1.7	0.8	0.2	2.0	0.3	0.7
Sample 2	$\theta / ^\circ$	61.6	49.7	49.2	51.2	68.9	61.5	80.8
	$\Delta\theta / ^\circ$	0.9	0.2	0.5	0.3	0.3	0.5	1.0
Reference	$\theta / ^\circ$	61.9	56.0	43.2	43.1	35.2	34.8	30.1
	$\Delta\theta / ^\circ$	2.0	3.6	0.3	0.5	4.1	1.9	2.8

Table S3. pH Dependent Contact Angle Measurements of Sample 1 and 2 and References 1 and 2.

pH		5.0	7.0	9.0
Sample 1	$\theta / ^\circ$	50.3	54.7	74.6
	$\Delta\theta / ^\circ$	0.9	1.7	0.3
Sample 2	$\theta / ^\circ$	47.1	49.7	72.4
	$\Delta\theta / ^\circ$	1.7	0.2	0.2
Reference 2	$\theta / ^\circ$	46.2	56.0	43.2
	$\Delta\theta / ^\circ$	0.2	3.6	2.2