Supporting Information

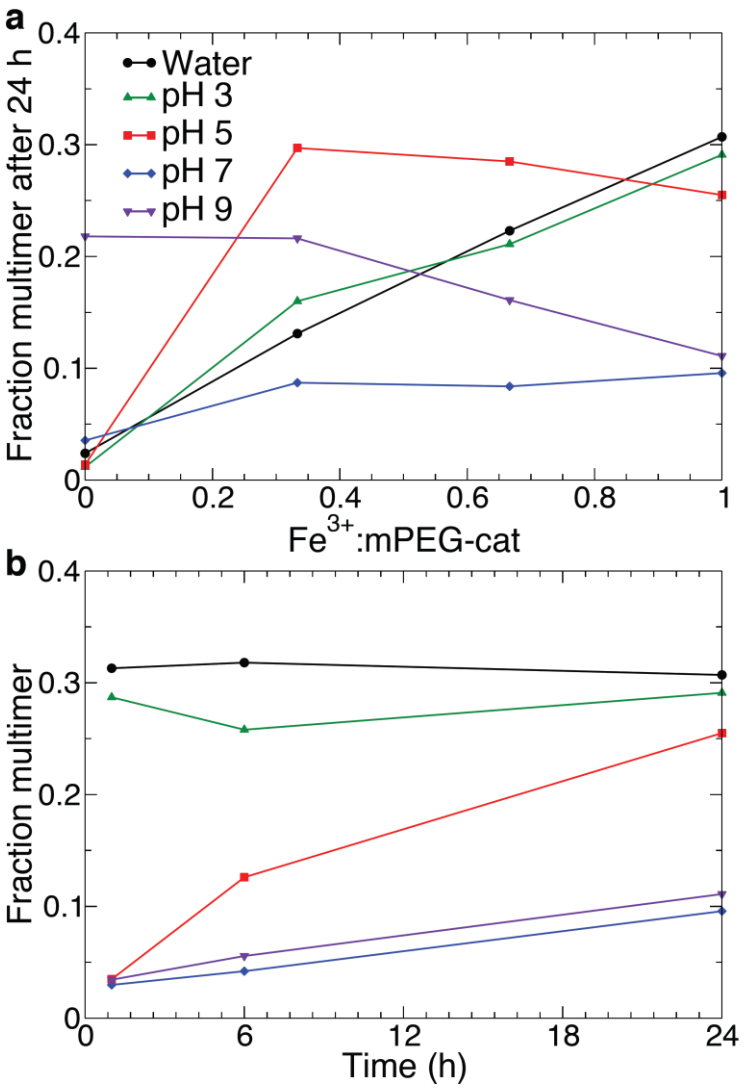

Figure S1. Quantification of multimers formed by GPC as function of pH. The monomer fraction was defined as the value of [1 – multimer fraction]. (a) Fraction of multimer formed after 24 h. (b) Time-dependence of multimer formation at a 1:1 Fe^{3+}:catechol ratio (legend same as in (a)).

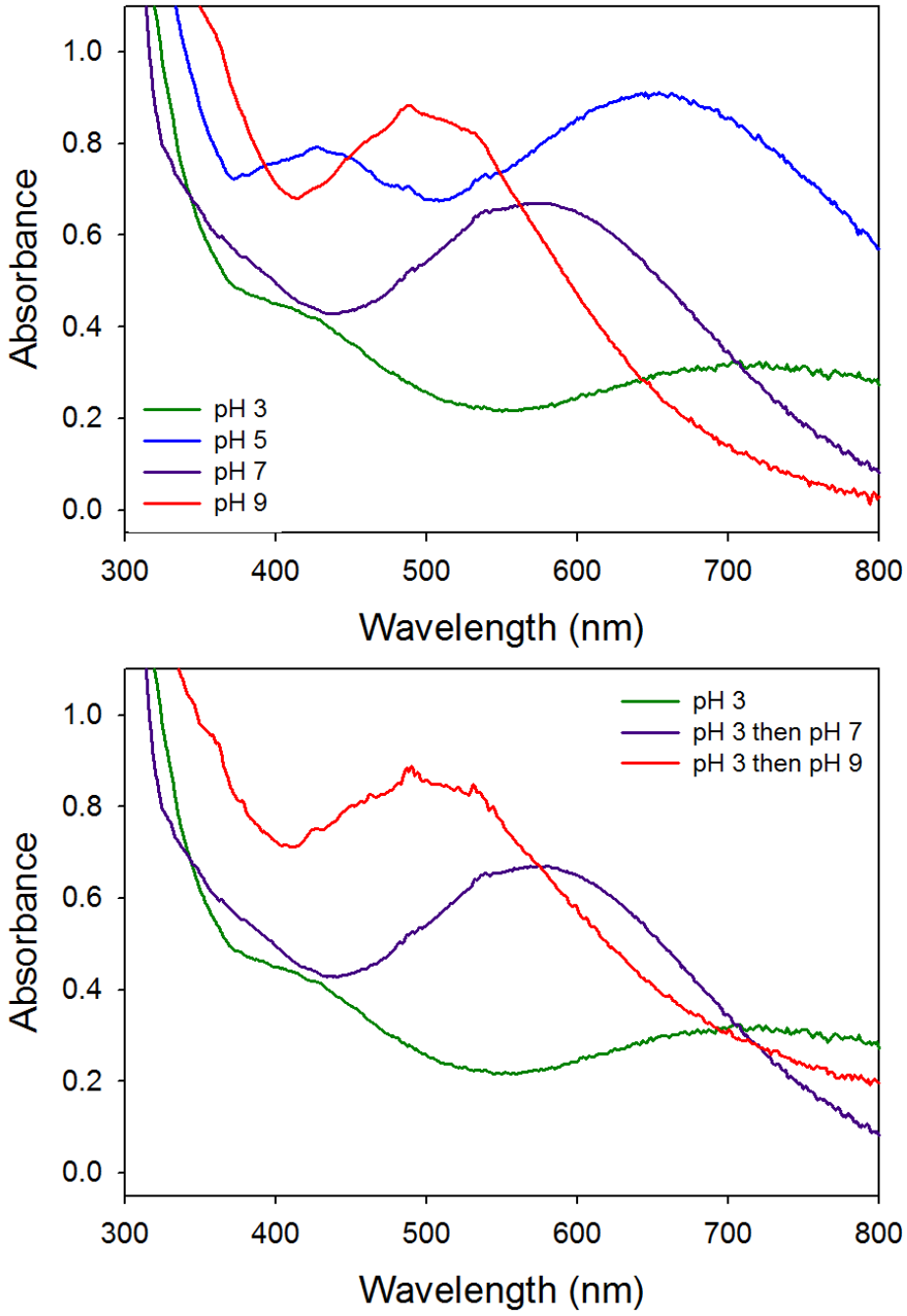

Figure S2. UV-visible spectra of solutions of Fe^{3+} and mPEG-cat. Spectra of Fe^{3+} and mPEG-cat in buffers of various pH (top). Spectra of Fe^{3+} and mPEG-cat incubated at pH 3 for 2 h before adjustment to pH 7 or 9 (bottom).

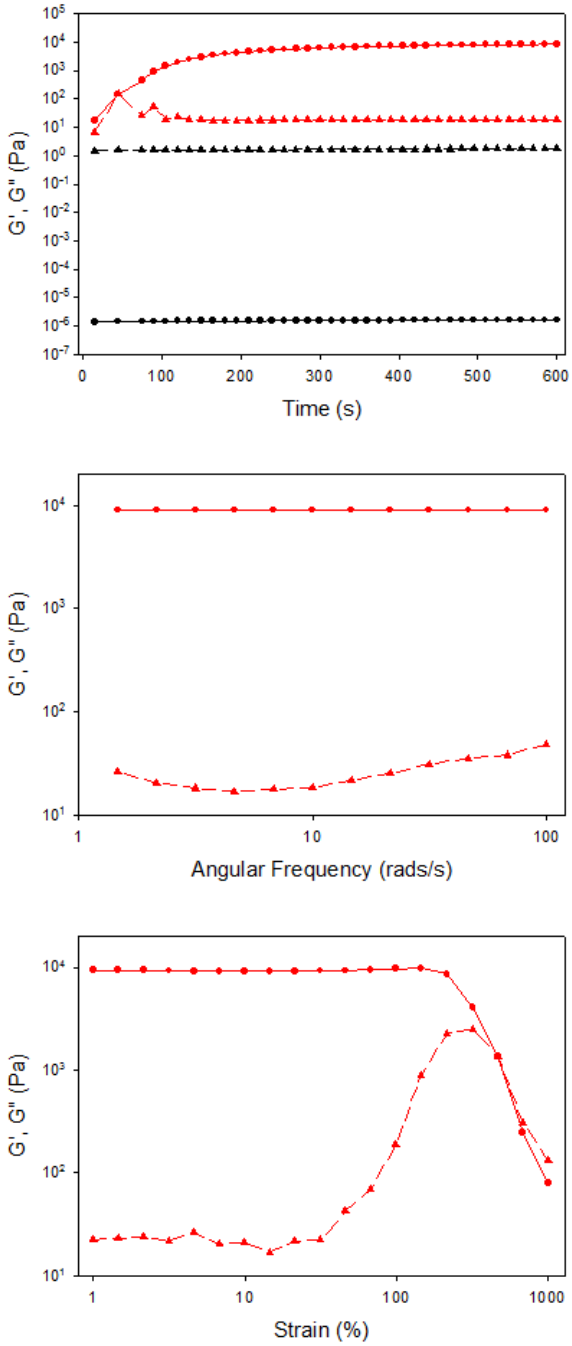

Figure S3. Rheometry of gels composed of 8cPEGa in unbuffered water. Gel formation with Fe^{3+}:catechol of 2:3 (red) was studied as a function of time (top), frequency (middle) and strain (bottom); as shown in the time sweep, Fe^{3+}:catechol of 1:3 (black) does not produce a gel. *G′*: solid line with circles; *G″*: dashed line with triangles (bottom).

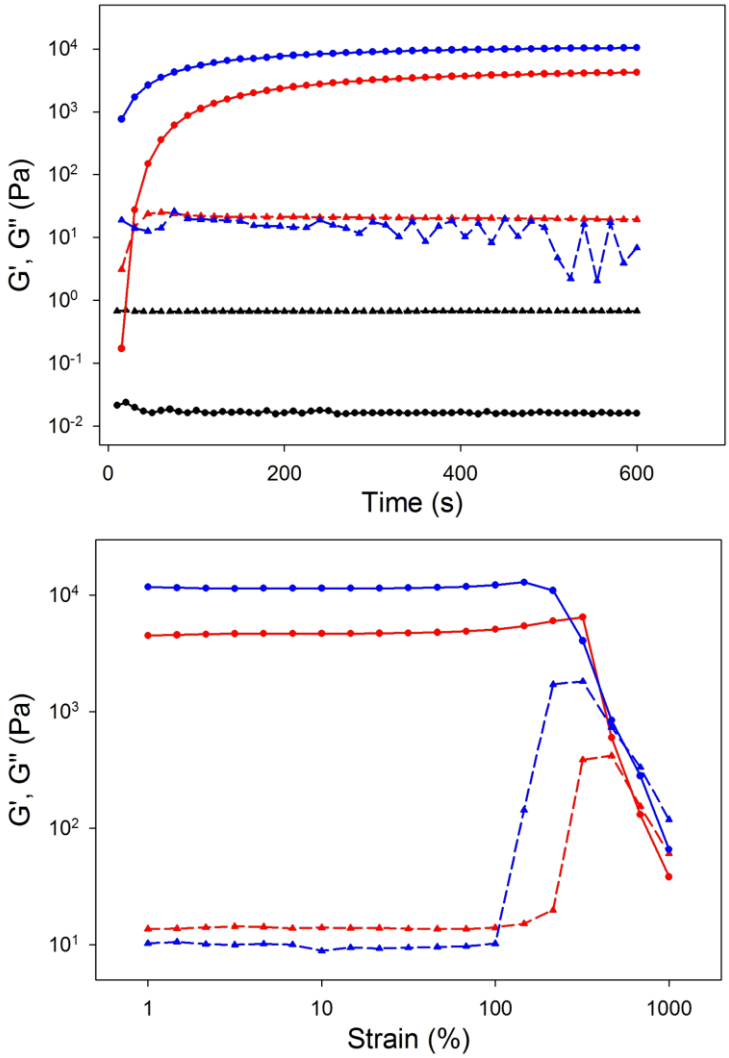

Figure S4. Time and strain sweep experiments of gels formed at pH 3 composed of 8cPEGa with Fe^{3+}:catechol of 1:3 (black), 2:3 (red), and 3:3 (blue). Gel formation was studied as a function of time (top) and, for gels with Fe^{3+}:catechol of 2:3 and 3:3, of strain (bottom) for gels with Fe^{3+}:catechol of 2:3 and 3:3. *G′*: solid line with circles; *G″*: dashed line with triangles.

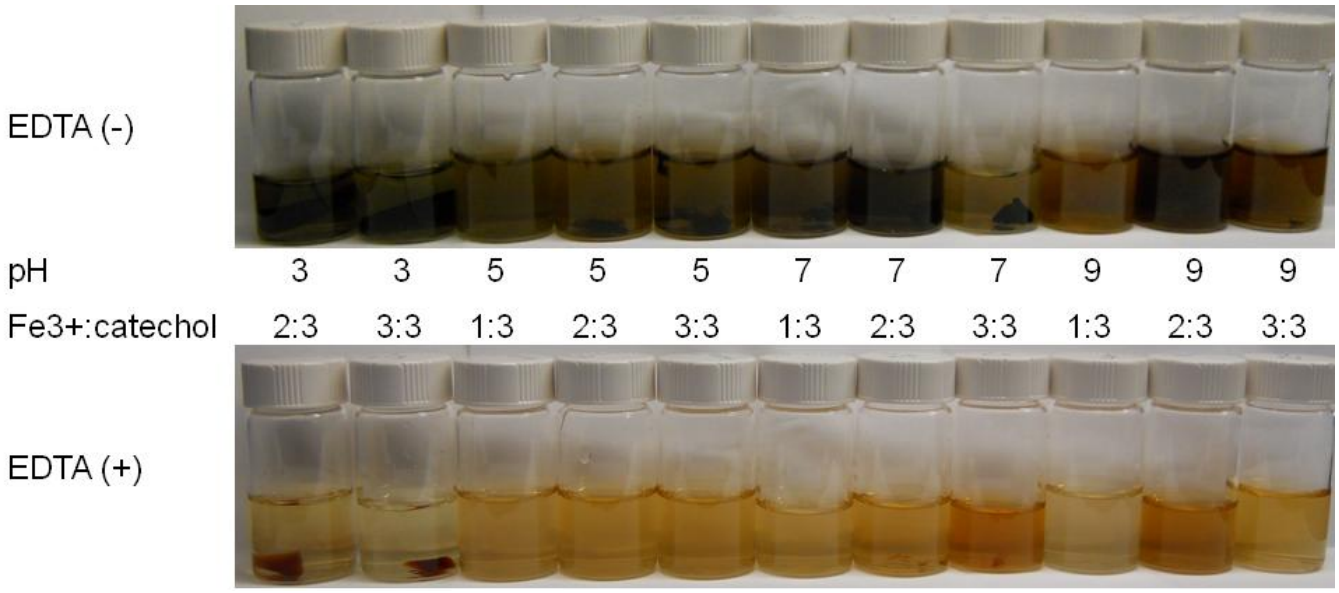

Figure S5. Digital images depicting the stability of hydrogels in water and aqueous EDTA. Gels were formed at the indicated pH values and Fe^{3+}:catechol stoichiometries

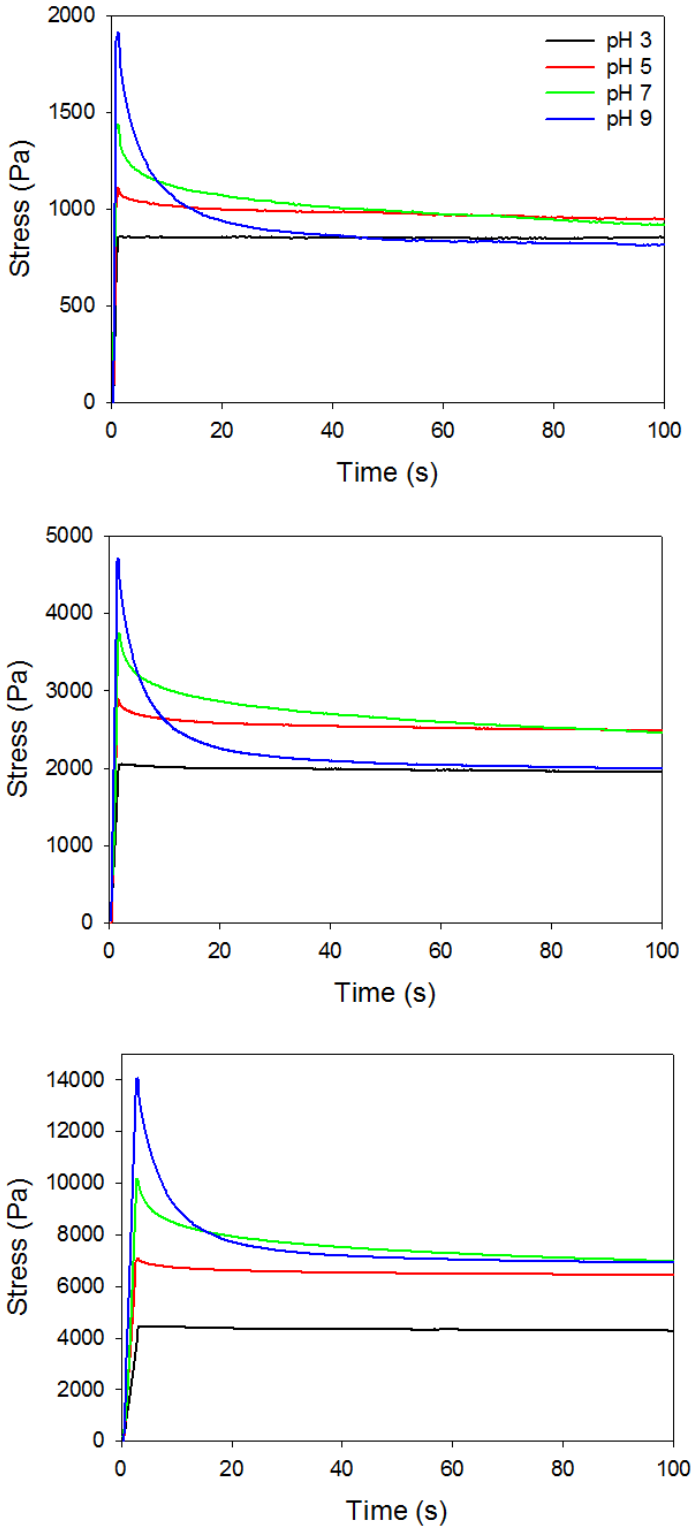

Figure S6. pH-dependent relaxation of two-step hydrogels containing covalent and coordination bonds. These samples were strained to 5 % (top), 10 % (middle), or 20 % (bottom) compression, and the stress was monitored for 100 s.

Table S1. Measured pH of reaction between Fe^{3+} and mPEG-cat

Fe^{3+}:mPEG-cat	**pH 3**	**pH 5**	**pH 7**	**pH 9**
1:3	3.0	5.1	6.6	8.6
2:3	2.7	4.8	6.3	8.2
3:3	2.5	4.7	6.1	8.0

Table S2. Gel times associated with one-step cross-linking of 8cPEGa by Fe^{3+}

Fe^{3+}:catechol	**Water**	**pH 3**	**pH 5**	**pH 7**	**pH 9**
1:3	NA	NA	NA	immediate	immediate
2:3	50 s	85 s	NA	immediate	immediate
3:3	20 s	45 s	NA	immediate	immediate

Gel formation assessed by vial inversion method. NA = no gel formed within 60 minutes.

Table S3. Stability of Fe^{3+}-8cPEGa gels incubated in water or EDTA solution after 24 h

Solvent	**Fe^{3+}:catechol**	**pH 3**	**pH 5**	**pH 7**	**pH 9**
Water	1:3	NA*	Unstable	Mostly Stable	Unstable
	2:3	Stable	Mostly Unstable	Mostly Stable	Unstable
	3:3	Stable	Mostly Stable	Stable	Mostly Unstable
100 mM EDTA in Water	1:3	NA	Unstable	Mostly Unstable	Unstable
	2:3	Stable	Unstable	Mostly Unstable	Unstable
	3:3	Stable	Unstable	Mostly Unstable	Unstable

1.5 h allowed for gel formation. *NA: gel does not form within 20 minutes

Table S4. Physical Characterization of Two-Step Hybrid Gels After Equilibration

		pH 3	pH 5	pH 7	pH 9
Color		yellow-brown	black	black	black
Swelling (%)		159.8 ± 3.8	108.7 ± 6.7	98.3 ± 1.3	88.8 ± 8.3
Initial Modulus (kPa)[a]		8.7 ± 5.6	18.8 ± 4.6	47.8 ± 6.9	39.5 ± 2.8
Initial Modulus (kPa)[b]	**5 % strain**	15.8 ± 4.7	25.8 ± 3.6	24.4 ± 3.8	55.4 ± 9.4
	10 % strain	18.7 ± 3.9	33.0 ± 2.5	38.8 ± 4.5	60.4 ± 9.2
	20 % strain	21.2 ± 4.0	37.5 ± 2.2	55.3 ± 3.9	66.6 ± 9.7
Steady State Modulus (kPa)[c]	**5 % strain**	15.4 ± 4.4	18.7 ± 2.1	12.2 ± 2.7	22.7 ± 3.6
	10 % strain	17.3 ± 3.8	24.6 ± 1.8	19.2 ± 2.4	25.6 ± 4.7
	20 % strain	19.2 ± 3.9	31.0 ± 1.3	31.6 ± 2.0	30.6 ± 4.6
Relaxation (%)[d]	**5 % strain**	--[f]	13.6 ± 1.1[g]	35.9 ± 1.2[g]	55.3 ± 0.7[g]
	10 % strain	--[f]	13.3 ± 0.9	35.5 ± 1.6	56.1 ± 1.4
	20 % strain	--[f]	9.7 ± 0.8	32.3 ± 1.2	51.2 ± 0.6
Relaxation Time, τ (s)[e]	**5 % strain**	--[f]	218 ± 56[g]	58.4 ± 40.4[g]	4.9 ± 0.3[g]
	10 % strain	--[f]	12 ± 1	37.4 ± 6.9	4.5 ± 0.2
	20 % strain	--[f]	25 ± 16	18.4 ± 0.4	4.9 ± 0.2
α[e]	**5 % strain**	--[f]	0.3 ± 0.02[g]	0.30 ± 0.04[g]	0.62 ± 0.03[g]
	10 % strain	--[f]	0.4 ± 0.05	0.35 ± 0.01	0.64 ± 0.003
	20 % strain	--[f]	0.38 ± 0.02	0.39 ± 0.02	0.67 ± 0.004

[a] initial modulus calculated from slope of linear portion of stress-strain curves (from compression loops) with cross-head speed of 10 mm/min; [b] initial modulus calculated from slope of linear portion of stress-strain curves (from relaxation tests) with cross-head speed of 40 mm/min; [c] steady-state modulus (A_1/ε_{100}) calculated from fit of relaxation tests; [d] percent stress relaxed after 100 s; [e] calculated from fit of relaxation tests by expanded exponential model; [f] relaxation data were not calculated for materials equilibrated to pH 3 because of the absence of coordination bonds; [g] larger error for calculations associated with 5 % strain were due to the significance of instrumental drift.