Electronic Supplementary Material (ESI) for Soft Matter.
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– Supporting Information –

Self-Organization of Metallo-Supramolecular Polymer Networks by Free Formation of Pyridine–Phenanthroline Heteroleptic Complexes

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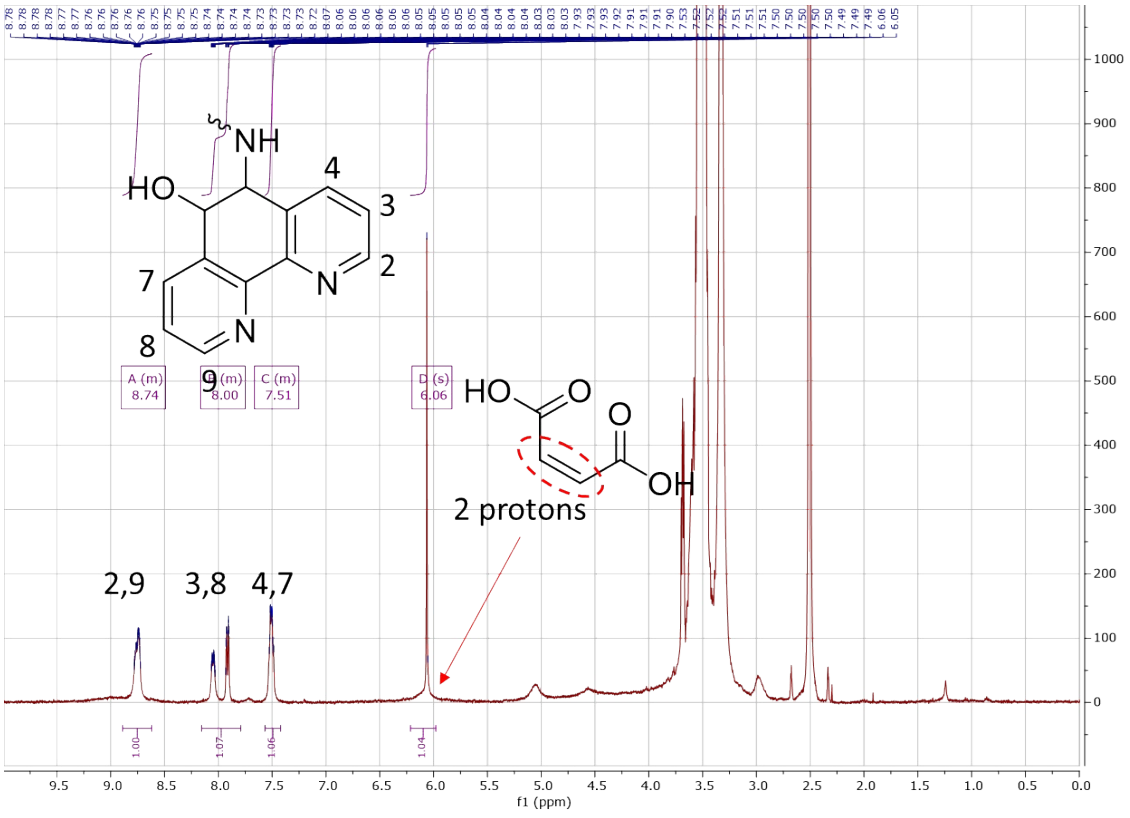

Figure S1. ^{1}H NMR spectra (400 MHz, DMSO-d_6) of tetraEPhen20k along with the stoichiometric amount of maleic acid as the external standard.

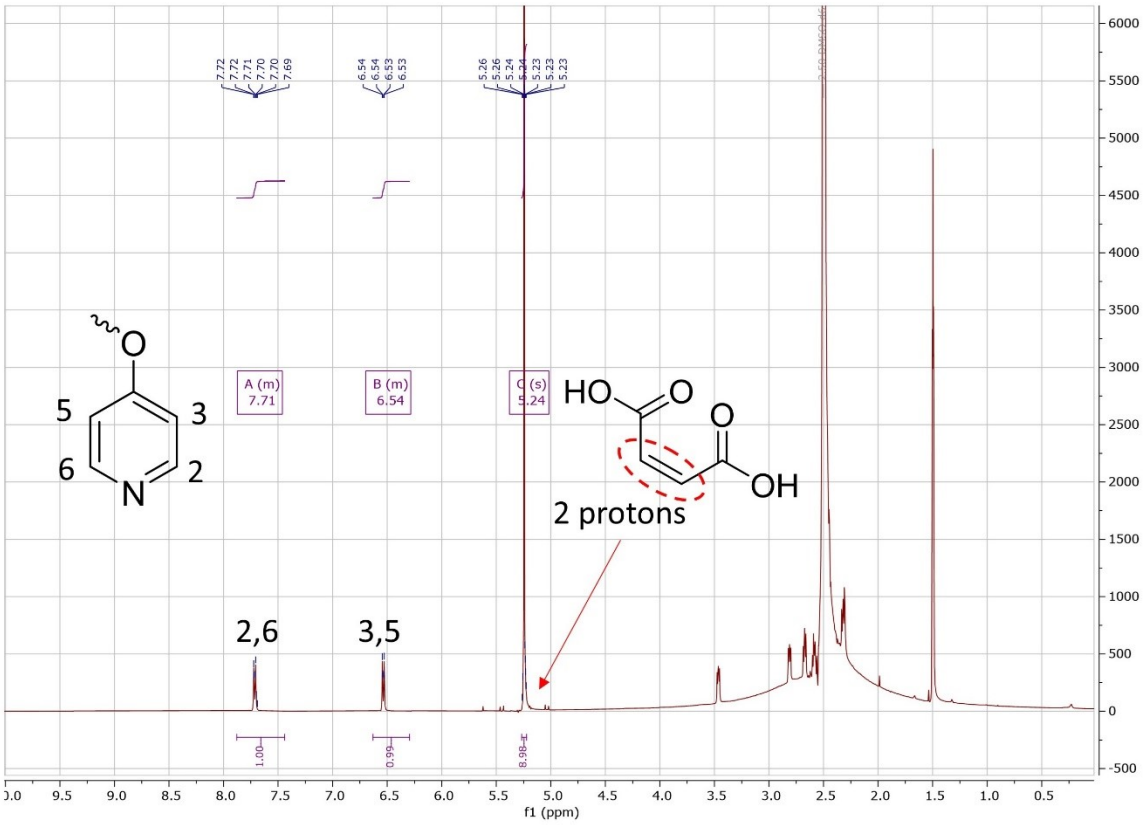

Figure S2. ^{1}H NMR spectra (400 MHz, DMSO-d_6) of tetraPy20k along with maleic acid as the external standard added 9 times of the equilibrium.

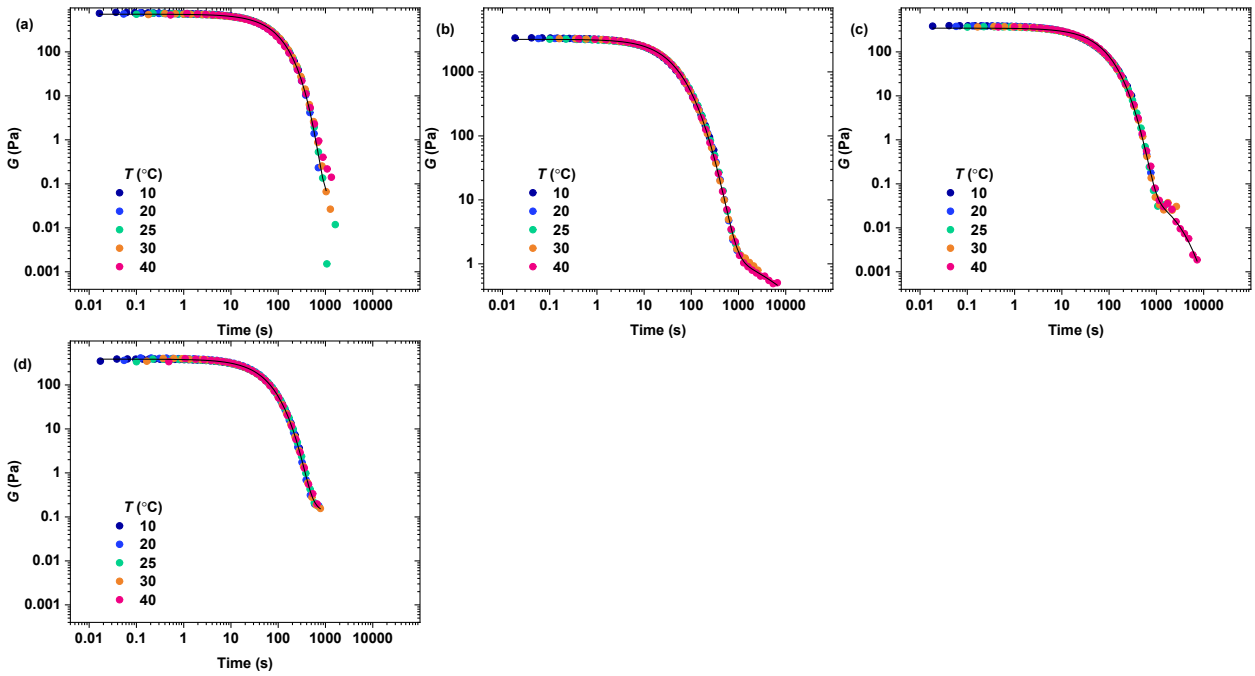

Figure S3. Shear stress mater-curves of tetraPy(40)Py(X) samples series (symbols) and the corresponding fit of the generalized Maxwell modes (curves) for (a) X = 1, (b) X = 2, (c) X = 4, and (d) X = 6.

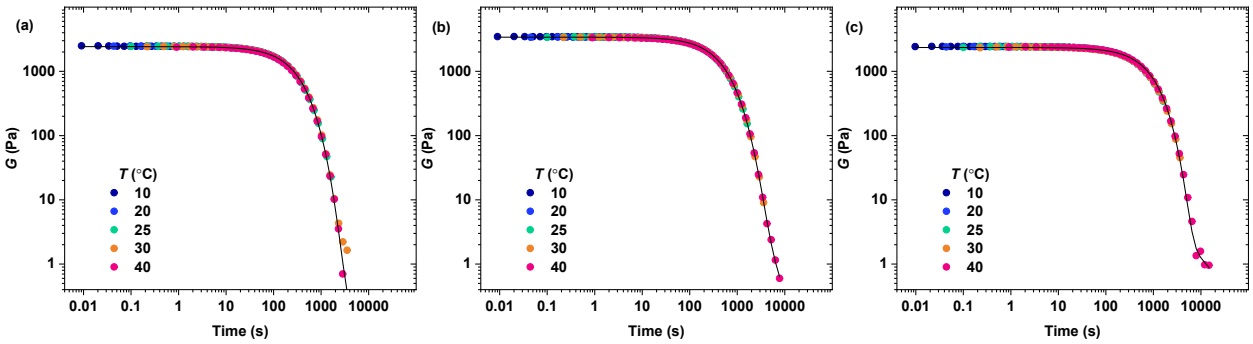

Figure S4. Shear stress mater-curves of tetraEPhen(40)Fe(X) samples series (symbols) and the corresponding fit of the generalized Maxwell modes (curves) for (a) X = 2, (b) X = 4, and (c) X = 6.

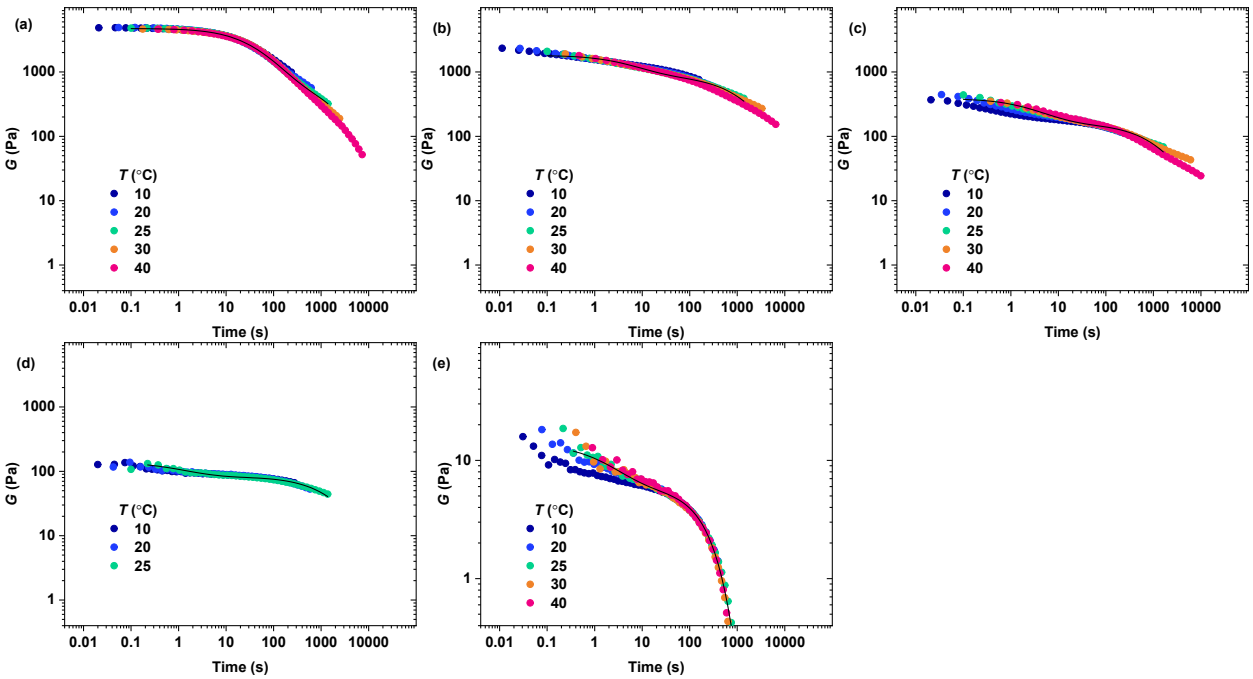

Figure S5. Shear stress mater-curves of tetraEPhen(40)Pd(X) samples series (symbols) and the corresponding fit of the generalized Maxwell modes (curves) for (a) X = 2, (b) X = 3, (c) X = 4, (d) X = 5, and (e) X = 6.

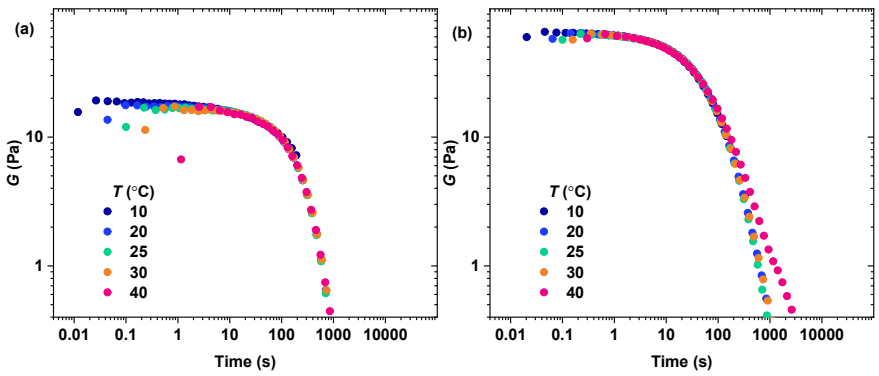

Figure S6. Shear stress mater-curves of (a) tetraEPhen(20)Fe(2) and (b) tetraEPhen(20)Pd(2).

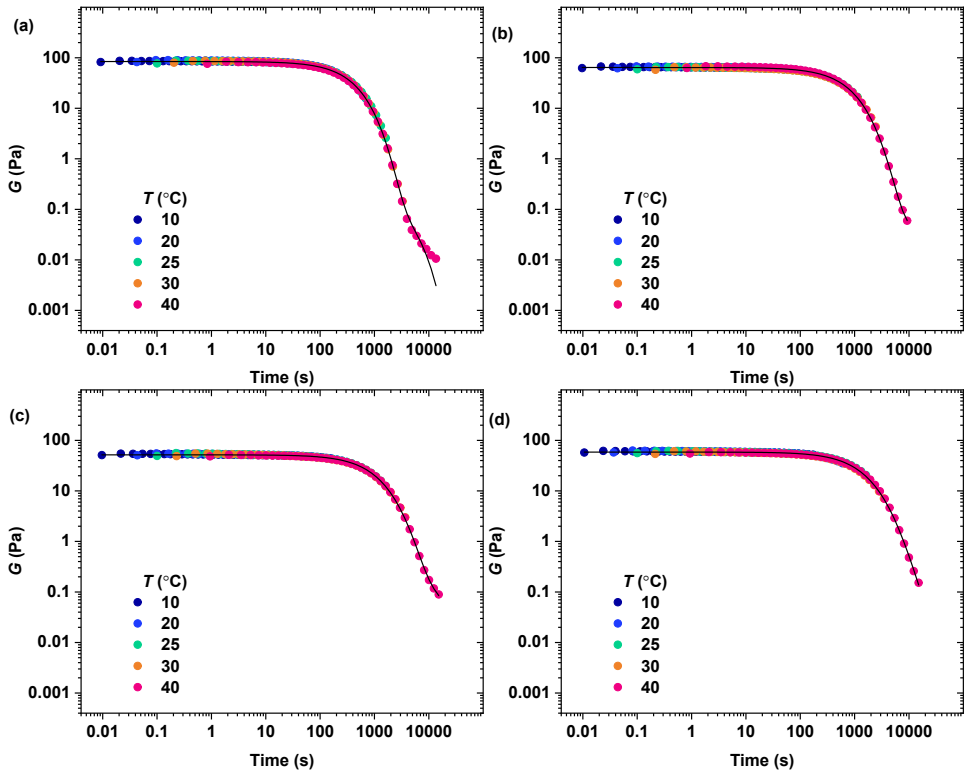

Figure S7. Shear modulus of mixed tetraPy/tetraEPhen networks (symbols) and the corresponding fit of the generalized Maxwell modes (curves) at EPhen:Fe^{2+} = 1, 25 °C, and varying Py:EPhen ratios of (a) 1:1, (b) 2:1, (c) 3:1, and (d) 4:1.

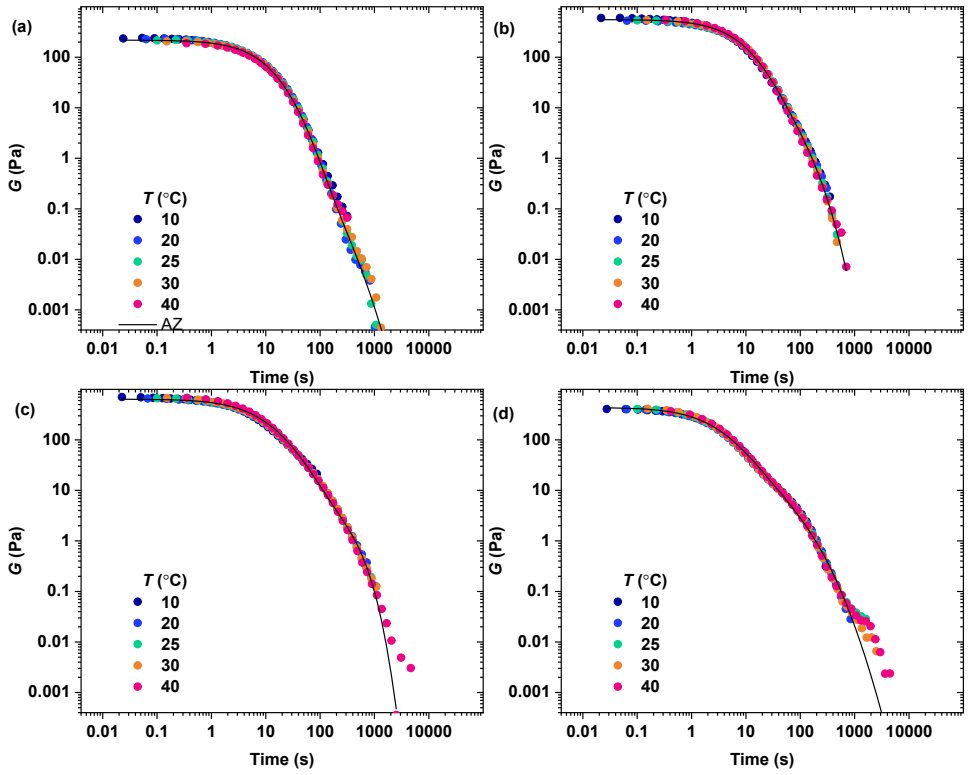

Figure S8. Shear modulus of mixed tetraPy/tetraEPhen networks (symbols) and the corresponding fit of the generalized Maxwell modes (curves) at EPhen:Pd^{2+} = 1, 25 °C, and varying Py:EPhen ratios of (a) 1:1, (b) 2:1, (c) 3:1, and (d) 4:1.

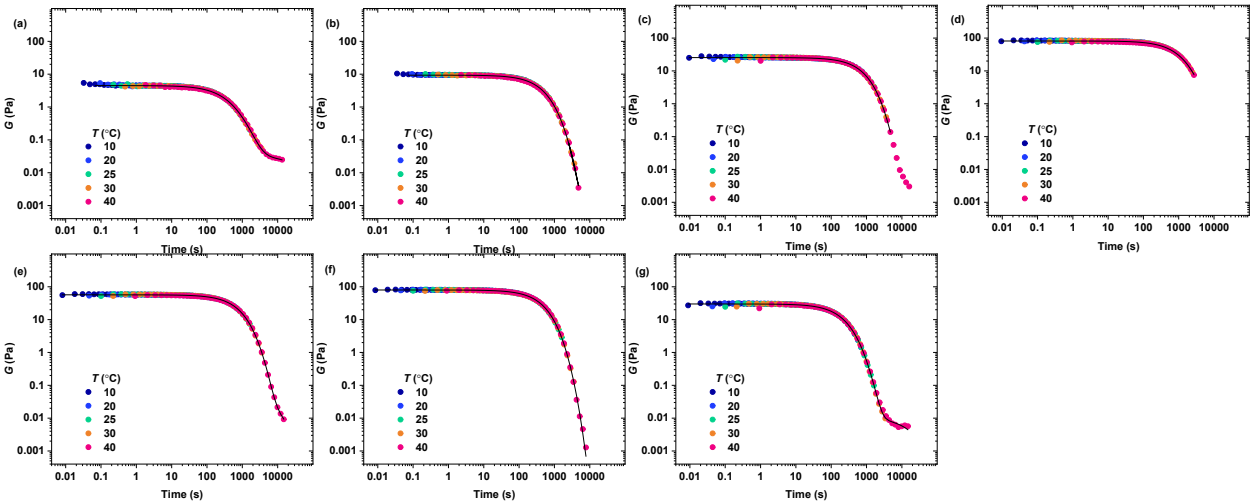

Figure S9. Shear modulus of mixed tetraPy/tetraEPhen networks (symbols) and the corresponding fit of the generalized Maxwell modes (curves) at Py:EPhen = 1:1, 25 °C, and varying EPhen:Fe^{2+} ratios: (a) X = 8, (b) X = 7, (c) X = 6, (d) X = 5, (e) X = 4, (f) X = 3, (g) and X = 2.

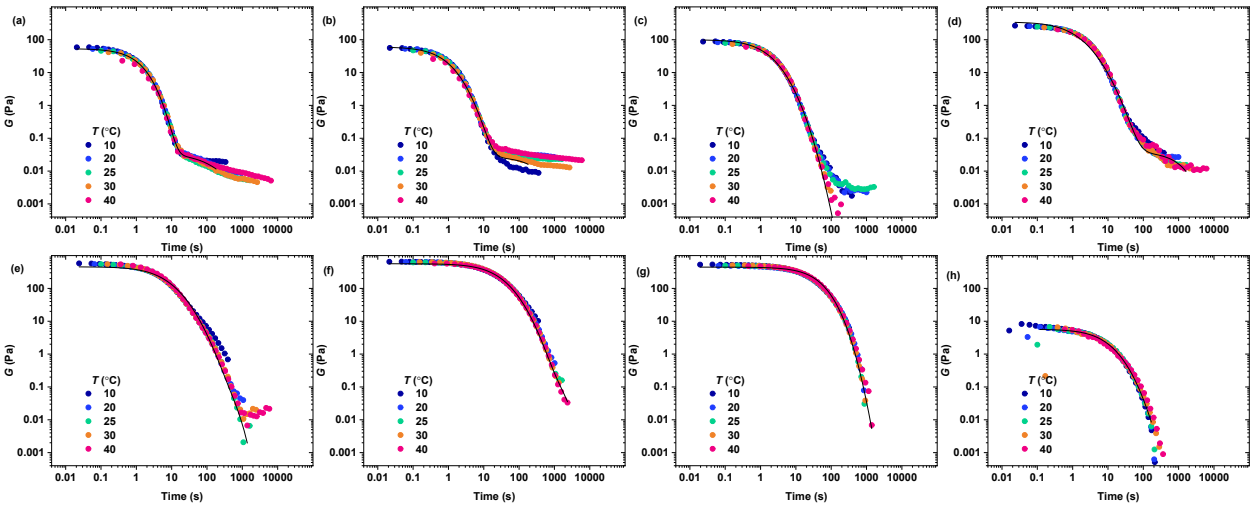

Figure S10. Shear modulus of mixed tetraPy/tetraEPhen networks (symbols) and the corresponding fit of the generalized Maxwell modes (curves) at Py:EPhen = 2:1, 25 °C, and varying EPhen:Pd^{2+} ratios: (a) X = 8, (b) X = 7, (c) X = 6, (d) X = 5, (e) X = 4, (f) X = 3, (g) X = 2, and (h) X = 1.

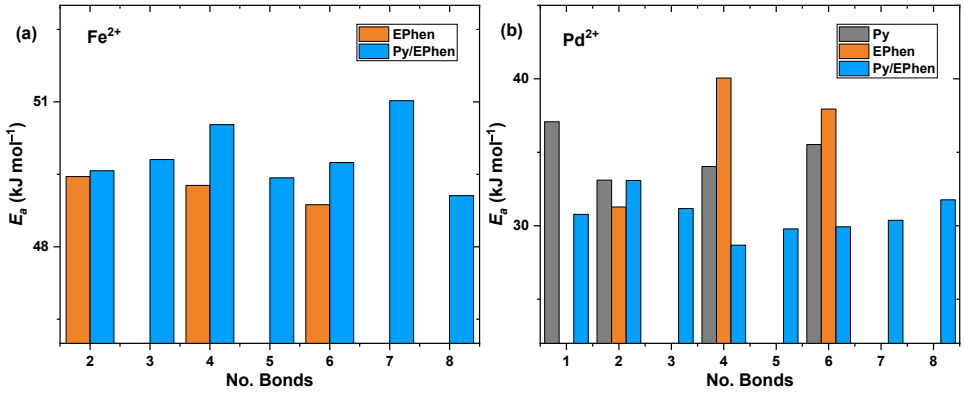

Figure S11. Activation energies obtained from time-temperature superposition of shear moduli of parent and mixed networks in the presence of (a) Fe^{2+} and (b) Pd^{2+}.

Table S1. Complexation energies in kcal mol^{-1} relative to the free metal ions (M^{2+}).*

	Fe	Co	Ni	Cu	Zn	Pd
$M(Py)_1$	1.0	-5.0	-54.9	-17.2	-3.2	-89.0
$M(Py)_2$	-29.2	-7.9	-74.5	-27.5	-7.6	-114.1
$M(Py)_3$	-3.8	-19.3	-95.0	-35.0	-9.9	-140.3
$M(Py)_4$	-10.5	-19.5	-108.1	-41.8	-12.1	-161.7
$M(Py)_6$	-13.7	-15.5	-114.1	-29.0	1.7	-151.9
$M(EPhen)_1$	-12.4	-20.2	-85.5	-21.2	-11.1	-128.1
$M(EPhen)_2$	-26.1	-33.9	-126.4	-59.3	-27.6	-173.3
$M(EPhen)_3$	-46.2	-55.0	-154.6	-61.2	-32.5	-167.0
M(EPhen)(Py)	3.3	-26.2	-105.2	-45.0	-18.1	-148.4
$M(EPhen)(Py)_2$	-17.7	-35.1	-120.6	-51.1	-18.9	-172.6
$M(EPhen)_2(Py)_2$	-30.0	-43.2	-142.6	-52.0	-22.4	-160.0

* $E_{Complexation} = E_{Complex} - \left(E_{Organics} + E_{M^{2+}}\right)$

Table S2. Complexation energies in kcal mol^{-1} of the metal ions (M^{2+}) relative to the metal ions (M^{2+}) included in the $M(NO_3)_2$ salts.*

	Fe	Co	Ni	Cu	Zn	Pd
$M(Py)_1$	14.8	10.2	30.4	19.7	3.9	39.5
$M(Py)_2$	-15.5	7.3	10.8	9.3	-0.5	14.4
$M(Py)_3$	10.0	-4.1	-9.7	1.9	-2.8	-11.8
$M(Py)_4$	3.3	-4.2	-22.8	-4.9	-5.0	-33.2
$M(Py)_6$	10.1	-0.3	-28.8	7.9	8.8	-23.3
$M(EPhen)_1$	1.4	-4.9	-0.2	15.7	-4.0	0.4
$M(EPhen)_2$	-12.3	-18.6	-41.1	-22.4	-20.5	-44.8
$M(EPhen)_3$	-32.5	-39.8	-69.3	-24.3	-25.4	-38.5
M(EPhen)(Py)	17.1	-11.0	-19.9	-8.1	-11.0	-19.9
$M(EPhen)(Py)_2$	-3.9	-19.9	-35.3	-14.3	-11.8	-44.1
$M(EPhen)_2(Py)_2$	-16.2	-28.0	-57.3	-15.2	-15.3	-31.5

* $E_{Complexation} = E_{Complex} - \left(E_{Organics} + E_{InterSalt}\right), E_{InterSalt} = E_{Salt} - \left(E_{Couterion} + E_{M^{2+}}\right)$

Table S3. Bond distances (in Å) of the metal ions with the atoms of the ligands (the second column corresponds to the ground state: S = singlet, D = doublet, T = triplet, Qua = quartet, Qui = quintet).

Fe	Qui	$M(Py)_1$	1.901					
	Qui	$M(Py)_2$	1.930					
	Qui	$M(Py)_3$	1.987					
	Qui	$M(Py)_4$	2.034	2.032	2.033	2.034		
	Qui	$M(Py)_6$	2.289	2.211	2.211	2.206		
	Qui	$M(EPhen)_1$	1.990	1.993				
	Qui	$M(EPhen)_2$	2.021	2.035	2.022	2.034		
	S	$M(EPhen)_3$	1.955	1.950	1.955	1.948	1.956	1.950
	Qui	M(EPhen)(Py)	2.022	2.029	1.967			
	Qui	$M(EPhen)(Py)_2$	2.055	2.056	2.010	2.010		
	S	$M(EPhen)_2(Py)_2$	1.967	1.949	1.967	1.949	2.009	2.009
Co	Qua	$M(Py)_1$	1.860					
	Qua	$M(Py)_2$	1.894					
	Qua	$M(Py)_3$	1.945					
	Qua	$M(Py)_4$	2.068					
	Qua	$M(Py)_6$	2.259	2.177	2.263	2.178		
	Qua	$M(EPhen)_1$	1.936	1.970				
	D	$M(EPhen)_2$	1.936	1.904	1.905	1.936		
	D	$M(EPhen)_3$	1.953	2.151	1.950	1.943	1.952	2.150
	Qui	M(EPhen)(Py)	2.022	1.978	1.929			
	D	$M(EPhen)(Py)_2$	1.939	1.940	1.915	1.916		
	D	$M(EPhen)_2(Py)_2$	1.953	2.173	1.958	1.951	1.969	2.346
Ni	T	$M(Py)_1$	1.856					

	T	$M(Py)_2$	1.866					
	T	$M(Py)_3$	1.919					
	T	$M(Py)_4$	1.903	1.903	1.903	1.903		
	T	$M(Py)_6$	2.269	2.273	2.158	2.158		
	T	$M(EPhen)_1$	1.910	1.914				
	T	$M(EPhen)_2$	1.996	1.983	1.982	2.004		
	T	$M(EPhen)_3$	2.080	2.076	2.081	2.075	2.081	2.075
	T	M(EPhen)(Py)	1.981	1.945	1.911			
	S	$M(EPhen)(Py)_2$	1.914	1.911	1.890	1.889		
	T	$M(EPhen)_2(Py)_2$	2.096	2.094	2.096	2.094	2.101	2.106
Cu	D	$M(Py)_1$	1.911					
	D	$M(Py)_2$	1.886					
	D	$M(Py)_3$	1.942	1.931	1.930			
	D	$M(Py)_4$	2.026					
	D	$M(Py)_6$	2.079	2.078	2.073	2.073		
	D	$M(EPhen)_1$	1.991	1.991				
	D	$M(EPhen)_2$	2.030	2.031	2.030	2.031		
	D	$M(EPhen)_3$	2.332	2.051	2.327	2.048	2.064	2.058
	D	M(EPhen)(Py)	2.042	2.016	1.921			
	D	$M(EPhen)(Py)_2$	2.050	2.048	2.012	2.012		
	D	$M(EPhen)_2(Py)_2$	2.071	2.361	2.077	2.063	2.038	2.391
Zn	S	$M(Py)_1$	1.947					
	S	$M(Py)_2$	1.885					
	S	$M(Py)_3$	1.962					
	S	$M(Py)_4$	2.022	2.020	2.021	2.021		

	S	$M(Py)_6$	2.204	2.201	2.207	2.204		
	S	$M(EPhen)_1$	2.004	2.005				
	S	$M(EPhen)_2$	2.031	2.027	2.031	2.027		
	S	$M(EPhen)_3$	2.175	2.165	2.171	2.161	2.176	2.165
	S	M(EPhen)(Py)	1.998	1.993	1.929			
	S	$M(EPhen)(Py)_2$	2.053	2.049	2.001	2.001		
	S	$M(EPhen)_2(Py)_2$	2.184	2.206	2.183	2.206	2.152	2.157
Pd	S	$M(Py)_1$	1.980					
	S	$M(Py)_2$	2.022					
	S	$M(Py)_3$	1.997	2.027	2.028			
	S	$M(Py)_4$	2.047					
	S	$M(Py)_6$	2.058	2.044	2.056	2.045		
	S	$M(EPhen)_1$	2.110	2.110				
	S	$M(EPhen)_2$	2.057	2.057	2.057	2.057		
	S	$M(EPhen)_3$	2.072	2.730	2.045	2.041	2.744	2.072
	S	M(EPhen)(Py)	1.998	1.993	1.929			
	S	$M(EPhen)(Py)_2$	2.043	2.039	2.043	2.042		
	S	$M(EPhen)_2(Py)_2$	2.055	2.808	2.058	2.767	2.043	2.061

Table S4. Mayer Bond Orders of the metal ions with the atoms of the ligands.

Fe	$M(Py)_1$	0.759					
	$M(Py)_2$	0.654	0.654				
	$M(Py)_3$	0.586	0.586	0.586			
	$M(Py)_4$	0.511	0.511	0.512	0.511		
	$M(Py)_6$	0.363	0.371	0.372	0.342	0.336	0.363
	$M(EPhen)_1$	0.575	0.567				
	$M(EPhen)_2$	0.529	0.517	0.530	0.516		
	$M(EPhen)_3$	0.675	0.679	0.673	0.679	0.676	0.682
	M(EPhen)(Py)	0.535	0.526	0.609			
	$M(EPhen)(Py)_2$	0.493	0.491	0.540	0.539		
	$M(EPhen)_2(Py)_2$	0.677	0.695	0.677	0.695	0.606	0.606
Co	$M(Py)_1$	0.775					
	$M(Py)_2$	0.675	0.675				
	$M(Py)_3$	0.600	0.600	0.600			
	$M(Py)_4$	0.467					
	$M(Py)_6$	0.375	0.377	0.377	0.353	0.348	0.375
	$M(EPhen)_1$	0.603	0.563				
	$M(EPhen)_2$	0.640	0.646	0.648	0.642		
	$M(EPhen)_3$	0.617	0.389	0.618	0.390	0.629	0.637
	M(EPhen)(Py)	0.503	0.548	0.617			
	$M(EPhen)(Py)_2$	0.626	0.625	0.628	0.629		
	$M(EPhen)_2(Py)_2$	0.618	0.378	0.624	0.636	0.591	0.288
Ni	$M(Py)_1$	0.733					
	$M(Py)_2$	0.681	0.681				

	$M(Py)_3$	0.610	0.610	0.610			
	$M(Py)_4$	0.619	0.619	0.619	0.619		
	$M(Py)_6$	0.382	0.384	0.384	0.351	0.349	0.382
	$M(EPhen)_1$	0.590	0.581				
	$M(EPhen)_2$	0.515	0.498	0.517	0.520		
	$M(EPhen)_3$	0.424	0.427	0.424	0.427	0.424	0.428
	M(EPhen)(Py)	0.503	0.545	0.604			
	$M(EPhen)(Py)_2$	0.627	0.630	0.626	0.628		
	$M(EPhen)_2(Py)_2$	0.418	0.417	0.418	0.417	0.411	0.412
Cu	$M(Py)_1$	0.668					
	$M(Py)_2$	0.645	0.645				
	$M(Py)_3$	0.613	0.542	0.614			
	$M(Py)_4$	0.494					
	$M(Py)_6$	0.203	0.201	0.450	0.440	0.438	0.449
	$M(EPhen)_1$	0.514	0.510				
	$M(EPhen)_2$	0.478	0.474	0.479	0.474		
	$M(EPhen)_3$	0.267	0.456	0.444	0.448	0.273	0.457
	M(EPhen)(Py)	0.453	0.475	0.630			
	$M(EPhen)(Py)_2$	0.467	0.465	0.495	0.494		
	$M(EPhen)_2(Py)_2$	0.444	0.251	0.439	0.451	0.469	0.254
Zn	$M(Py)_1$	0.833					
	$M(Py)_2$	0.792	0.792				
	$M(Py)_3$	0.640	0.640	0.640			
	$M(Py)_4$	0.526	0.526	0.526	0.526		
	$M(Py)_6$	0.351	0.353	0.353	0.320	0.313	0.351

	$M(EPhen)_1$	0.599	0.591				
	$M(EPhen)_2$	0.527	0.532	0.527	0.532		
	$M(EPhen)_3$	0.362	0.368	0.361	0.368	0.364	0.370
	M(EPhen)(Py)	0.594	0.601	0.702			
	$M(EPhen)(Py)_2$	0.496	0.500	0.559	0.558		
	$M(EPhen)_2(Py)_2$	0.358	0.341	0.359	0.340	0.383	0.384
Pd	$M(Py)_1$	0.781					
	$M(Py)_2$	0.675	0.675				
	$M(Py)_3$	0.618	0.725	0.621			
	$M(Py)_4$	0.581					
	$M(Py)_6$	0.561	0.564	0.066	0.554	0.590	0.054
	$M(EPhen)_1$	0.461	0.457				
	$M(EPhen)_2$	0.590	0.593	0.590	0.593		
	$M(EPhen)_3$	0.569	0.571	0.133	0.547	0.547	0.135
	M(EPhen)(Py)	0.640	0.580	0.610			
	$M(EPhen)(Py)_2$	0.596	0.600	0.576	0.579		
	$M(EPhen)_2(Py)_2$	0.553	0.100	0.552	0.111	0.573	0.539

Table S5. HOMO-LUMO gap (in a.u.).

	Fe	Co	Ni	Cu	Zn	Pd
$M(Py)_1$	0.051	0.066	0.058	0.072	0.012	0.003
$M(Py)_2$	0.086	0.086	0.081	0.080	0.125	0.002
$M(Py)_3$	0.089	0.095	0.092	0.077	0.144	0.044
$M(Py)_4$	0.069	0.066	0.088	0.092	0.152	0.113
$M(Py)_6$	0.052	0.062	0.095	0.078	0.147	0.098
$M(EPhen)_1$	0.032	0.035	0.036	0.037	0.005	0.034
$M(EPhen)_2$	0.028	0.014	0.028	0.032	0.049	0.017
$M(EPhen)_3$	0.028	0.040	0.057	0.030	0.028	0.045
M(EPhen)(Py)	0.030	0.031	0.035	0.037	0.041	0.005
$M(EPhen)(Py)_2$	0.033	0.025	0.036	0.033	0.050	0.025
$M(EPhen)_2(Py)_2$	0.028	0.045	0.056	0.029	0.057	0.053

Table S6. NPA charges on the metal ion of the complexes.

	Fe	Co	Ni	Cu	Zn	Pd
$M(Py)_1$	2.449	1.863	1.287	0.618	1.349	0.917
$M(Py)_2$	2.461	1.855	1.252	0.523	1.365	0.764
$M(Py)_3$	2.371	1.820	1.228	0.688	1.265	0.727
$M(Py)_4$	2.321	1.865	0.667	0.690	1.163	0.587
$M(Py)_6$	2.426	1.851	1.283	0.736	1.245	0.560
$M(EPhen)_1$	2.300	1.684	1.074	0.515	1.208	0.692
$M(EPhen)_2$	-0.313	0.164	-0.141	-0.324	0.152	-0.287
$M(EPhen)_3$	2.272	0.877	1.068	0.548	1.162	0.630
M(EPhen)(Py)	2.347	1.722	1.093	0.519	1.273	0.689
$M(EPhen)(Py)_2$	2.322	0.920	0.676	0.635	1.163	0.598
$M(EPhen)_2(Py)_2$	0.380	0.781	1.185	0.695	1.178	0.583

Table S7. XYZ coordinates and absolute energies (in a.u.) of all computed species by DFT (T = triplet, Q = quartet or quintet, and without a final letter means singlet or doublet for even and odd electron metals)

(**attached as a separate file, labelled SIcoordinates.xyz)**