

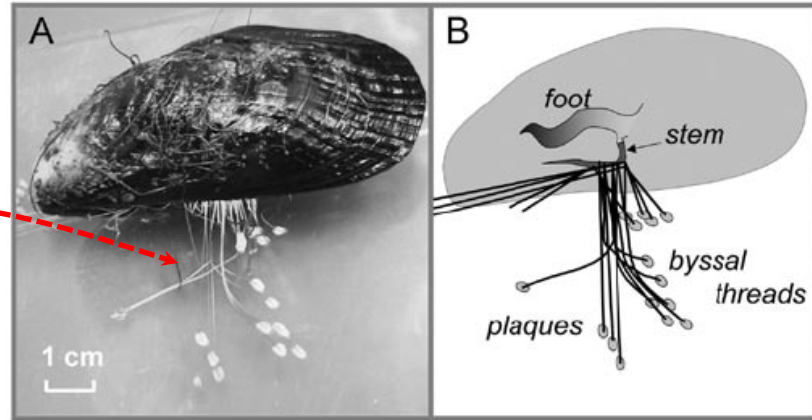


**Bio-inspired metal-coordination crosslinking:
easy access to broad dynamics for new
engineering of polymer mechanics**



Bio-inspired metal-coordination crosslinking:
easy access to broad **dynamics** for new
engineering of polymer **mechanics**

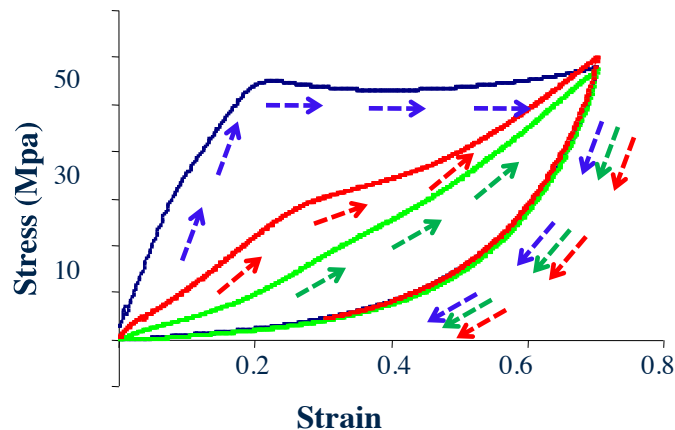
Mechanical energy dissipation in mussel threads



Holten-Andersen & Waite, *J. Dental Research*. **87**, 701-709, (2008)

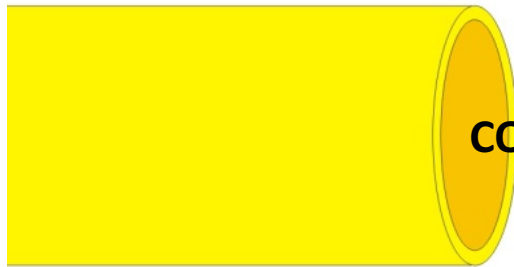


Repeated stress-strain cycles



Toughness
Self-healing

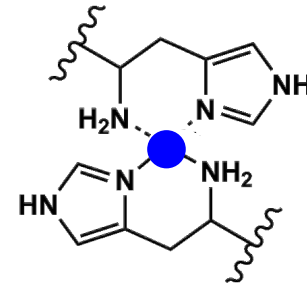
Metal-ion coordinate crosslinking in mussel threads



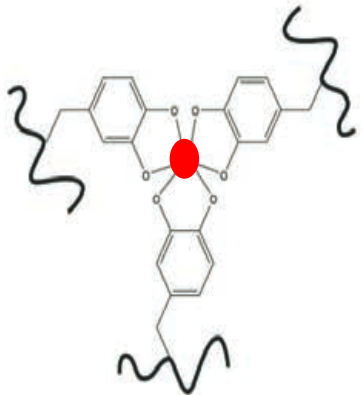
CORE

COATING

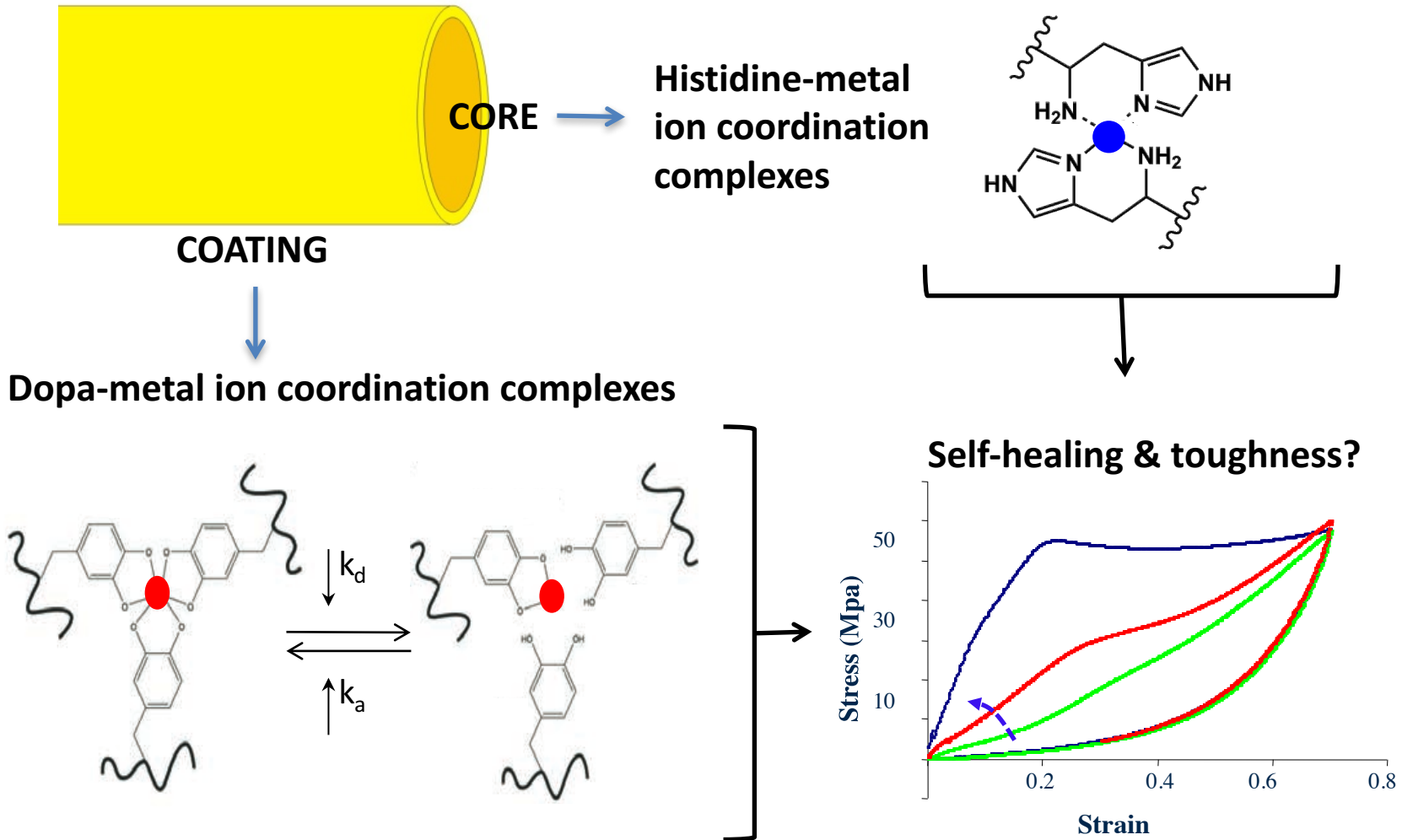
Histidine-metal
ion coordination
complexes



Dopa-metal ion coordination complexes

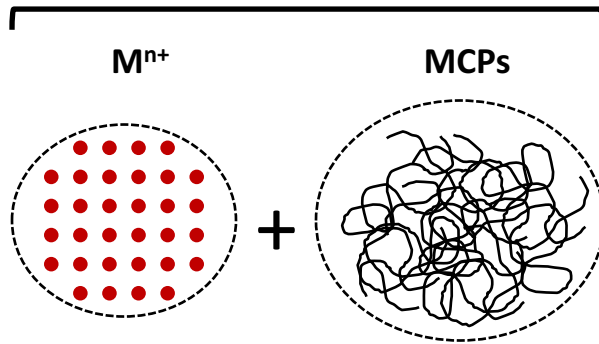


Metal-ion coordinate crosslinking in mussel threads



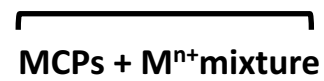
Metal-coordinated mussel thread assembly?

Intracellular storage at low pH (≤ 5)



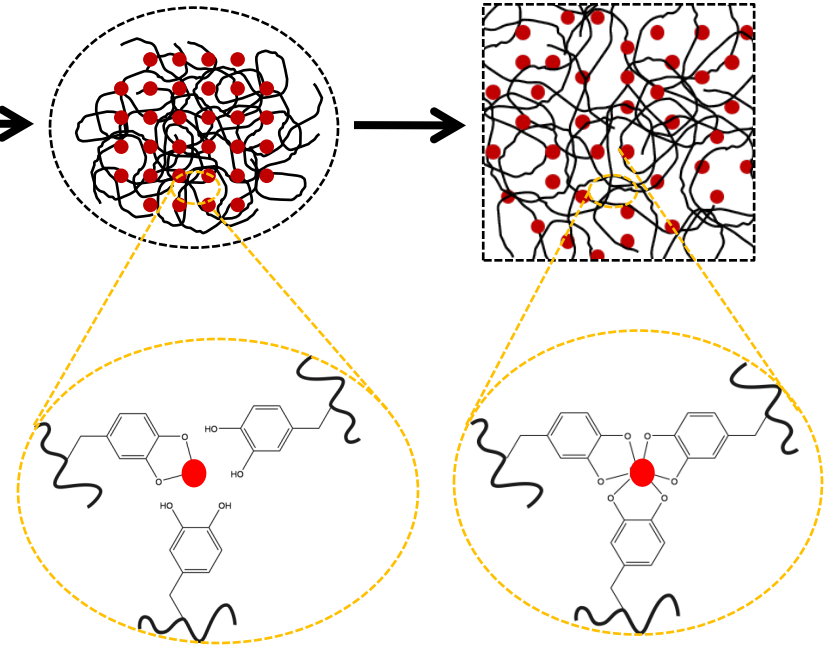
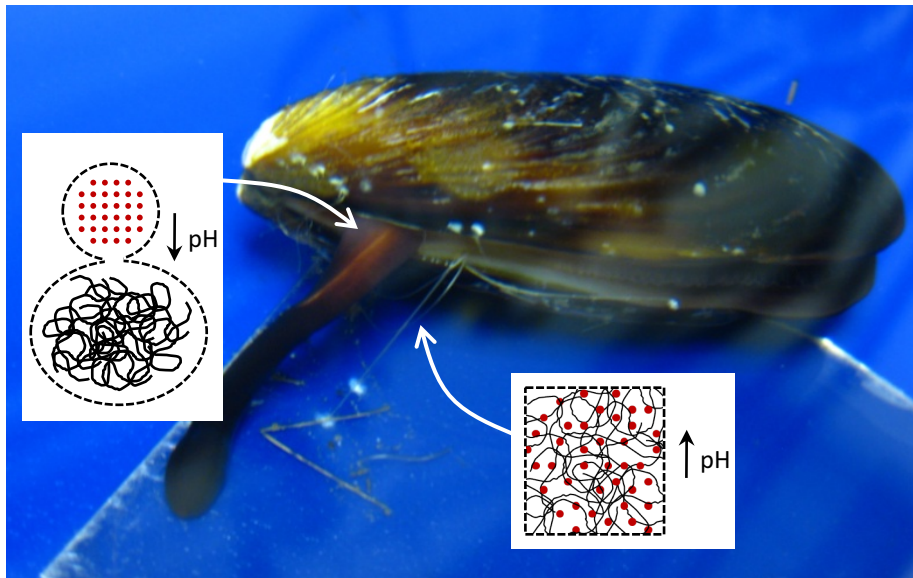
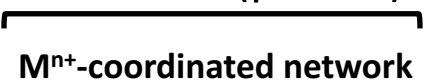
Mixing pH (≤ 5)

MCPs + M^{n+} mixture

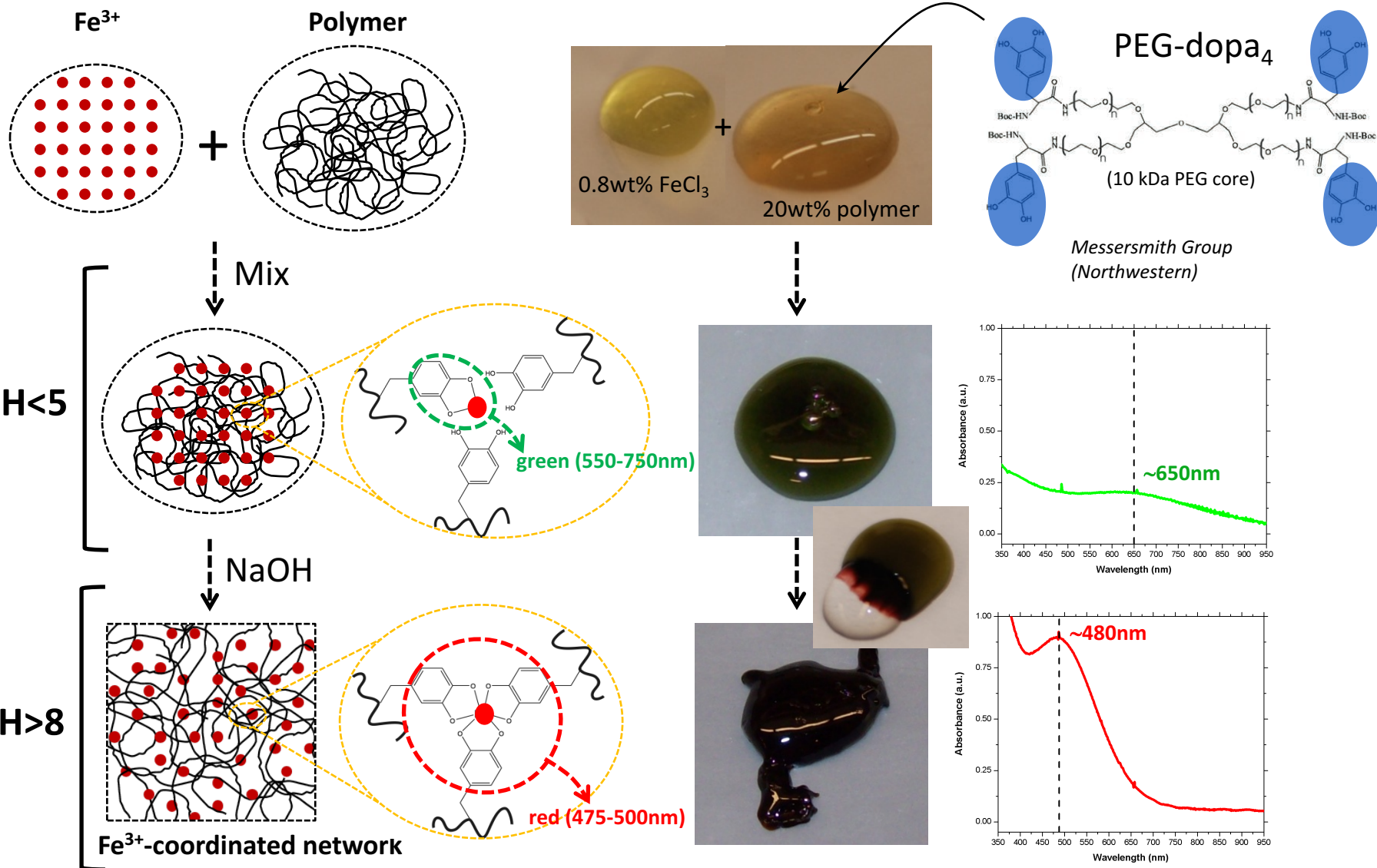


Exposure to seawater (pH ≈ 8)

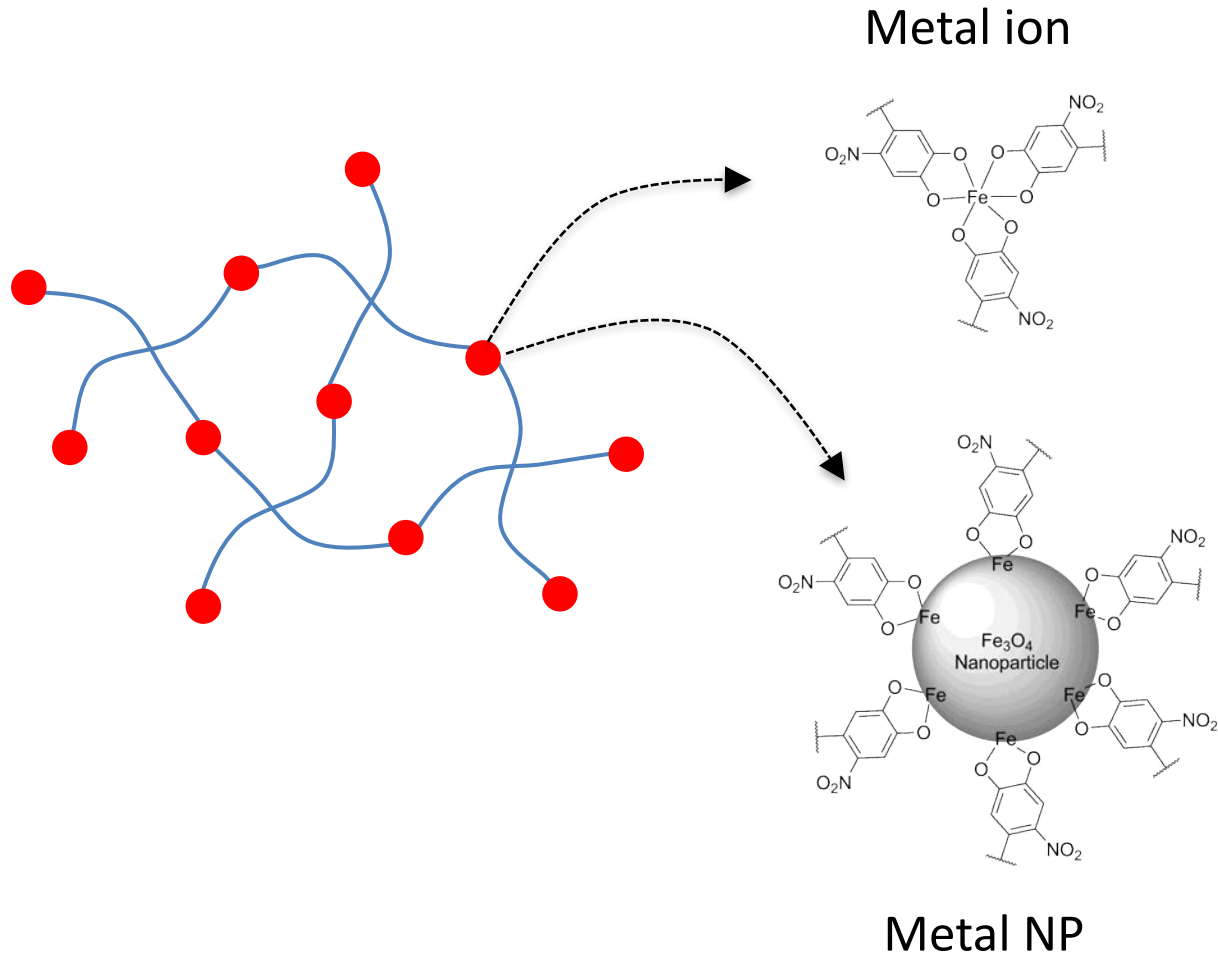
M^{n+} -coordinated network



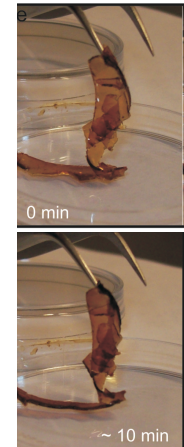
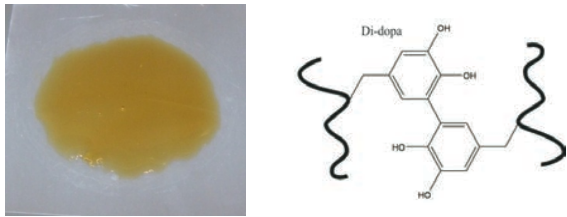
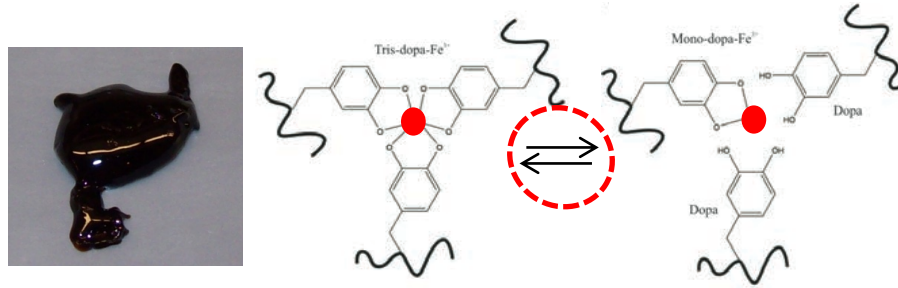
Metal-coordinated polymer network assembly



Bio-inspired metal-coordinate crosslinked networks

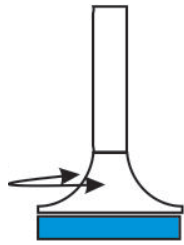
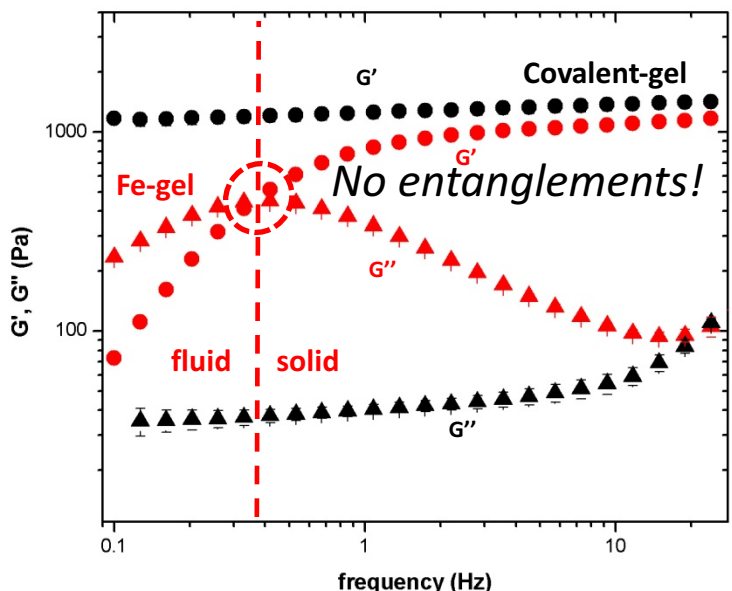


Metal ion-coordinate dynamics set gel mechanics

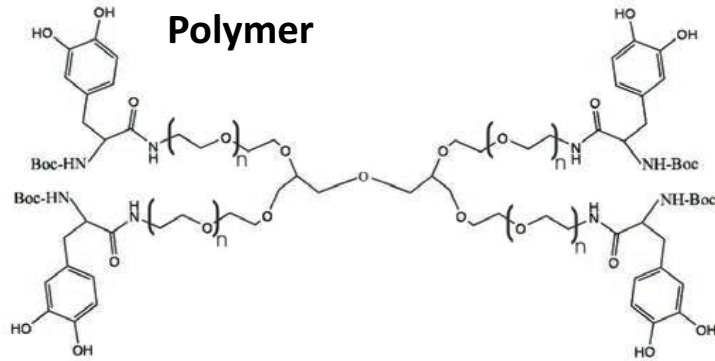


Elastic

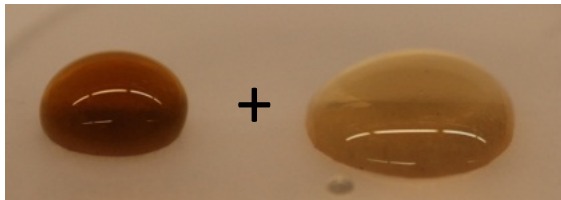
Visco-elastic



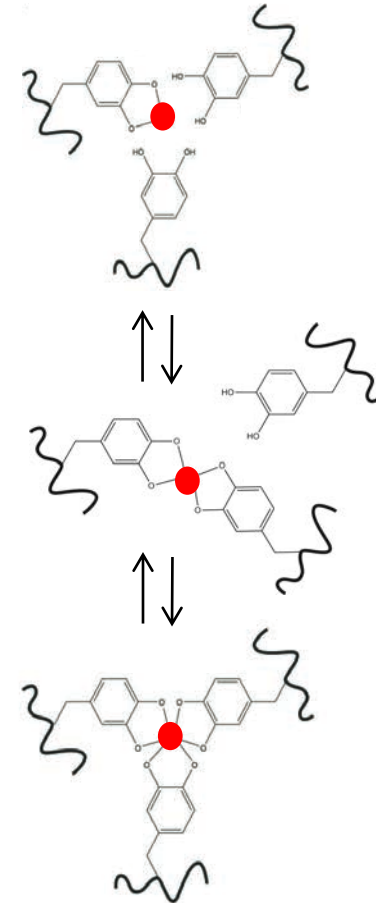
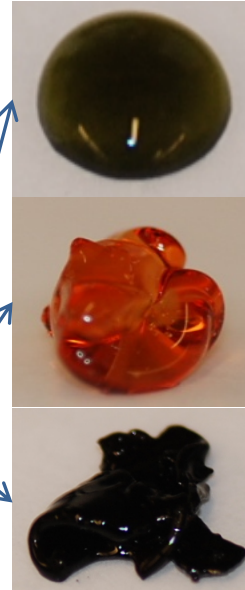
Metal ion-coordinate dynamics set gel mechanics



Metal



pH

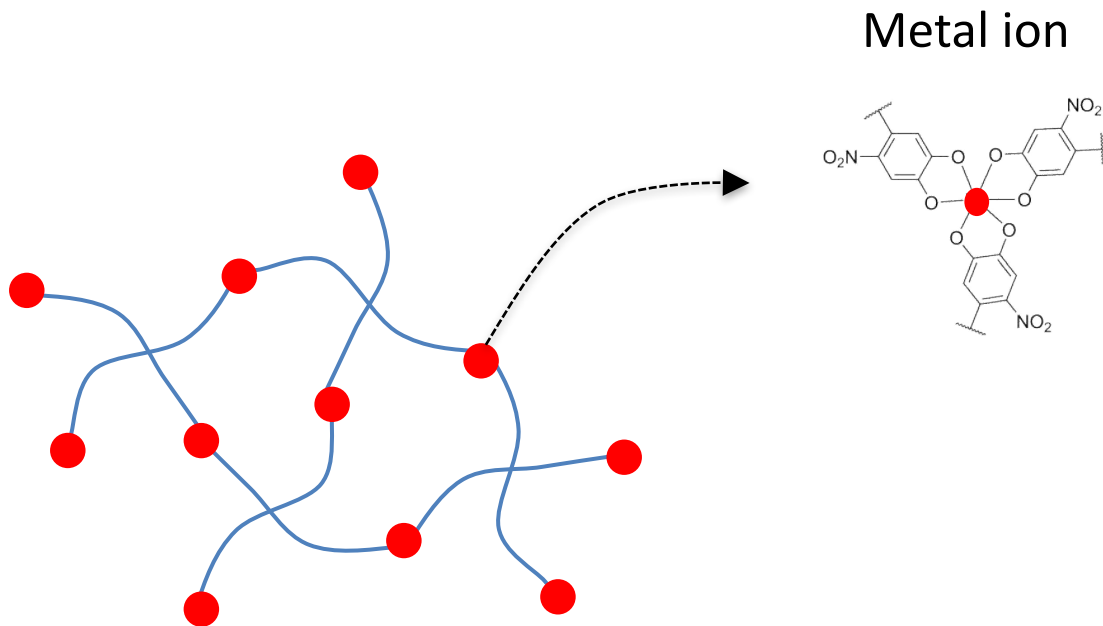


Periodic Table of the Elements

1 IA H Hydrogen	2 IIA He Helium																	18 VIIIA Ar Argon
3 IIIA Li Lithium	4 IVA Be Beryllium											13 IIIA B Boron	14 IVA C Carbon	15 VA N Nitrogen	16 VIA O Oxygen	17 VIIA F Fluorine	18 VIIIA Ne Neon	
11 IA Na Sodium	12 IIA Mg Magnesium											31 IIIA Al Aluminum	32 IVA Si Silicon	33 VA P Phosphorus	34 VIA S Sulfur	35 VIIA Cl Chlorine	36 VIIIA Ar Argon	
19 IA K Potassium	20 IIA Ca Calcium	21 Sc Scandium	22 Ti Titanium	23 V Vanadium	24 Cr Chromium	25 Mn Manganese	26 Fe Iron	27 Co Cobalt	28 Ni Nickel	29 Cu Copper	30 Zn Zinc	31 Ga Gallium	32 Ge Germanium	33 As Arsenic	34 Se Selenium	35 Br Bromine	36 Kr Krypton	
37 IA Rb Rubidium	38 IIA Sr Strontium	39 Y Yttrium	40 Zr Zirconium	41 Nb Niobium	42 Mo Molybdenum	43 Tc Technetium	44 Ru Ruthenium	45 Rh Rhodium	46 Pd Palladium	47 Ag Silver	48 Cd Cadmium	49 In Indium	50 Sn Tin	51 Sb Antimony	52 Te Tellurium	53 I Iodine	54 Xe Xenon	
55 IA Cs Cesium	56 IIA Ba Barium	57-71 Lanthanide Series	72 Hf Hafnium	73 Ta Tantalum	74 W Tungsten	75 Re Rhenium	76 Os Osmium	77 Ir Iridium	78 Pt Platinum	79 Au Gold	80 Hg Mercury	81 Tl Thallium	82 Pb Lead	83 Bi Bismuth	84 Po Polonium	85 At Astatine	86 Rn Radon	
87 IA Fr Francium	88 IIA Ra Radium	89-103 Actinide Series	104 Rf Rutherfordium	105 Db Dubnium	106 Sg Seaborgium	107 Bh Bohrium	108 Hs Hassium	109 Mt Meitnerium	110 Ds Darmstadtium	111 Rg Roentgenium	112 Cn Copernicium	113 Nh Nihonium	114 Fl Flerovium	115 Uup Ununpentium	116 Lv Livermorium	117 Uus Ununseptium	118 Uuo Ununoctium	
		101 La Lanthanum	102 Ce Cerium	103 Pr Praseodymium	104 Nd Neodymium	105 Pm Promethium	106 Sm Samarium	107 Eu Europium	108 Gd Gadolinium	109 Tb Terbium	110 Dy Dysprosium	111 Ho Holmium	112 Er Erbium	113 Tm Thulium	114 Yb Ytterbium	115 Lu Lutetium		
		119 Ac Actinium	120 Th Thorium	121 Pa Protactinium	122 U Uranium	123 Np Neptunium	124 Pu Plutonium	125 Am Americium	126 Cm Curium	127 Bk Berkelium	128 Cf Californium	129 Es Einsteinium	130 Fm Fermium	131 Md Mendelevium	132 No Nobelium	133 Lr Lawrencium		
		Alkali Metal	Alkaline Earth	Transition Metal	Basic Metal	Semi-metal	Nonmetal	Halogen	Noble Gas	Lanthanide	Actinide							

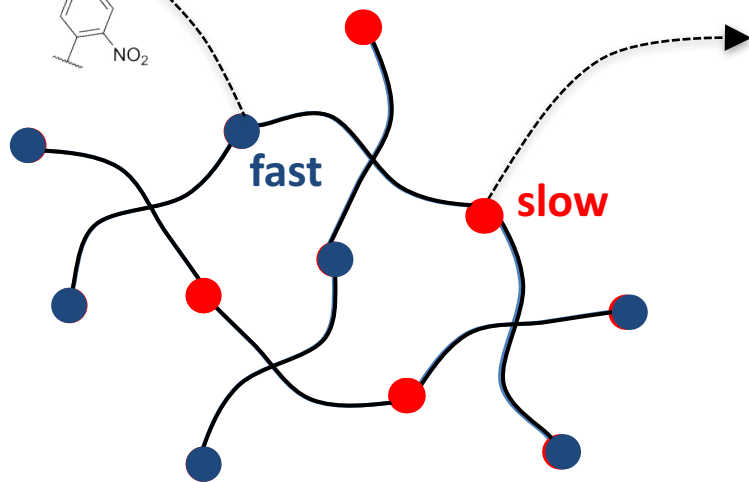
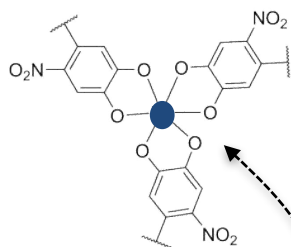
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Metal ion-coordinate dynamics set gel mechanics

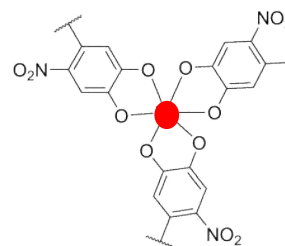


Metal ion-coordinate dynamics set gel mechanics

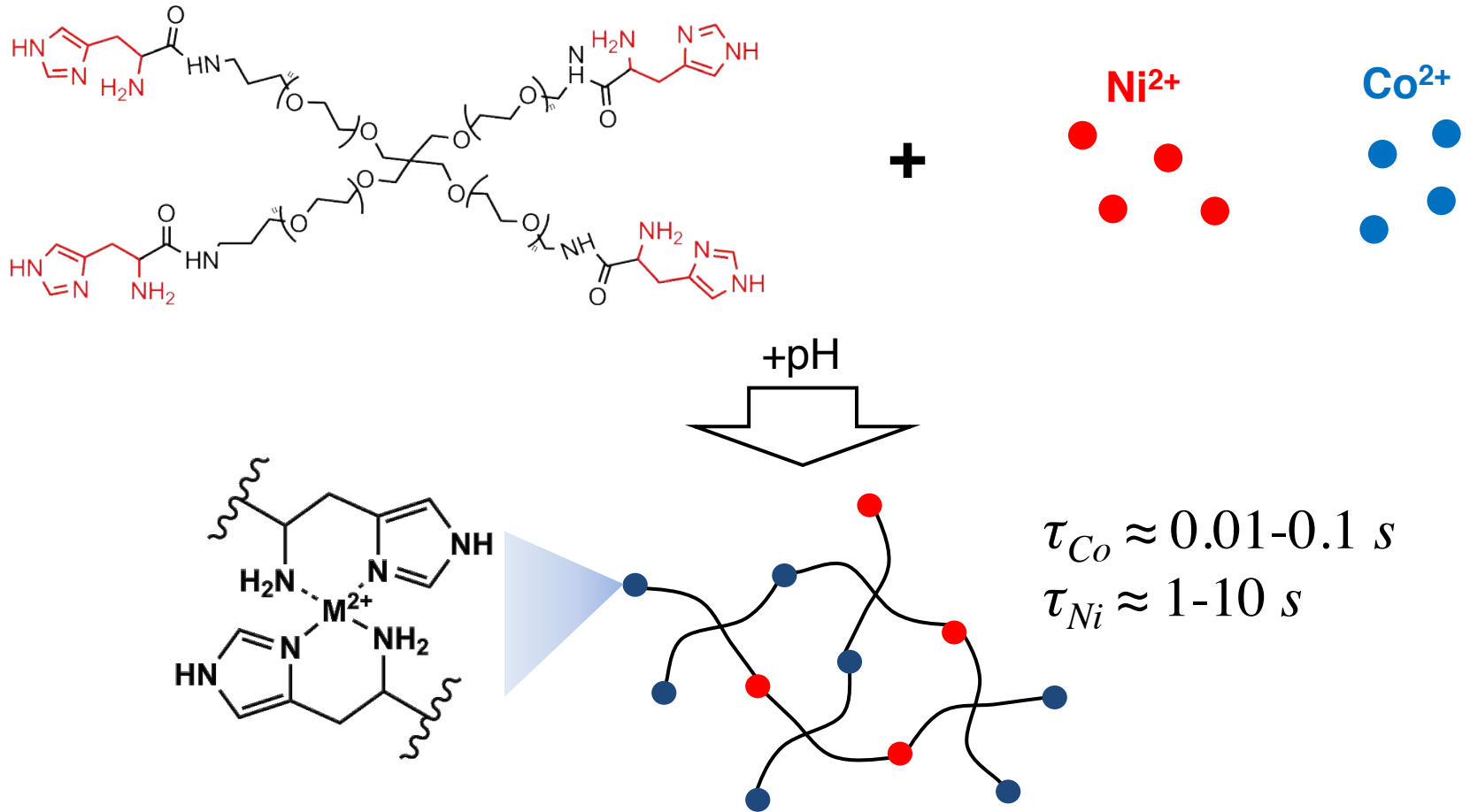
Metal ion B



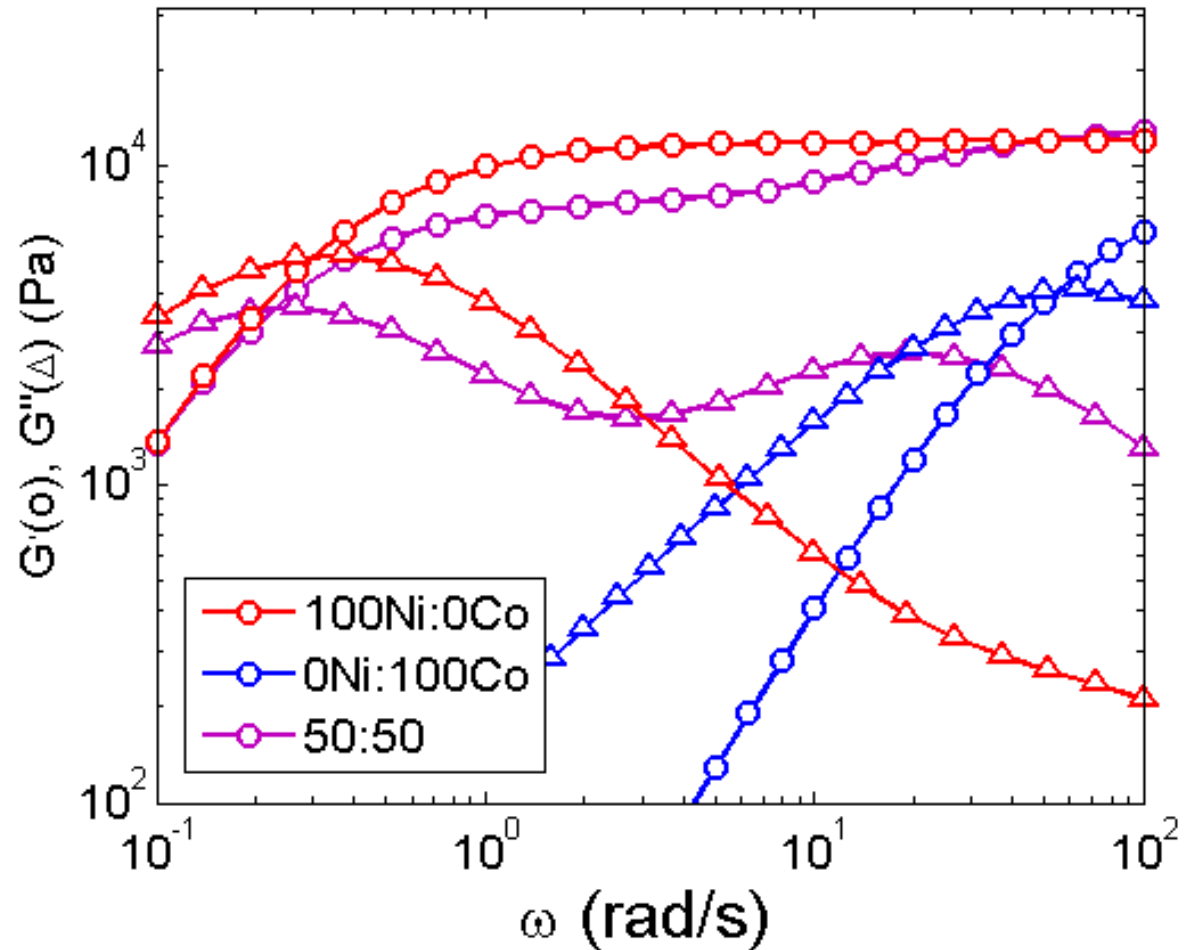
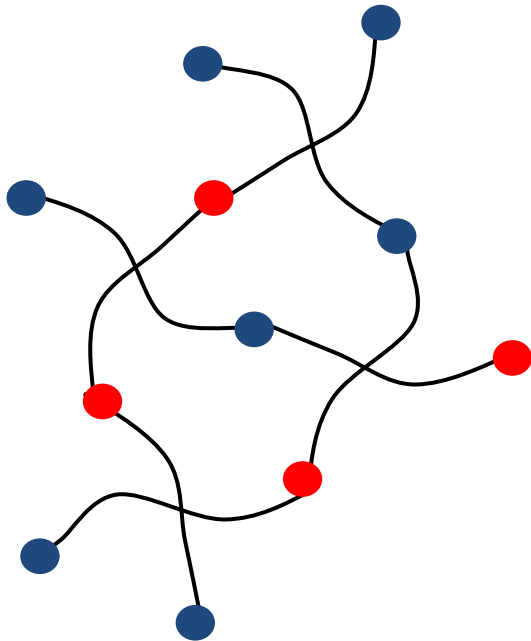
Metal ion A



Metal ion-coordinate dynamics set gel mechanics

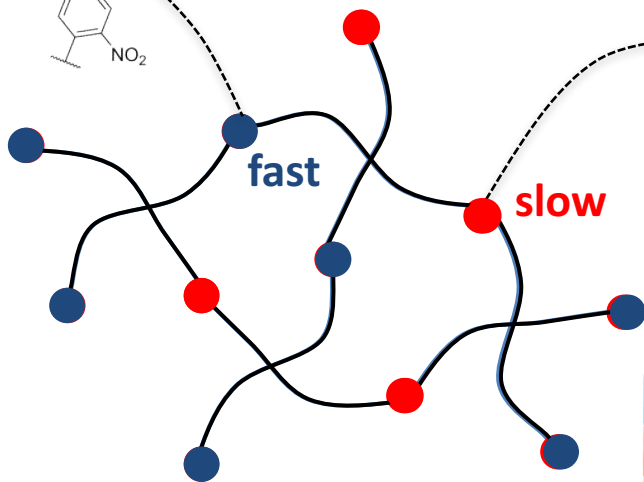
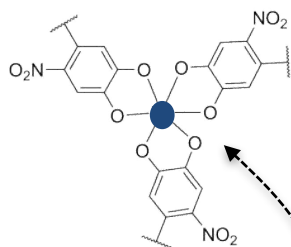


Metal ion-coordinate dynamics set gel mechanics

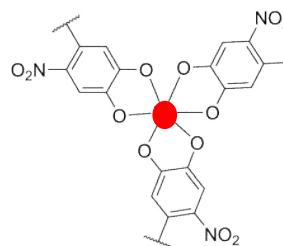


Metal ion-coordinate dynamics set gel mechanics

Metal ion B



Metal ion A

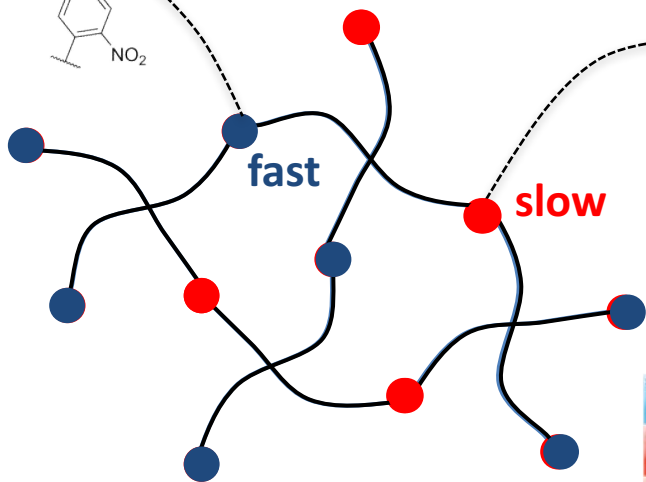
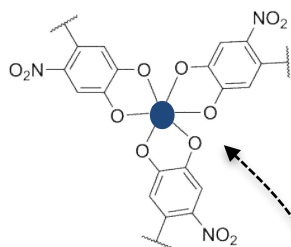


Periodic Table of the Elements

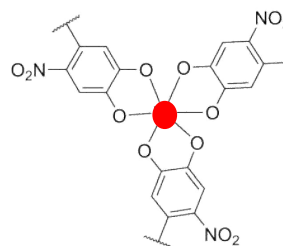
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3 IIIB Li Lithium 6.941	4 IIIB Mg Magnesium 24.305	5 IVB Na Sodium 22.990	6 VB Ca Calcium 40.078	7 VIB Sc Scandium 44.956	8 VIB Ti Titanium 47.88	9 VIB V Vanadium 50.942	10 VIB Cr Chromium 51.996	11 VIIB Mn Manganese 54.938	12 VIIB Fe Iron 55.845	13 VIIB Co Cobalt 58.933	14 VIIB Ni Nickel 58.693	15 VIIIB Cu Copper 63.546	16 VIIIB Zn Zinc 65.38	17 VIIIB Ga Gallium 69.723	18 VIIIB Ge Germanium 72.630	19 VIIIB As Arsenic 74.922	20 VIIIB Se Selenium 78.96	21 VIIIB Br Bromine 79.904	22 VIIIB Kr Krypton 83.798																
23 IIIB K Potassium 39.098	24 IIIB Ca Calcium 40.078	25 IIIB Sc Scandium 44.956	26 IIIB Ti Titanium 47.88	27 IIIB V Vanadium 50.942	28 IIIB Cr Chromium 51.996	29 IIIB Mn Manganese 54.938	30 IIIB Fe Iron 55.845	31 IIIB Co Cobalt 58.933	32 IIIB Ni Nickel 58.693	33 IIIB Cu Copper 63.546	34 IIIB Zn Zinc 65.38	35 IIIB Ga Gallium 69.723	36 IIIB Ge Germanium 72.630	37 IIIB As Arsenic 74.922	38 IIIB Se Selenium 78.96	39 IIIB Br Bromine 79.904	40 IIIB Kr Krypton 83.798	41 IIIB Rb Rubidium 85.468	42 IIIB Sr Strontium 87.62	43 IIIB Y Yttrium 88.906	44 IIIB Zr Zirconium 91.224	45 IIIB Nb Niobium 92.906	46 IIIB Mo Molybdenum 95.94	47 IIIB Tc Technetium 98.906	48 IIIB Ru Ruthenium 101.07	49 IIIB Rh Rhodium 102.905	50 IIIB Pd Palladium 106.42	51 IIIB Ag Silver 107.868	52 IIIB Cd Cadmium 112.411	53 IIIB In Indium 114.818	54 IIIB Sn Tin 118.710	55 IIIB Sb Antimony 121.757	56 IIIB Te Tellurium 127.6	57 IIIB I Iodine 126.905	58 IIIB Xe Xenon 131.29
59 IIIB Cs Cesium 132.905	60 IIIB Ba Barium 137.327	61-71 IIIB La-Lu Lanthanide Series	72 IIIB Hf Hafnium 178.49	73 IIIB Ta Tantalum 180.948	74 IIIB W Tungsten 183.84	75 IIIB Re Rhenium 186.207	76 IIIB Os Osmium 190.23	77 IIIB Ir Iridium 192.222	78 IIIB Pt Platinum 195.084	79 IIIB Au Gold 196.967	80 IIIB Hg Mercury 200.59	81 IIIB Tl Thallium 204.38	82 IIIB Pb Lead 207.2	83 IIIB Bi Bismuth 208.980	84 IIIB Po Polonium 209	85 IIIB At Astatine 209	86 IIIB Rn Radon 222	87 IIIB Fr Francium 223	88 IIIB Ra Radium 226	89-103 IIIB Ac-Lr Actinide Series	104 IIIB Rf Rutherfordium 261	105 IIIB Db Dubnium 262	106 IIIB Sg Seaborgium 263	107 IIIB Bh Bohrium 264	108 IIIB Hs Hassium 265	109 IIIB Mt Meitnerium 266	110 IIIB Ds Darmstadtium 267	111 IIIB Rg Roentgenium 268	112 IIIB Cn Copernicium 269	113 IIIB Uut Ununtrium 270	114 IIIB Fl Flerovium 271	115 IIIB Uup Ununpentium 272	116 IIIB Lv Livermorium 273	117 IIIB Uus Ununseptium 274	118 IIIB Uuo Ununoctium 276
89 IIIB La Lanthanum 138.905	90 IIIB Ce Cerium 140.12	91 IIIB Pr Praseodymium 140.908	92 IIIB Nd Neodymium 144.24	93 IIIB Pm Promethium 144.913	94 IIIB Sm Samarium 150.36	95 IIIB Eu Europium 151.964	96 IIIB Gd Gadolinium 157.25	97 IIIB Tb Terbium 158.925	98 IIIB Dy Dysprosium 162.50	99 IIIB Ho Holmium 164.930	100 IIIB Er Erbium 167.259	101 IIIB Tm Thulium 168.930	102 IIIB Yb Ytterbium 173.054	103 IIIB Lu Lutetium 174.967	104 IIIB Ac Actinium 227	105 IIIB Th Thorium 232.037	106 IIIB Pa Protactinium 231.036	107 IIIB U Uranium 238.029	108 IIIB Np Neptunium 237.048	109 IIIB Pu Plutonium 244.064	110 IIIB Am Americium 243.061	111 IIIB Cm Curium 247.070	112 IIIB Bk Berkelium 247.070	113 IIIB Cf Californium 251.083	114 IIIB Es Einsteinium 252.083	115 IIIB Fm Fermium 257.105	116 IIIB Md Mendelevium 258.105	117 IIIB No Nobelium 259.105	118 IIIB Lr Lawrencium 260.105						
Alkali Metal		Alkaline Earth		Transition Metal										Basis		Semimetal		Nonmetal		Halogen		Noble Gas		Lanthanide		Actinide									

Metal ion-coordinate dynamics set gel mechanics

Lanthanide Metal ion B



Lanthanide metal ion A

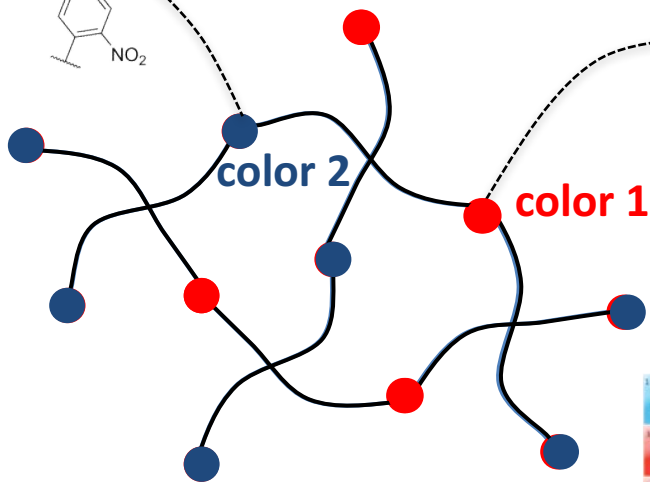
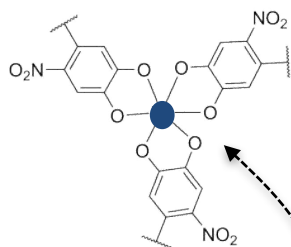


Periodic Table of the Elements

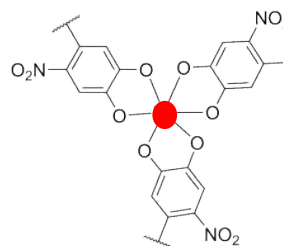
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3 IIIB Li Lithium 6.941	4 IIA Be Beryllium 9.012	5 IIIB Sc Scandium 44.956	6 IVB Ti Titanium 47.88	7 VB V Vanadium 50.942	8 VIB Cr Chromium 51.996	9 VIIB Mn Manganese 54.938	10 VIIIB Fe Iron 55.845	11 VIIIB Co Cobalt 58.933	12 VIIIB Ni Nickel 58.69	13 IB Cu Copper 63.546	14 IIB Zn Zinc 65.38	15 IIIB Ga Gallium 69.723	16 IIIVB Ge Germanium 72.63	17 IIIVB As Arsenic 74.922	18 IIIVB Se Selenium 78.96	19 IIIVB Br Bromine 79.904	20 IIIVB Kr Krypton 83.798								
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37 IIA Rb Rubidium 85.468	38 IIA Sr Strontium 87.62	39 IIIB Y Yttrium 88.906	40 IIIB Zr Zirconium 91.224	41 IIIB Nb Niobium 92.906	42 IIIB Mo Molybdenum 95.94	43 IIIB Tc Technetium 98.906	44 IIIB Ru Ruthenium 101.07	45 IIIB Rh Rhodium 102.905	46 IIIB Pd Palladium 106.42	47 IIIB Ag Silver 107.868	48 IIIB Cd Cadmium 112.411	49 IIIB In Indium 114.818	50 IIIB Sn Tin 118.710	51 IIIB Sb Antimony 121.757	52 IIIB Te Tellurium 127.6	53 IIIB I Iodine 126.905	54 IIIB Xe Xenon 131.29								
55 IIA Cs Cesium 132.905	56 IIA Ba Barium 137.327	57-71 Lanthanide Series La Lanthanum 138.905 Ce Cerium 140.12 Pr Praseodymium 140.908 Nd Neodymium 144.24 Pm Promethium 144.913 Sm Samarium 150.36 Eu Europium 151.964 Gd Gadolinium 157.25 Tb Terbium 158.925 Dy Dysprosium 162.50 Ho Holmium 164.930 Er Erbium 167.259 Tm Thulium 168.934 Yb Ytterbium 173.054 Lu Lutetium 174.967	72 IIIB Hf Hafnium 178.49	73 IIIB Ta Tantalum 180.948	74 IIIB W Tungsten 183.84	75 IIIB Re Rhenium 186.207	76 IIIB Os Osmium 190.23	77 IIIB Ir Iridium 192.222	78 IIIB Pt Platinum 195.084	79 IIIB Au Gold 196.967	80 IIIB Hg Mercury 200.59	81 IIIB Tl Thallium 204.38	82 IIIB Pb Lead 207.2	83 IIIB Bi Bismuth 208.980	84 IIIB Po Polonium 209	85 IIIB At Astatine 210	86 IIIB Rn Radon 222								
87 IIA Fr Francium [223]	88 IIA Ra Radium [226]	89-103 Actinide Series Rf Rutherfordium [261] Db Dubnium [262] Sg Seaborgium [263] Bh Bohrium [264] Hs Hassium [265] Mt Meitnerium [266] Ds Darmstadtium [267] Rg Roentgenium [268] Cn Copernicium [269] Uut Ununtrium [270] Fl Flerovium [271] Uup Ununpentium [272] Lv Livermorium [273] Uus Ununseptium [274] Uuo Ununoctium [275]	104 IIIB Rf Rutherfordium [261]	105 IIIB Db Dubnium [262]	106 IIIB Sg Seaborgium [263]	107 IIIB Bh Bohrium [264]	108 IIIB Hs Hassium [265]	109 IIIB Mt Meitnerium [266]	110 IIIB Ds Darmstadtium [267]	111 IIIB Rg Roentgenium [268]	112 IIIB Cn Copernicium [269]	113 IIIB Uut Ununtrium [270]	114 IIIB Fl Flerovium [271]	115 IIIB Uup Ununpentium [272]	116 IIIB Lv Livermorium [273]	117 IIIB Uus Ununseptium [274]	118 IIIB Uuo Ununoctium [275]								
		Lanthanide Series		Actinide Series		Alkali Metal		Alkaline Earth		Transition Metal		Block		Semimetal		Nonmetal		Halogen		Noble Gas		Lanthanide		Actinide	

Metal ion-coordinate dynamics set gel mechanics

Lanthanide Metal ion B



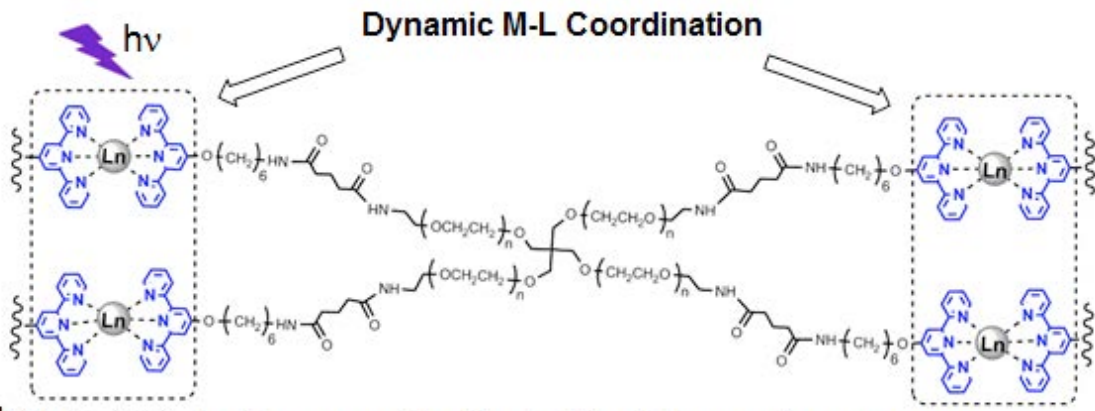
Lanthanide metal ion A



Periodic Table of the Elements

1 IA H Hydrogen 1.008	2 IIA Be Beryllium 9.012											13 IIIA B Boron 10.811	14 IVA C Carbon 12.011	15 VA N Nitrogen 14.007	16 VIA O Oxygen 15.999	17 VIIA F Fluorine 18.998	18 VIIIA Ne Neon 20.180
3 IA Li Lithium 6.941	4 IIA Be Beryllium 9.012	5 IIIB Sc Scandium 44.956	6 IVB Ti Titanium 47.88	7 VB V Vanadium 50.942	8 VIB Cr Chromium 51.996	9 VIIB Mn Manganese 54.938	10 VIII Fe Iron 55.845	11 VIII Co Cobalt 58.933	12 VIII Ni Nickel 58.693	13 IB Cu Copper 63.546	14 IIB Zn Zinc 65.38	15 IIIB Ga Gallium 69.723	16 IIIVB Ge Germanium 72.630	17 VB As Arsenic 74.922	18 VIB Se Selenium 78.96	19 VIIA Br Bromine 79.904	20 VIIIA Kr Krypton 83.798
19 IA K Potassium 39.098	20 IIA Ca Calcium 40.078	21 IIIB Sc Scandium 44.956	22 IVB Ti Titanium 47.88	23 VB V Vanadium 50.942	24 VIB Cr Chromium 51.996	25 VIIB Mn Manganese 54.938	26 VIII Fe Iron 55.845	27 VIII Co Cobalt 58.933	28 VIII Ni Nickel 58.693	29 IB Cu Copper 63.546	30 IIB Zn Zinc 65.38	31 IIIB Ga Gallium 69.723	32 IIIVB Ge Germanium 72.630	33 VB As Arsenic 74.922	34 VIB Se Selenium 78.96	35 VIIA Br Bromine 79.904	36 VIIIA Kr Krypton 83.798
37 IA Rb Rubidium 85.468	38 IIA Sr Strontium 87.62	39 IIIB Y Yttrium 88.906	40 IVB Zr Zirconium 91.224	41 VB Nb Niobium 92.906	42 VIB Mo Molybdenum 95.94	43 VIIB Tc Technetium 98.906	44 VIII Ru Ruthenium 101.07	45 VIII Rh Rhodium 102.905	46 VIII Pd Palladium 106.42	47 IB Ag Silver 107.868	48 IIB Cd Cadmium 112.411	49 IIIB In Indium 114.818	50 IIIVB Sn Tin 118.710	51 VB Sb Antimony 121.757	52 VIB Te Tellurium 127.6	53 VIIA I Iodine 126.905	54 VIIIA Xe Xenon 131.29
55 IA Cs Cesium 132.905	56 IIA Ba Barium 137.327	57-71 Lanthanide Series La Lanthanum 138.905 Ce Cerium 140.12 Pr Praseodymium 140.908 Nd Neodymium 144.24 Pm Promethium 144.913 Sm Samarium 150.36 Eu Europium 151.964 Gd Gadolinium 157.25 Tb Terbium 158.925 Dy Dysprosium 162.50 Ho Holmium 164.930 Er Erbium 167.255 Tm Thulium 168.934 Yb Ytterbium 173.054 Lu Lutetium 174.967	72 IVB Hf Hafnium 178.49	73 VB Ta Tantalum 180.948	74 VIB W Tungsten 183.84	75 VIIB Re Rhenium 186.207	76 VIII Os Osmium 190.23	77 VIII Ir Iridium 192.222	78 VIII Pt Platinum 195.084	79 IB Au Gold 196.967	80 IIB Hg Mercury 200.59	81 IIIB Tl Thallium 204.384	82 IIIVB Pb Lead 207.2	83 VB Bi Bismuth 208.980	84 VIB Po Polonium 209	85 VIIA At Astatine 209	86 VIIIA Rn Radon 222
87 IA Fr Francium [223]	88 IIA Ra Radium [226]	89-103 Actinide Series Rf Rutherfordium [261] Db Dubnium [262] Sg Seaborgium [263] Bh Bohrium [264] Hs Hassium [265] Mt Meitnerium [266] Ds Darmstadtium [267] Rg Roentgenium [268] Cn Copernicium [269] Uut Ununtrium [271] Fl Flerovium [277] Uup Ununpentium [278] Lv Livermorium [286] Uus Ununseptium [287] Uuo Ununoctium [288]	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [263]	107 Bh Bohrium [264]	108 Hs Hassium [265]	109 Mt Meitnerium [266]	110 Ds Darmstadtium [267]	111 Rg Roentgenium [268]	112 Cn Copernicium [269]	113 Nh Nihonium [270]	114 Fl Flerovium [277]	115 Mc Moscovium [278]	116 Lv Livermorium [286]	117 Ts Tennessine [287]	118 Og Oganesson [288]

Light-emitting stimuli-responsive polymer networks



Lanthanide salt

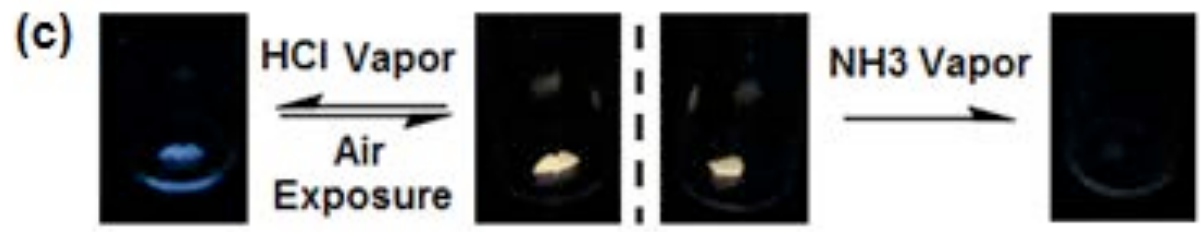
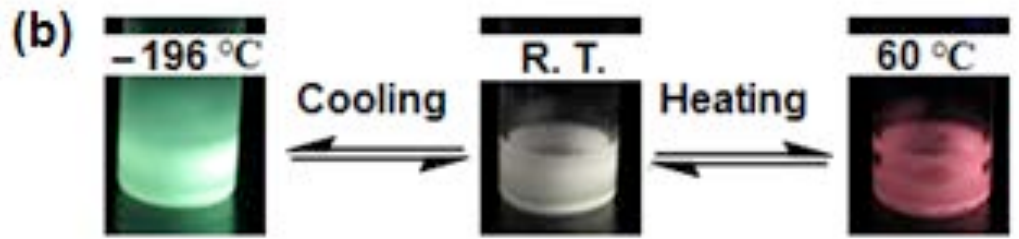
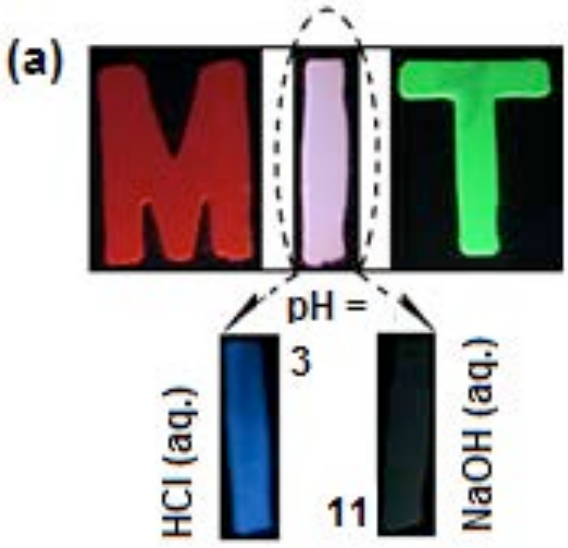
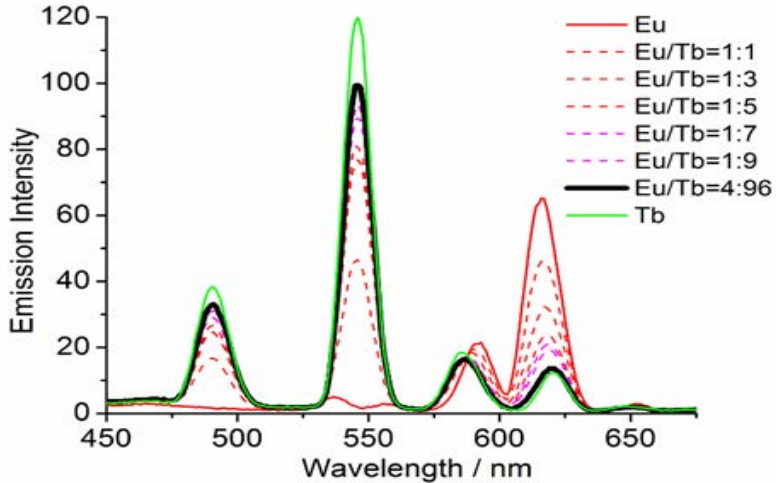
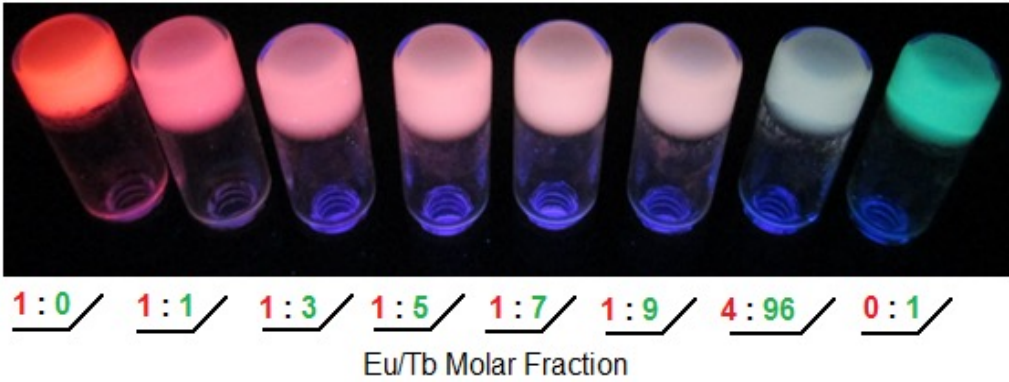


Polymer

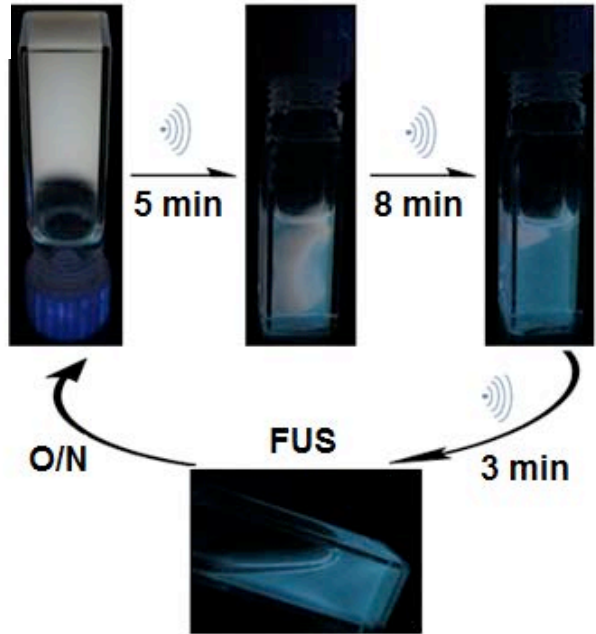
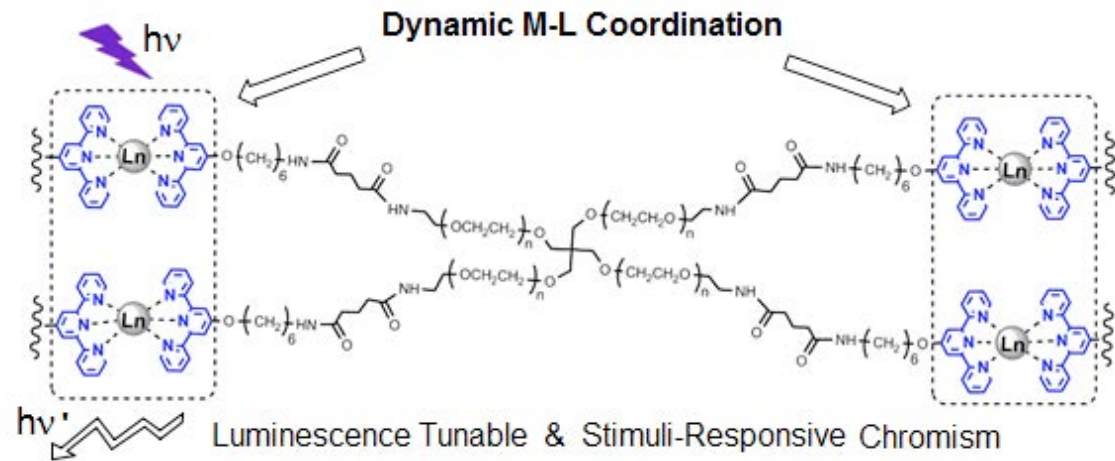


Ln(III) =		
Eu	Eu/Tb	Tb
RLGel	WLGel	GLGel

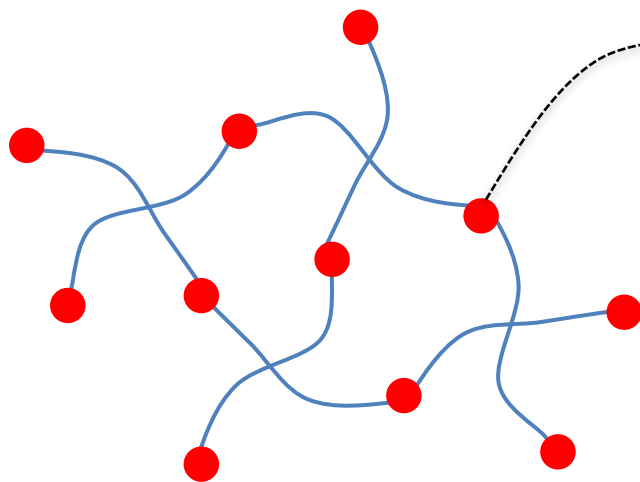
Light-emitting stimuli-responsive polymer networks



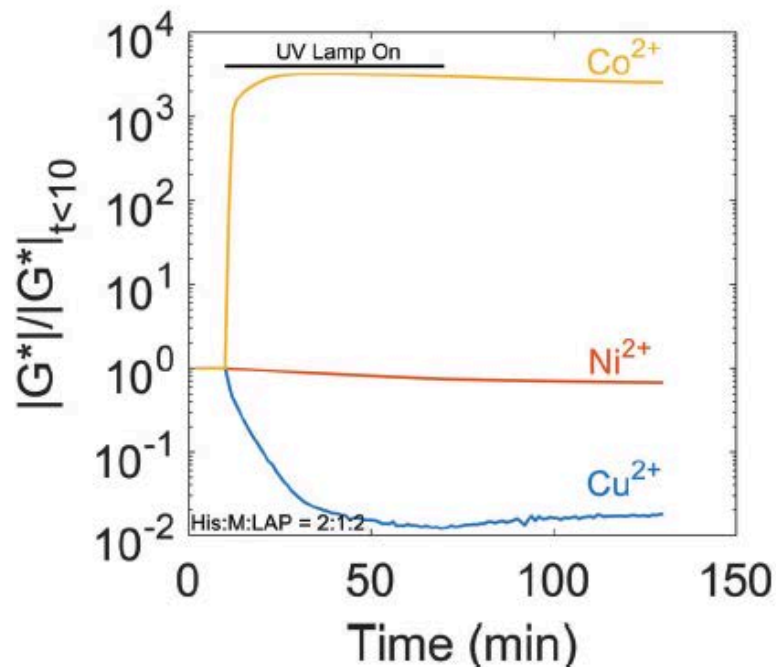
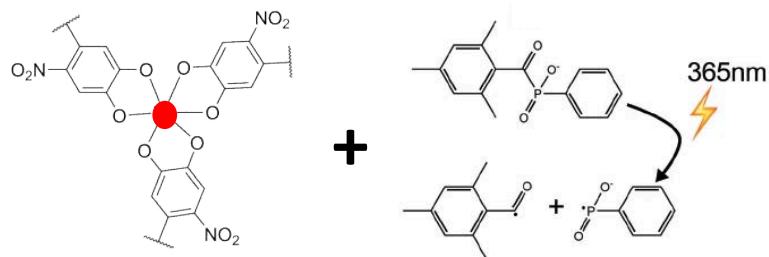
Light-emitting stimuli-responsive polymer networks



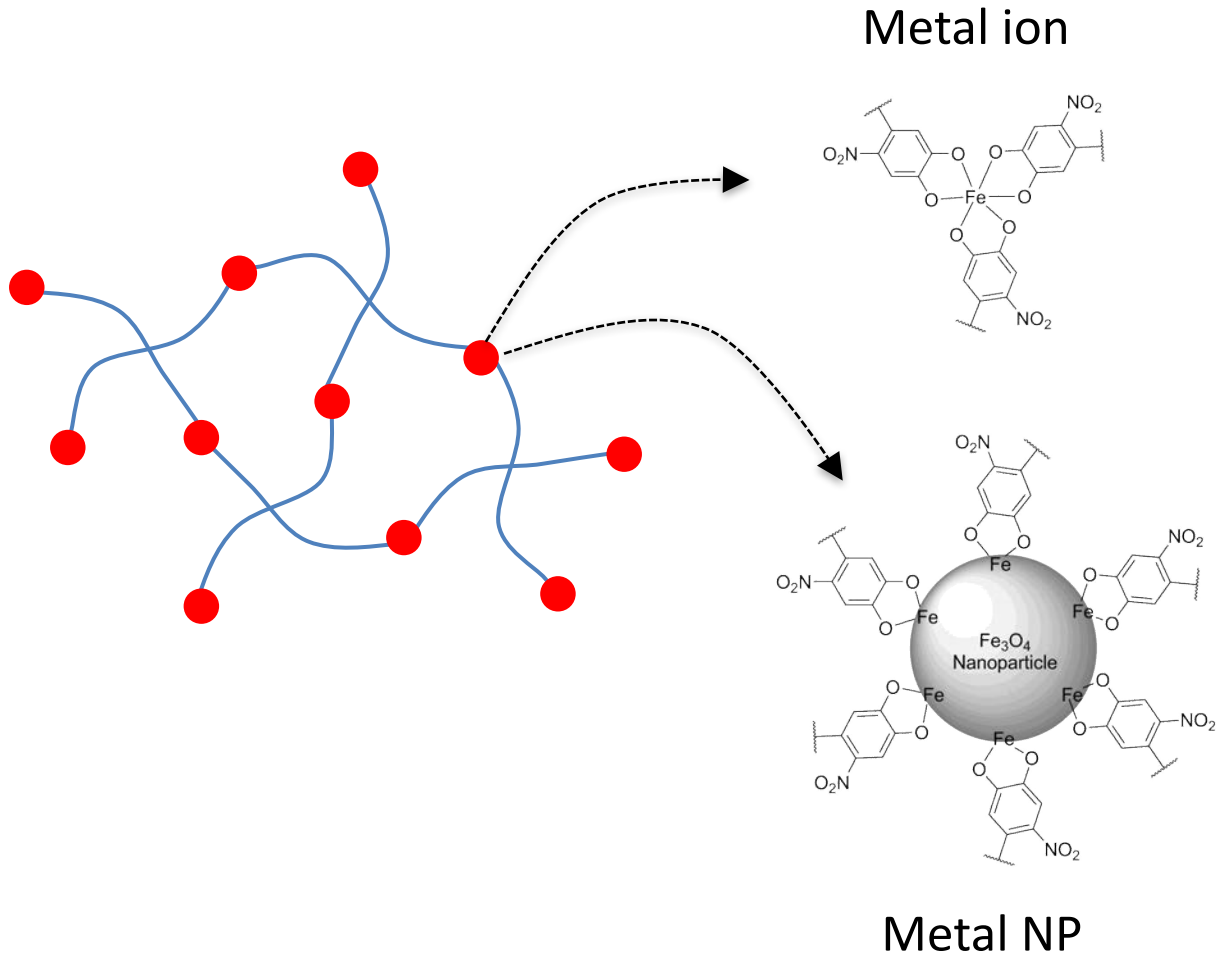
Metal ion-coordinate dynamics set gel mechanics



Metal ion

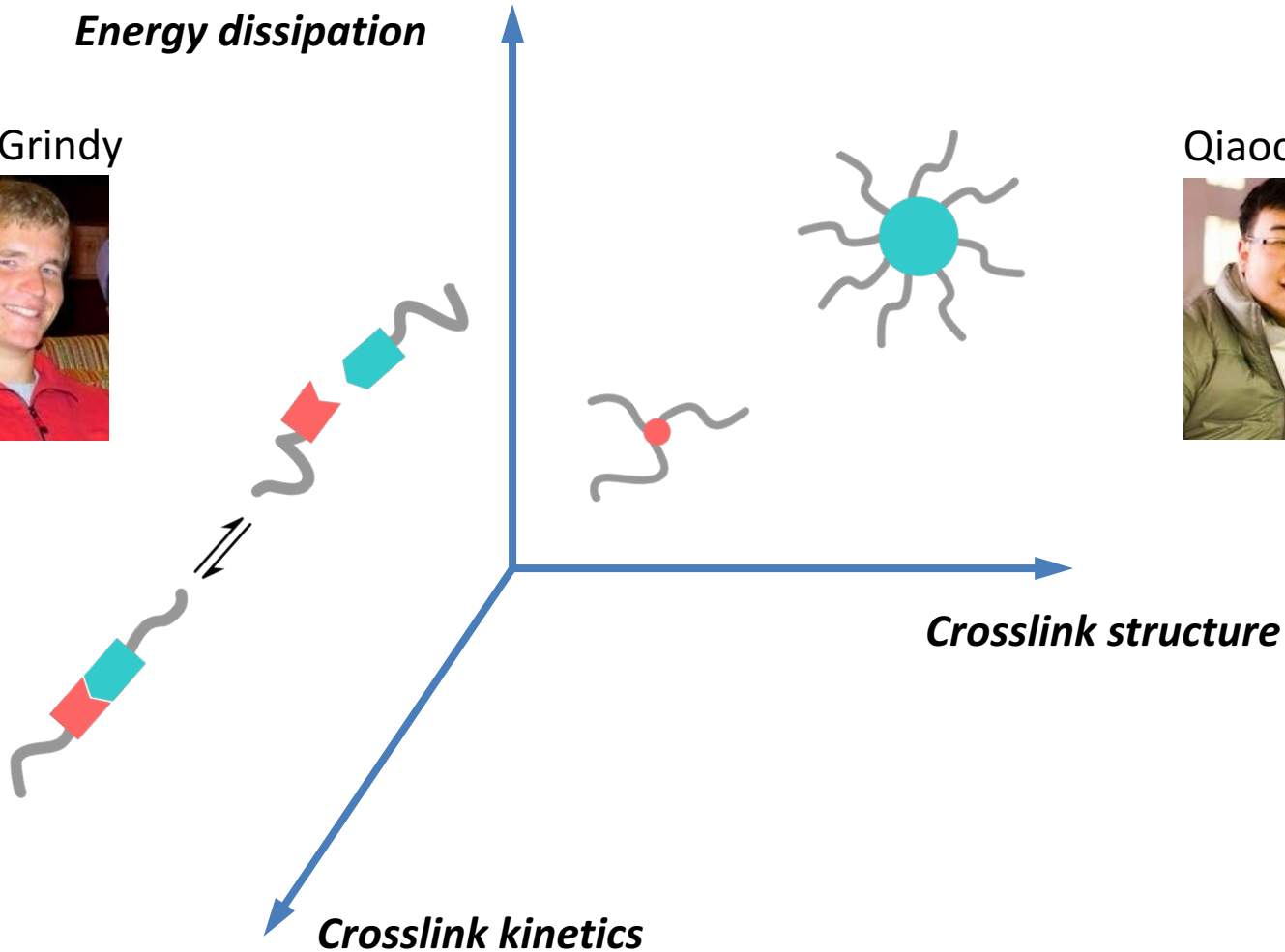


Bio-inspired metal-coordinate crosslinked networks



Energy dissipative crosslink engineering

Scott Grindy

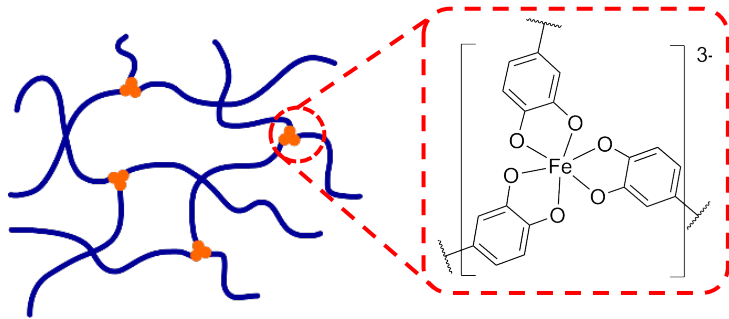


Qiaochu Li

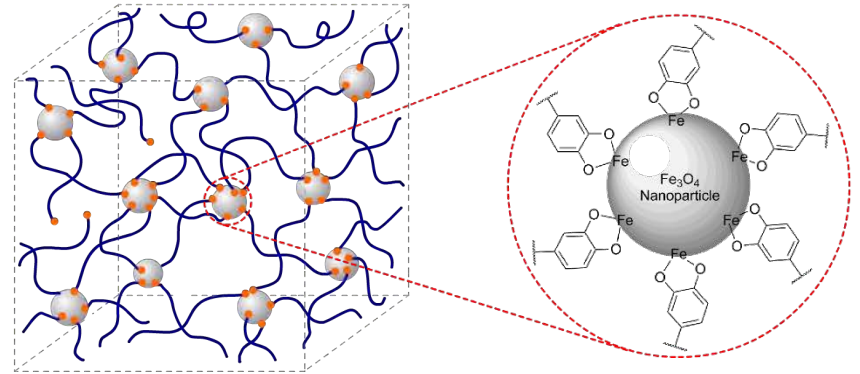


Energy dissipative crosslinks: Ions vs Nano-particles

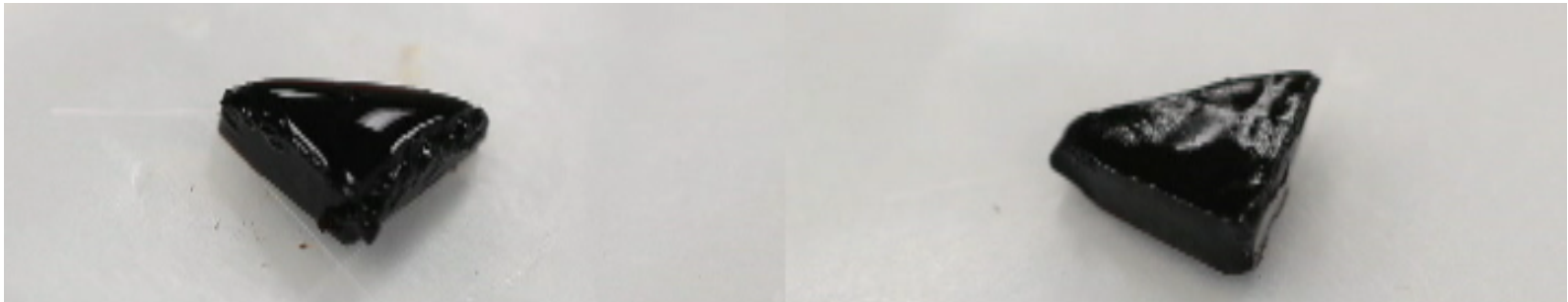
f : number of ligands at each crosslink



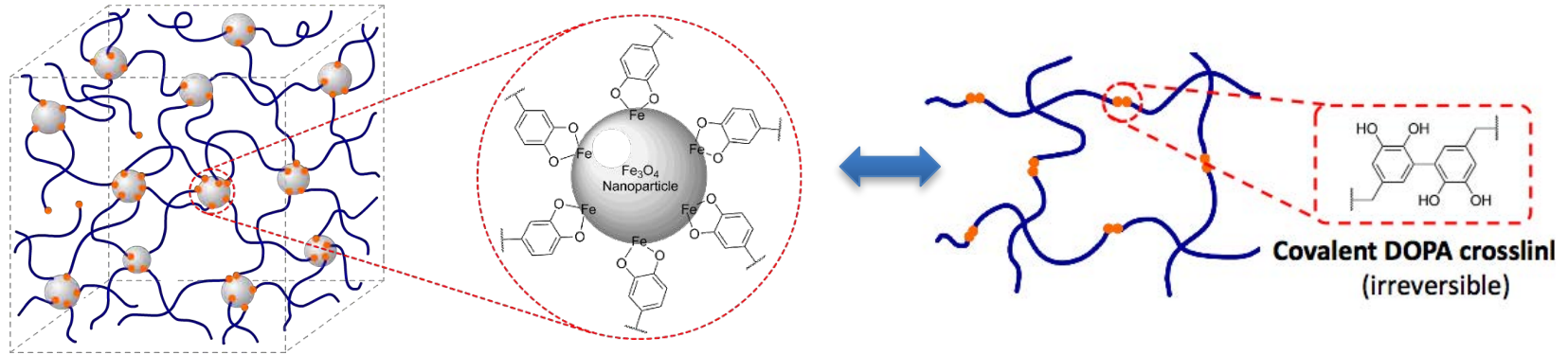
$f = 3$



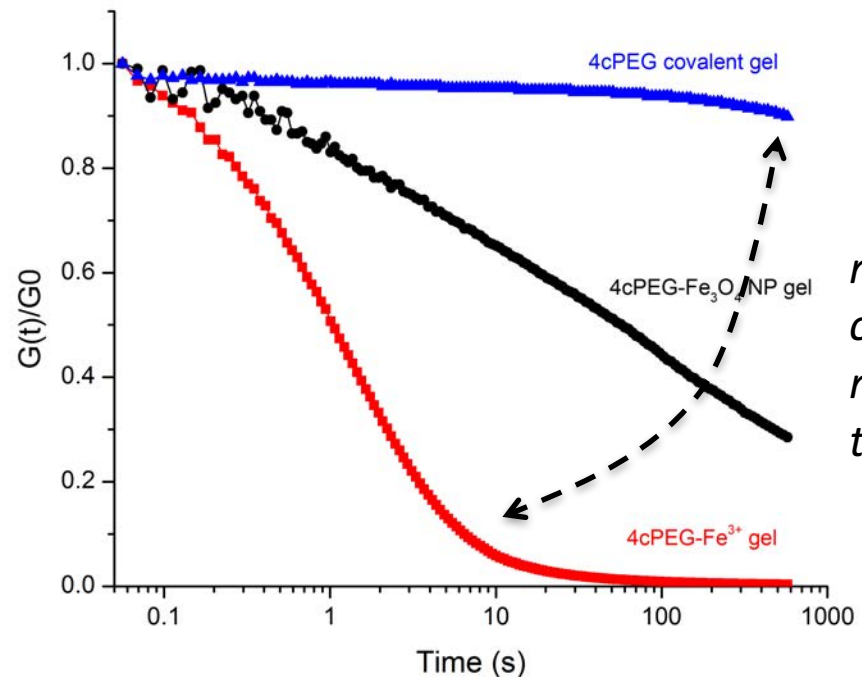
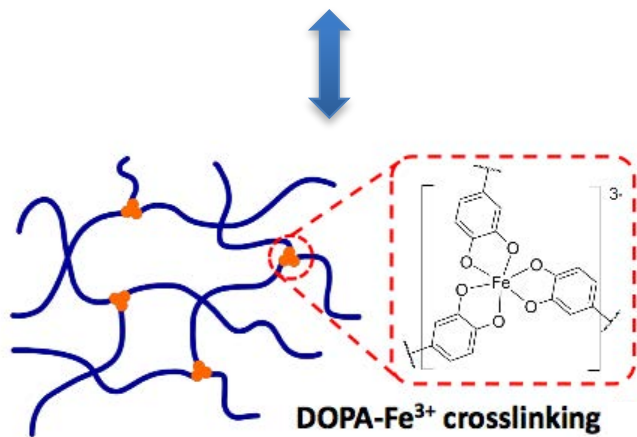
$f \sim 10^2$



Energy dissipative crosslinks: Ions vs Nano-particles



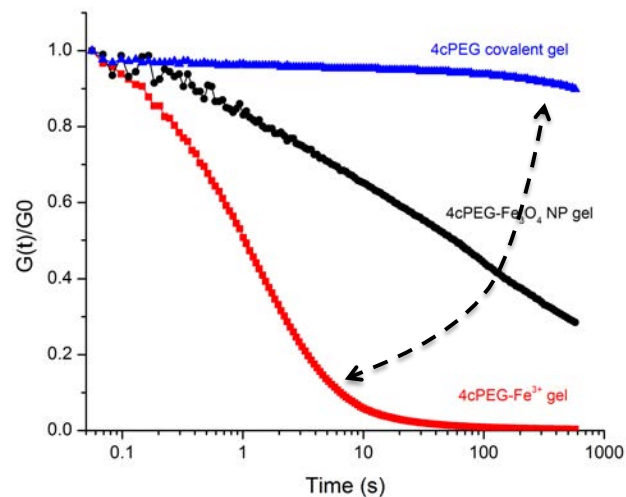
Self-assembled Hydrogel Network



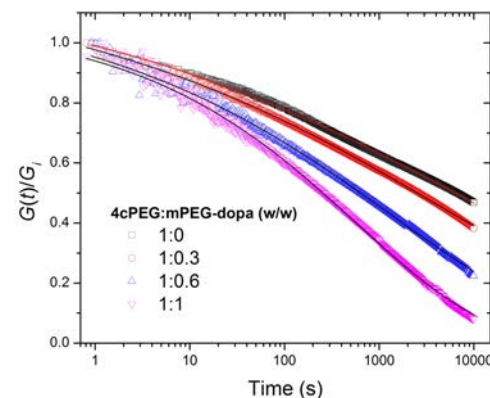
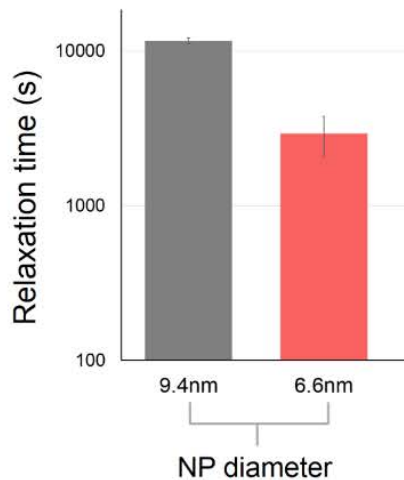
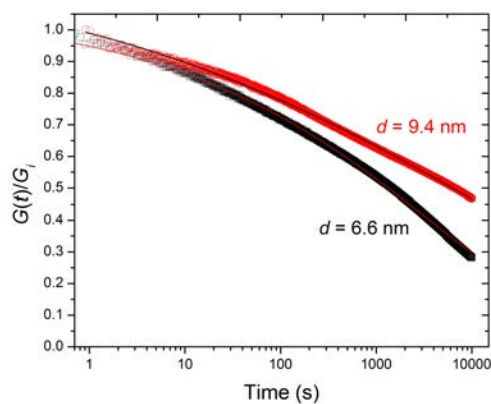
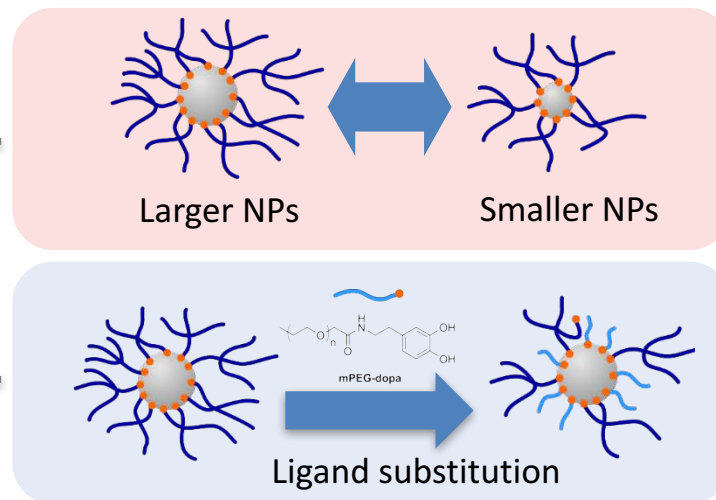
role of f in controlling relaxation time τ ?

Energy dissipative crosslinks:

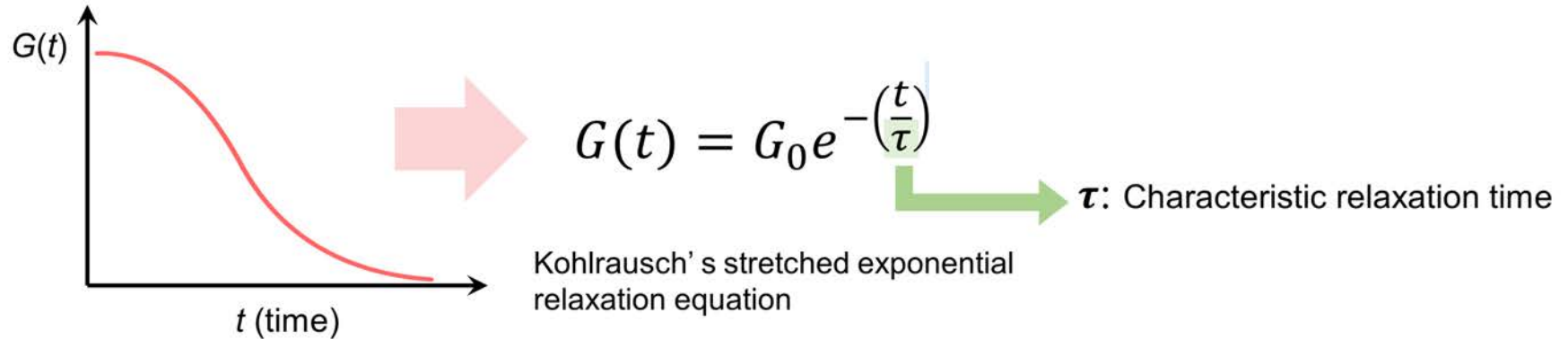
$$\tau \propto f$$



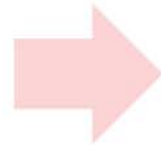
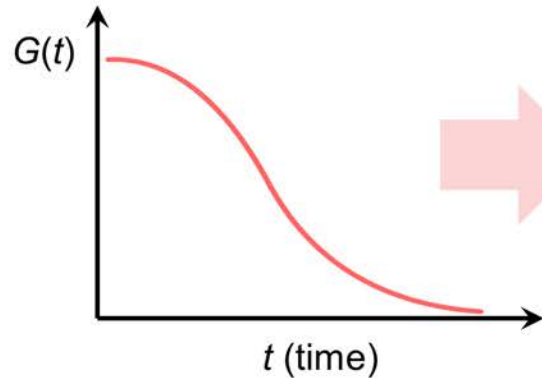
$$\tau \propto f$$



Energy dissipative crosslinks: $\tau \propto f$



Energy dissipative crosslinks: α

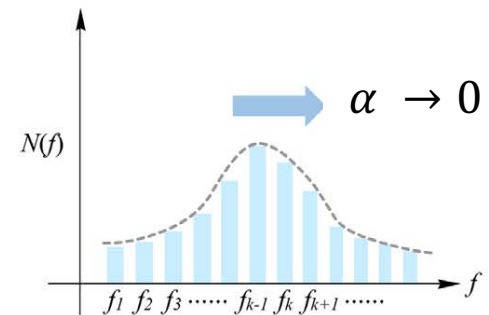
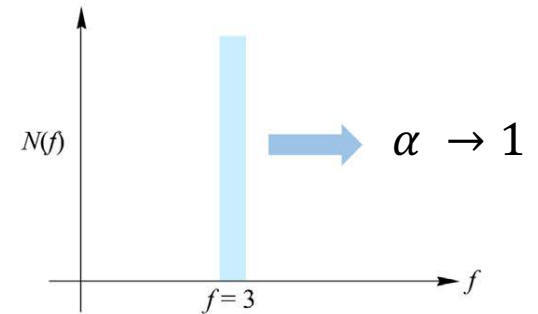


$$G(t) = G_0 e^{-\left(\frac{t}{\tau}\right)^\alpha}$$

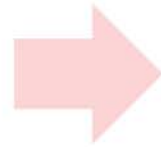
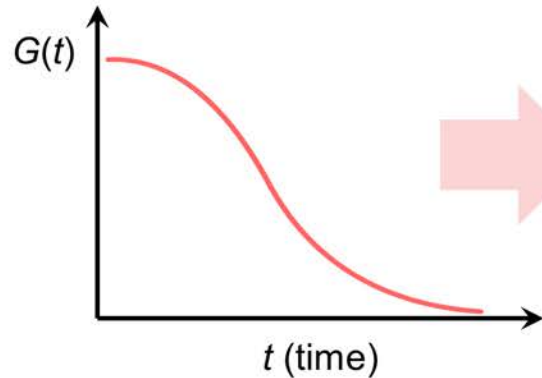
α : Kohlrausch's exponent

τ : Characteristic relaxation time

Kohlrausch's stretched exponential relaxation equation



Energy dissipative crosslinks: α

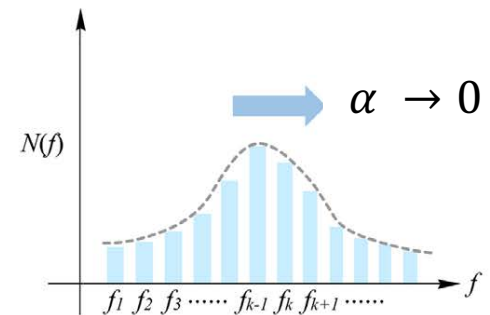
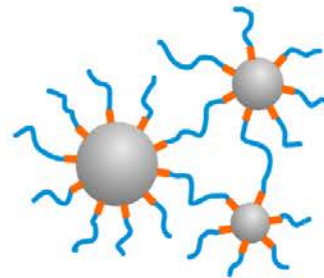
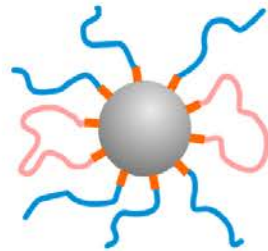
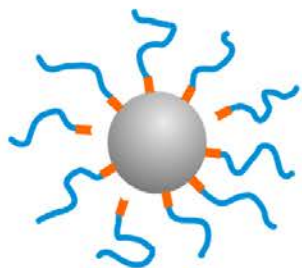
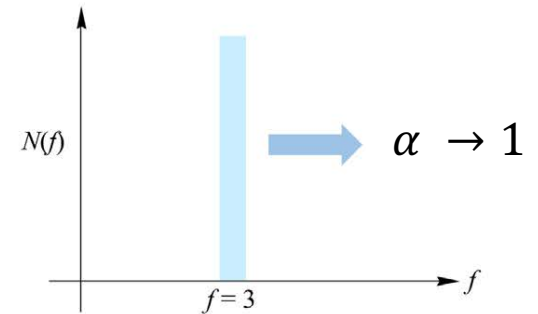
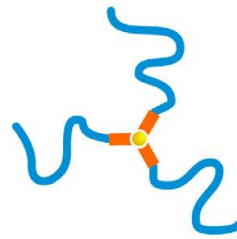


$$G(t) = G_0 e^{-\left(\frac{t}{\tau}\right)^\alpha}$$

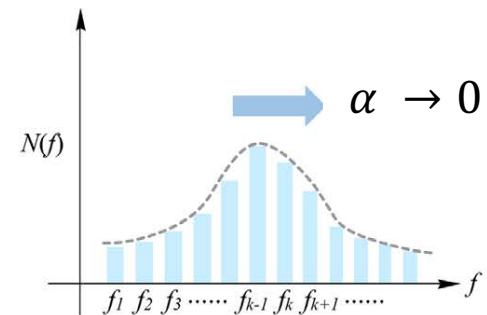
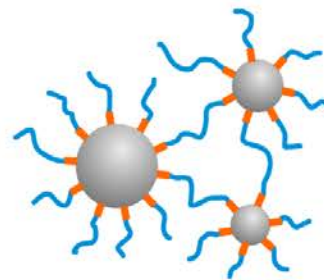
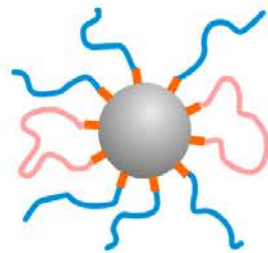
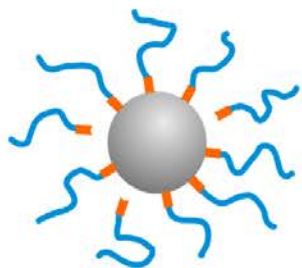
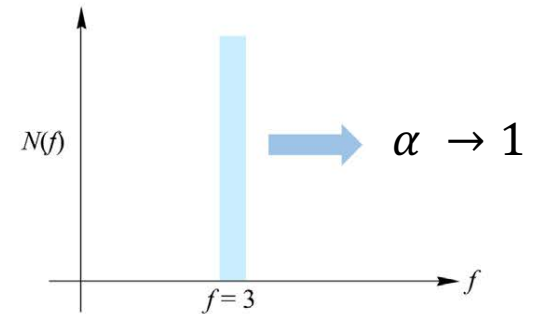
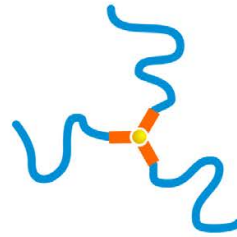
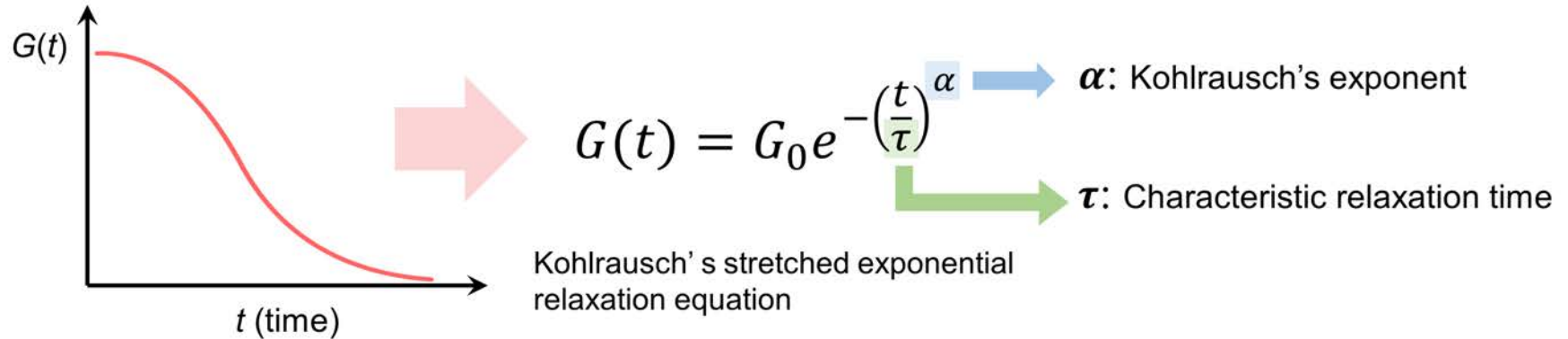
α : Kohlrausch's exponent

τ : Characteristic relaxation time

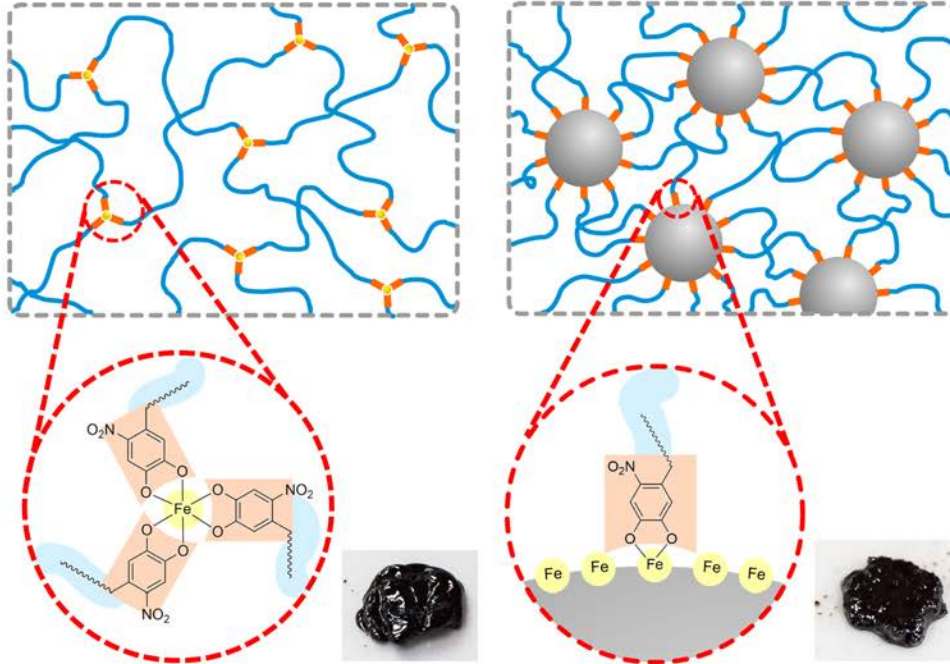
Kohlrausch's stretched exponential relaxation equation



Energy dissipative crosslinks: $\alpha \propto 1/(\Delta f)$

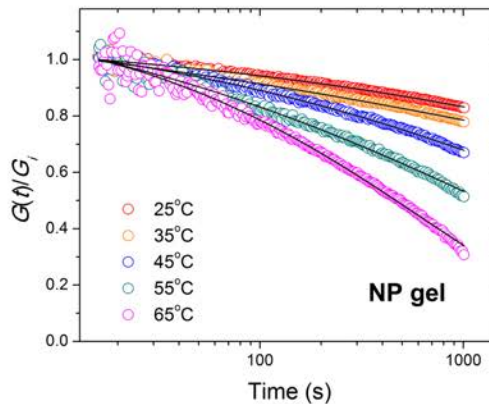
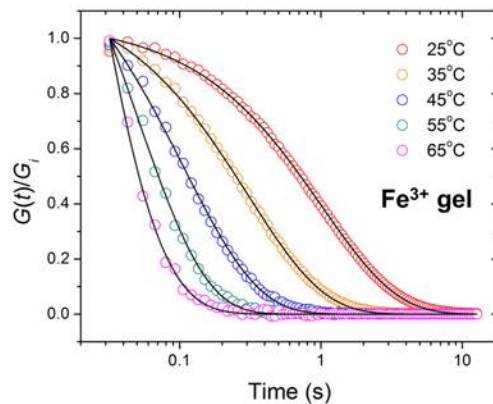


Energy dissipative crosslinks : tau vs alpha

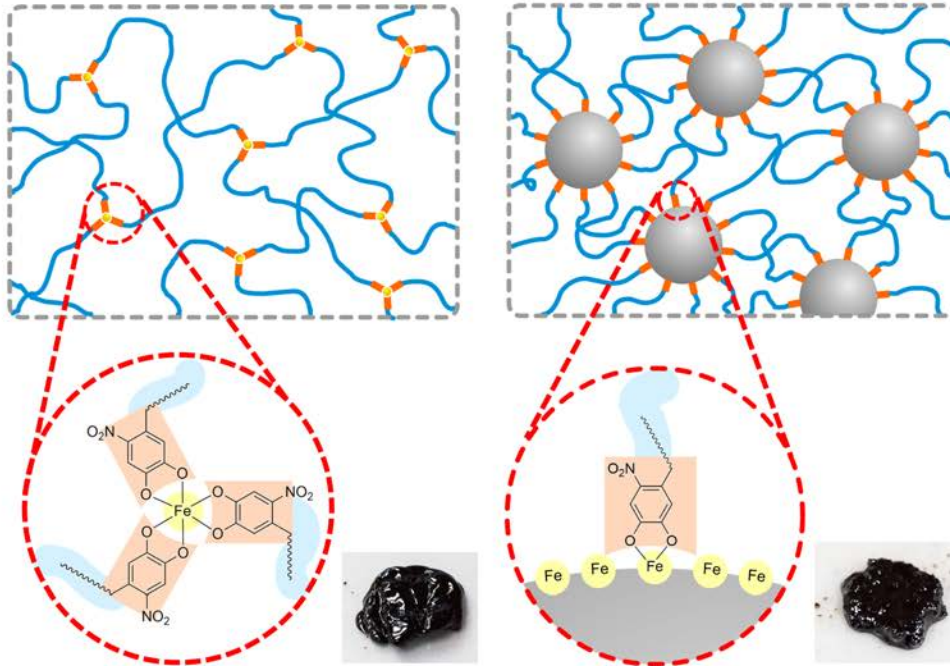


Fe³⁺ gel: ML₃ crosslink

NP gel: NP-L_n crosslink

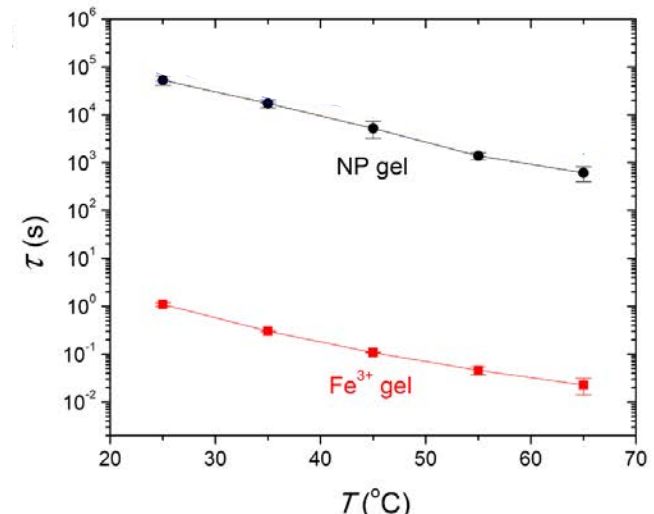
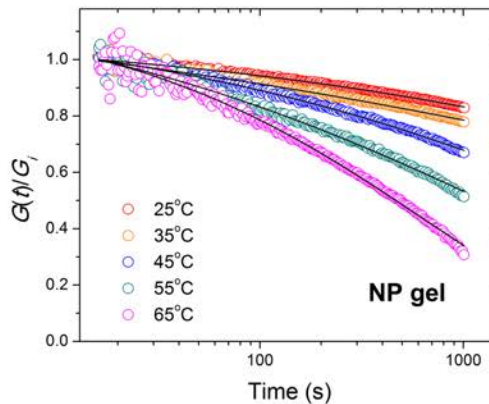
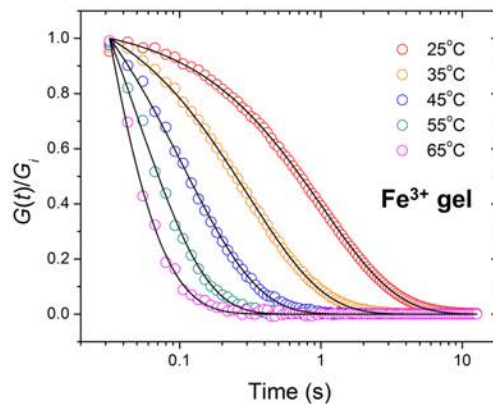


Energy dissipative crosslinks : tau vs alpha

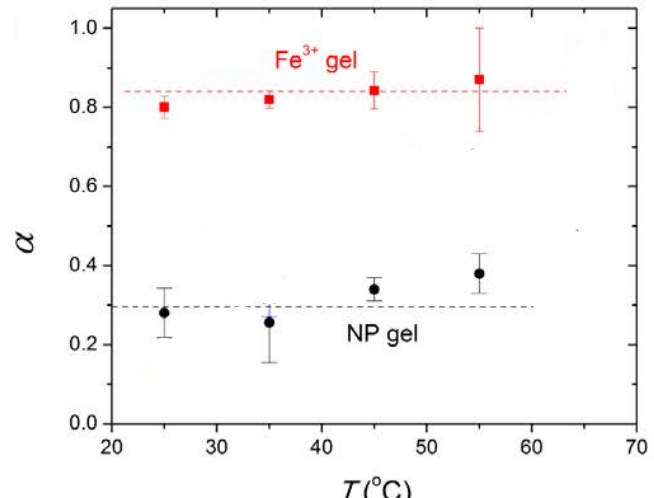
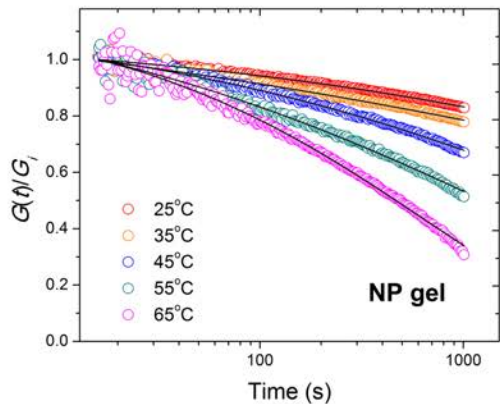
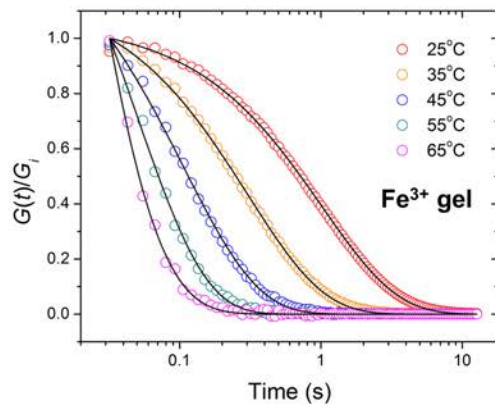
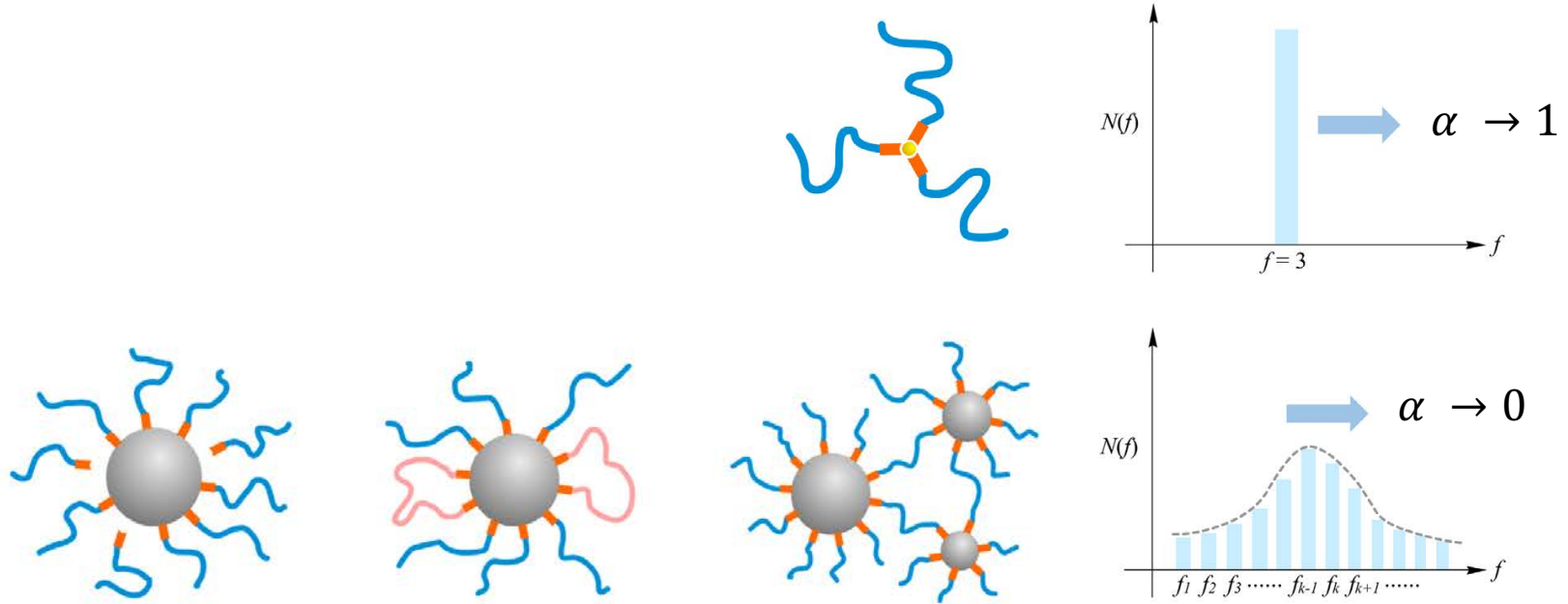


Fe³⁺ gel: ML₃ crosslink

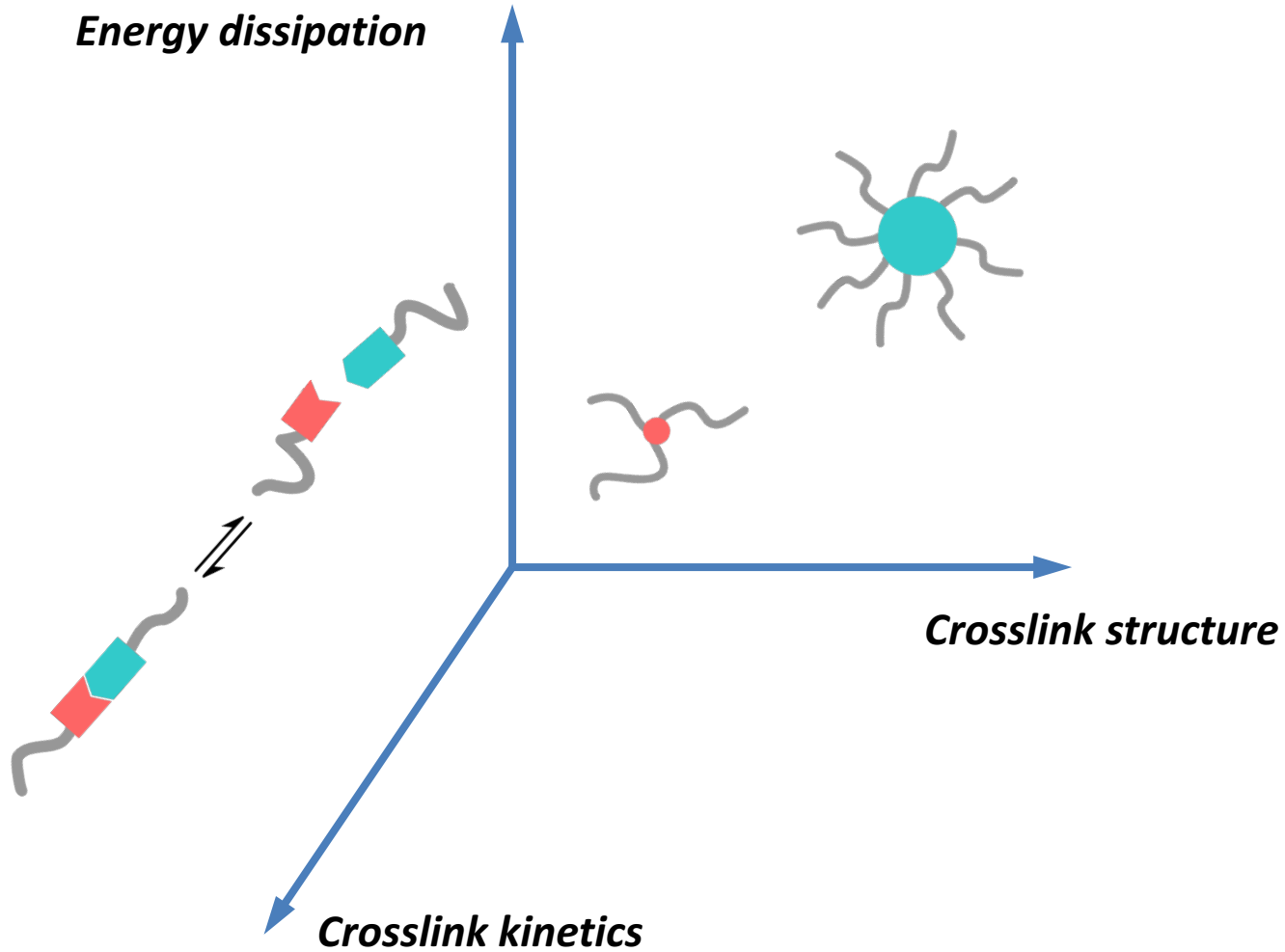
NP gel: NP-L_n crosslink



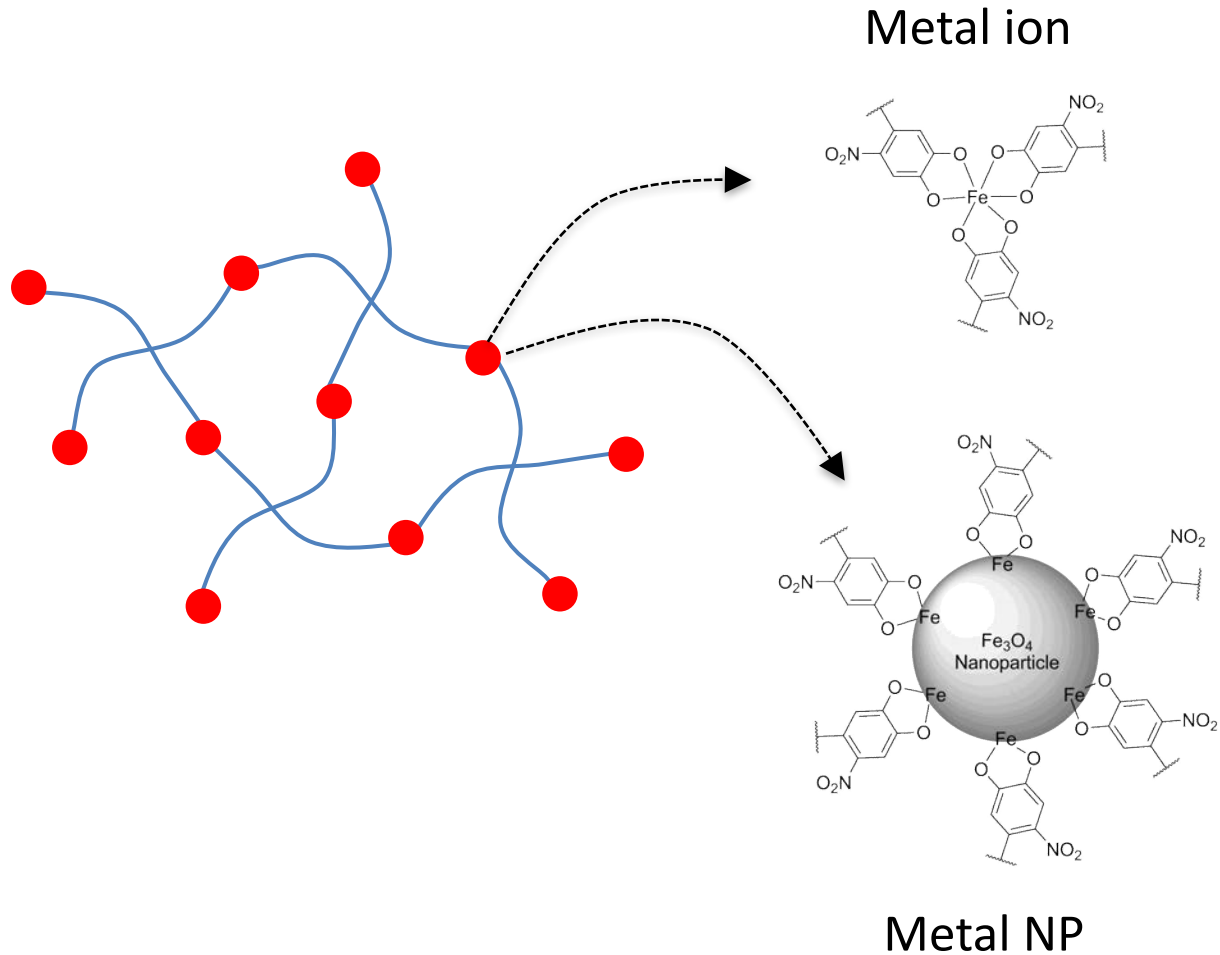
Energy dissipative crosslinks : tau vs alpha



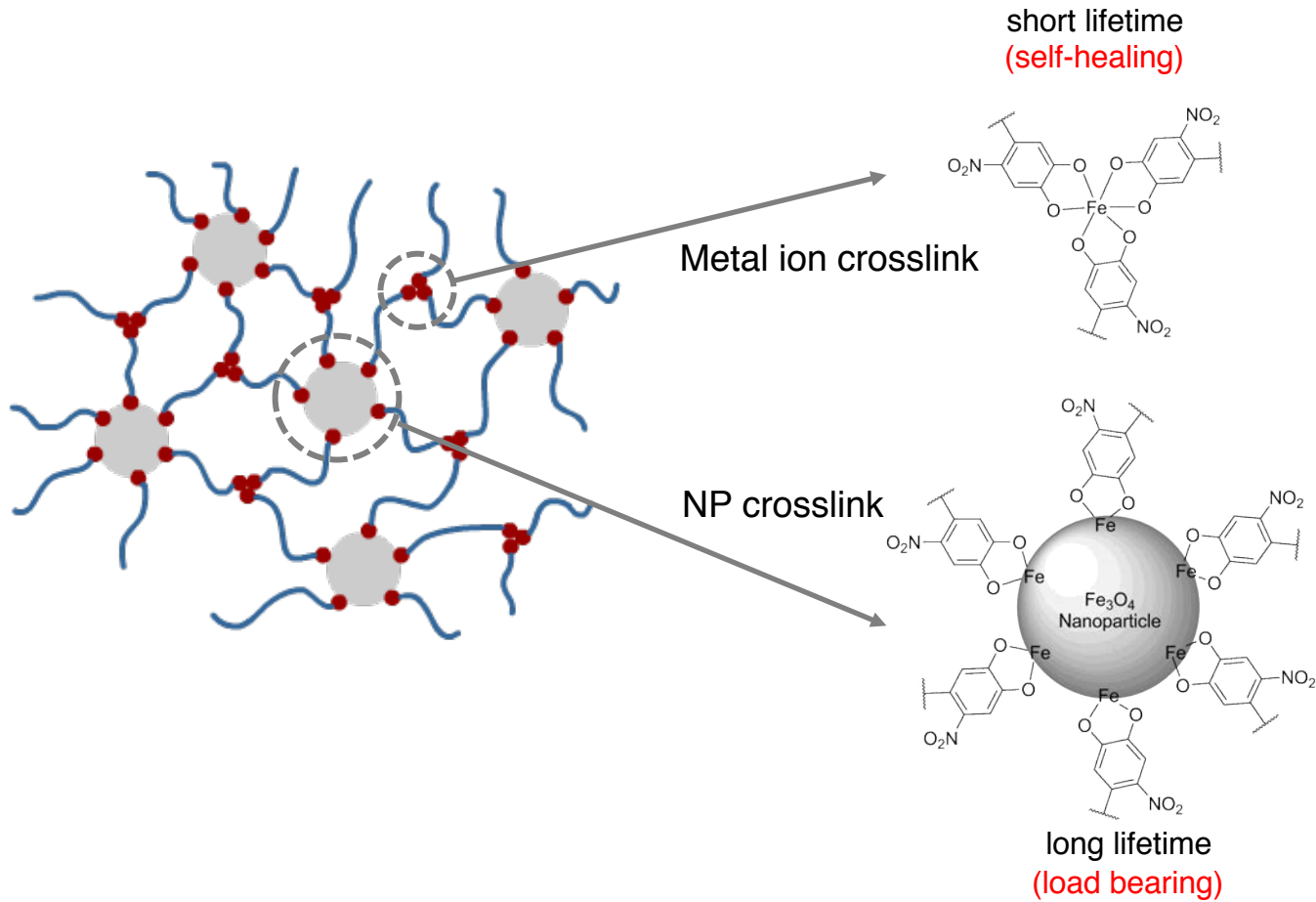
Energy dissipative crosslink engineering



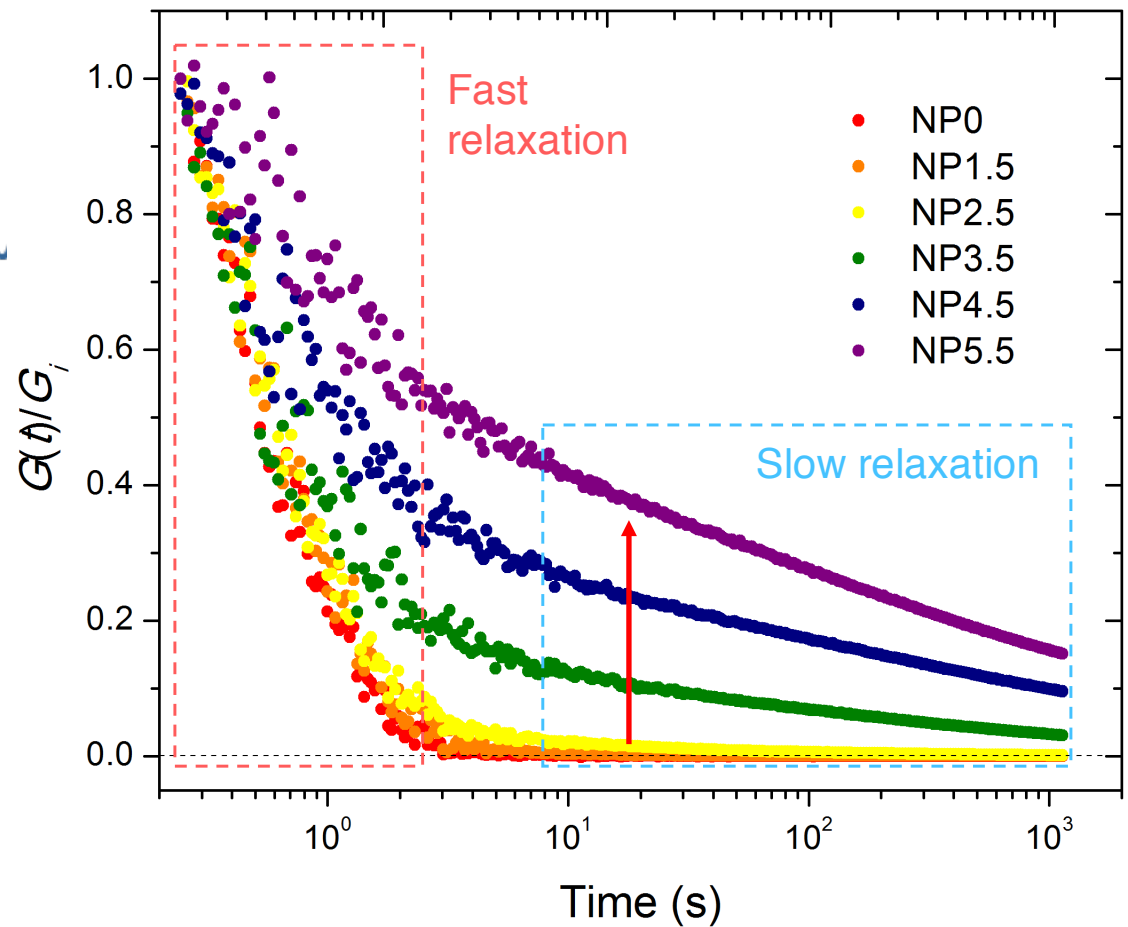
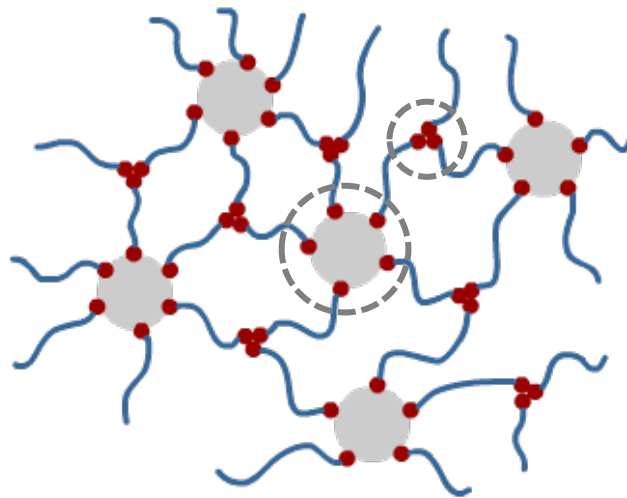
Energy dissipative crosslink engineering



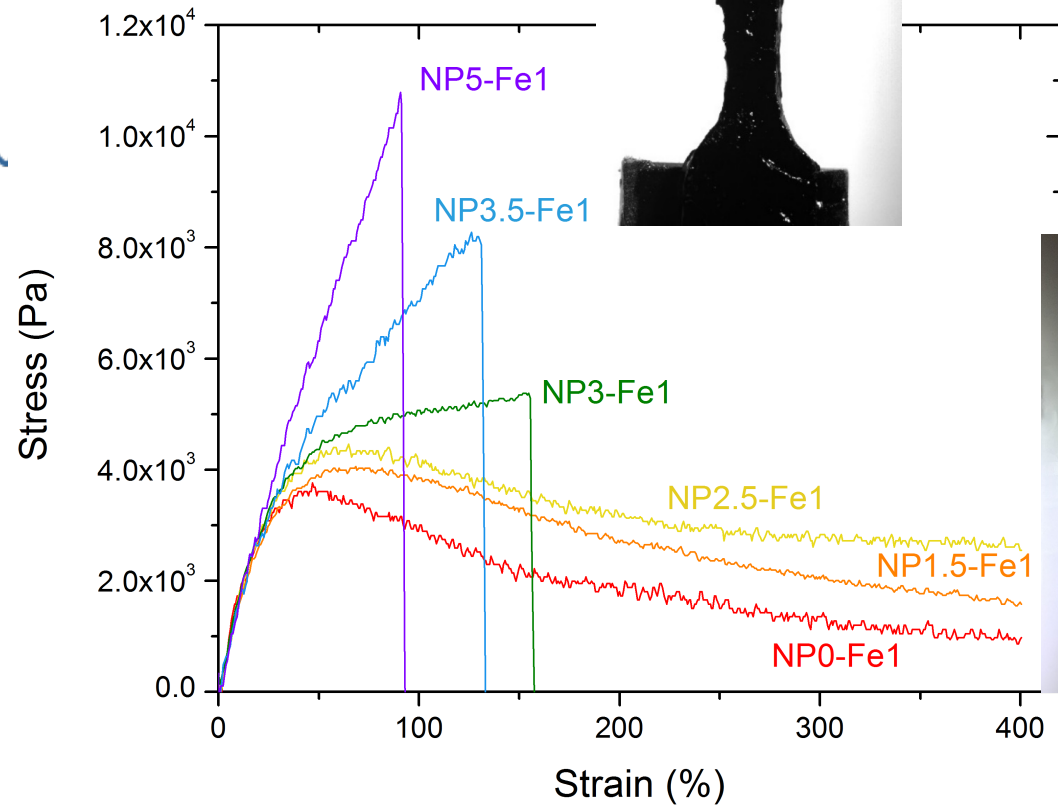
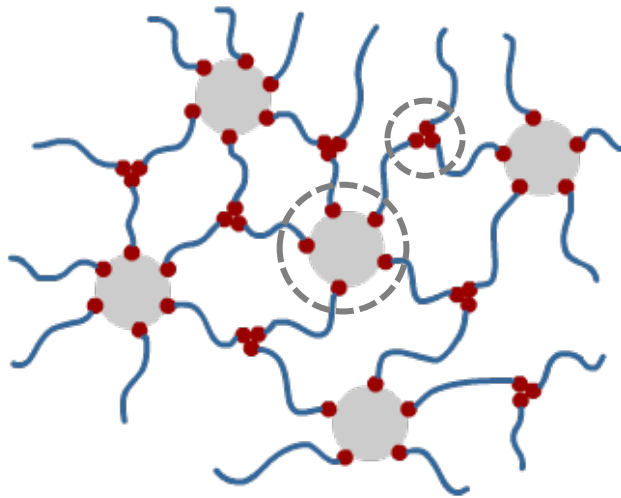
Energy dissipative crosslink engineering

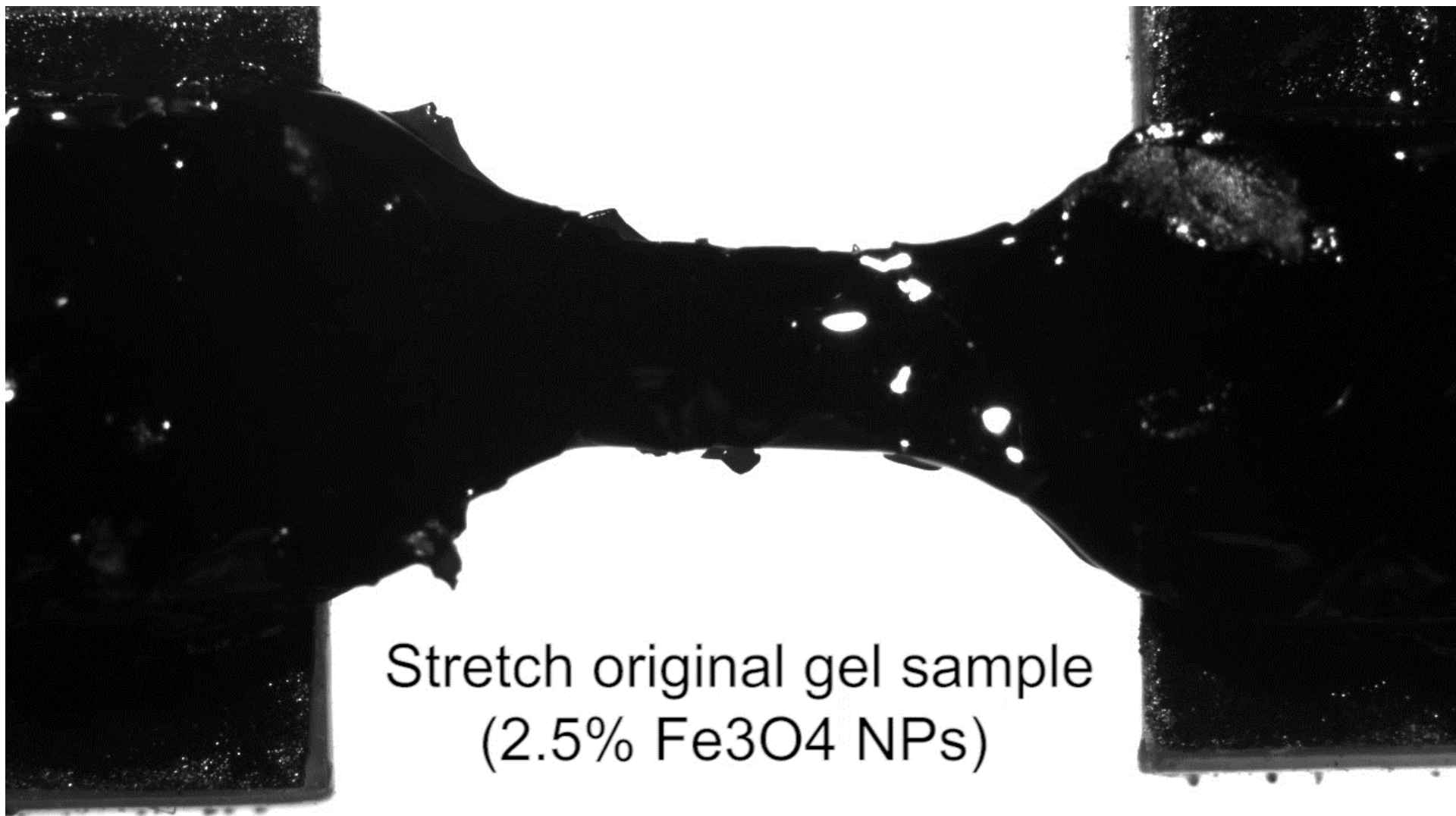


Energy dissipative crosslink engineering



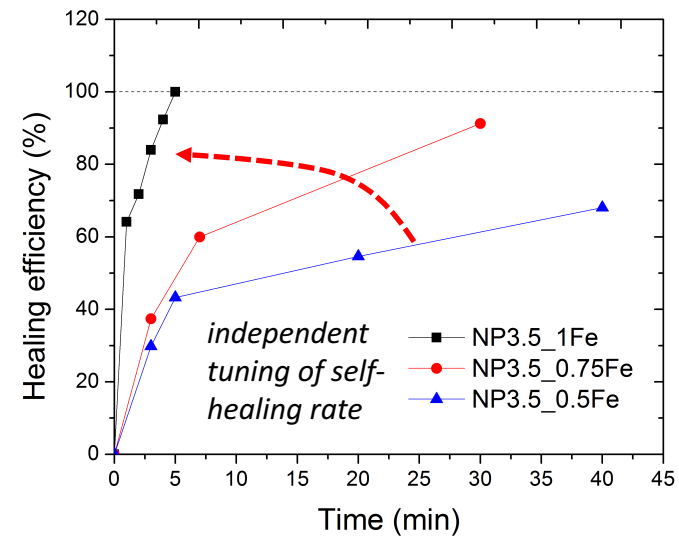
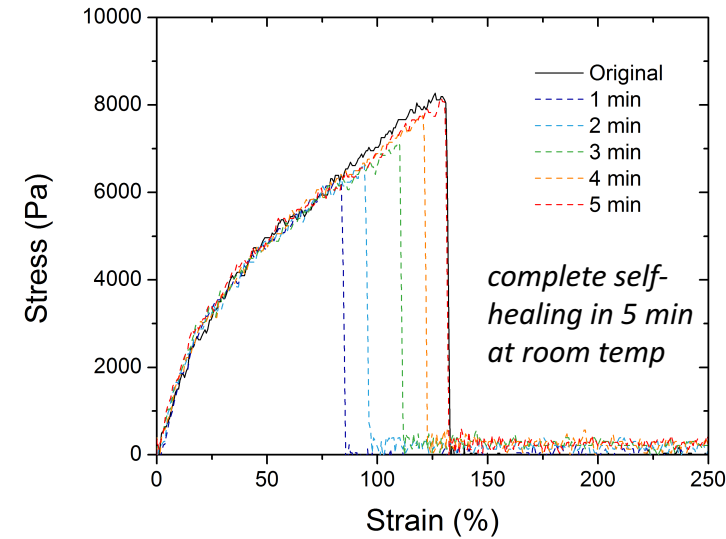
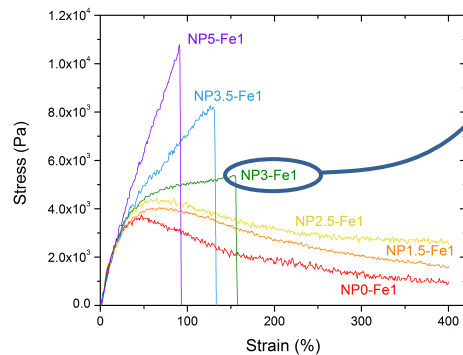
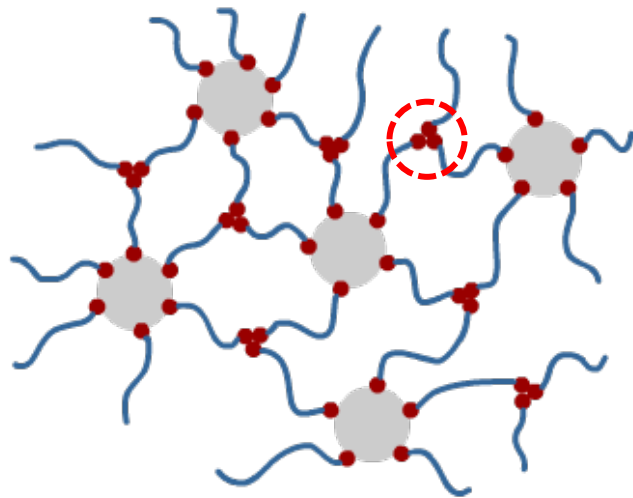
Energy dissipative crosslink engineering



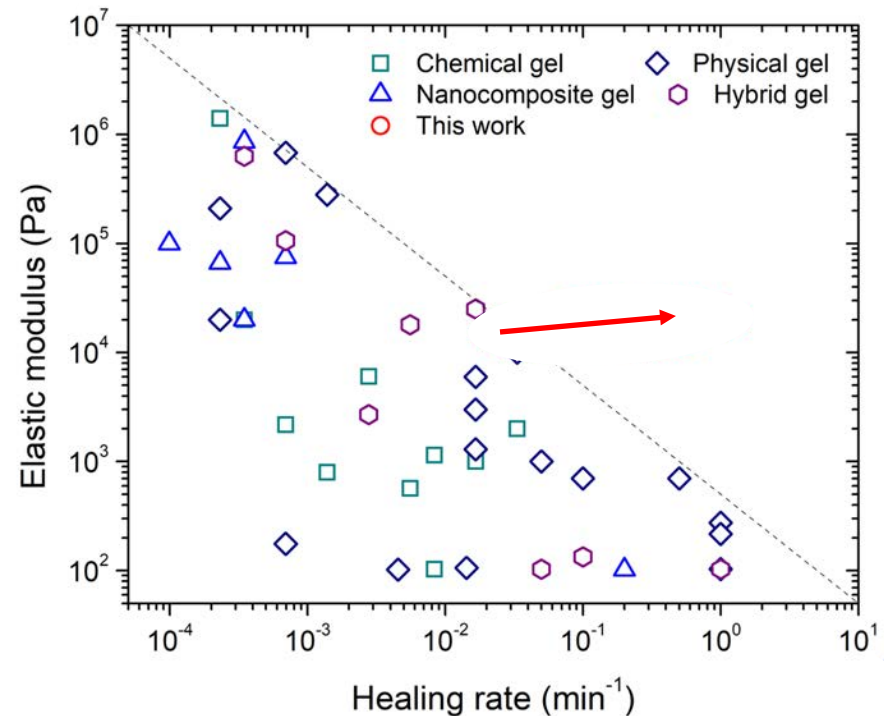
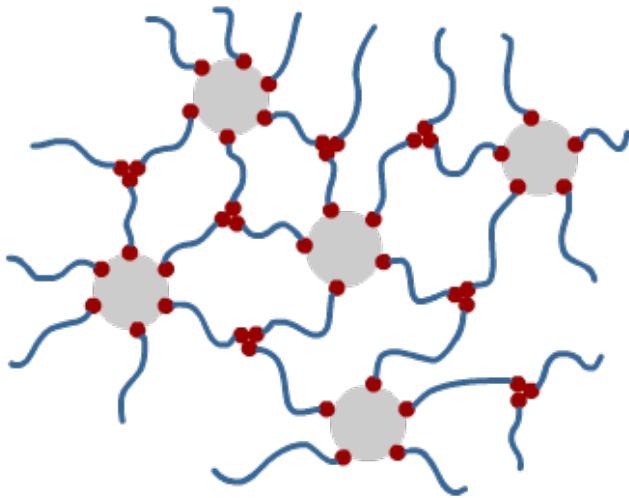


Stretch original gel sample
(2.5% Fe₃O₄ NPs)

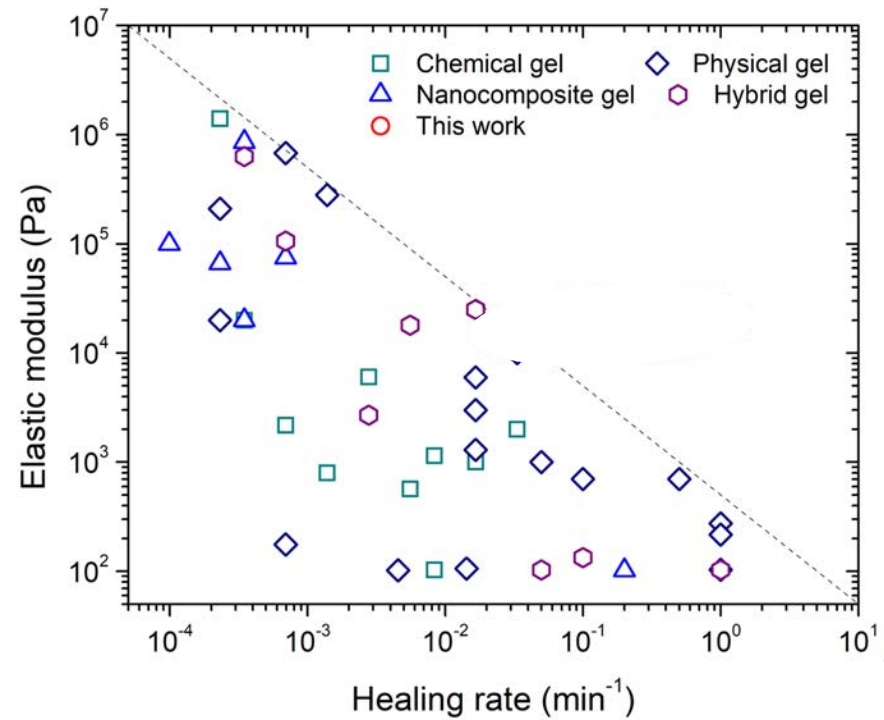
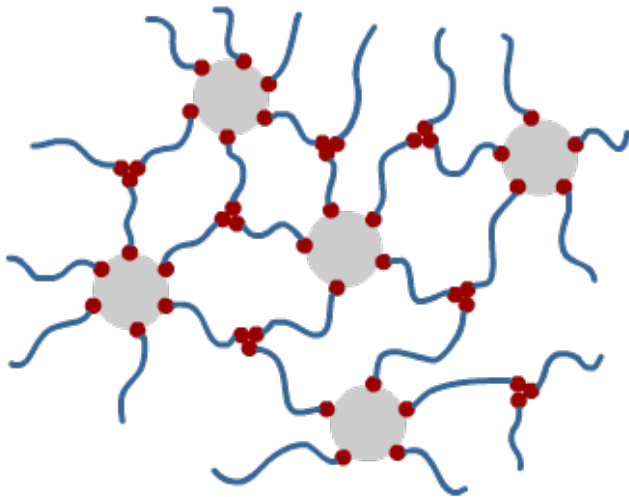
Energy dissipative crosslink engineering



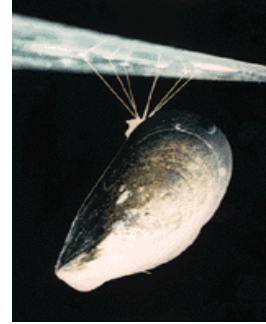
Energy dissipative crosslink engineering



Energy dissipative crosslink engineering

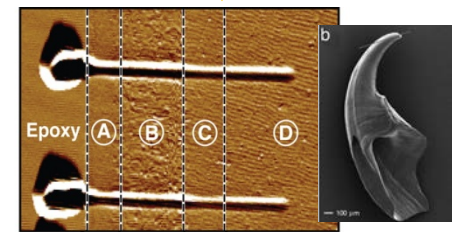
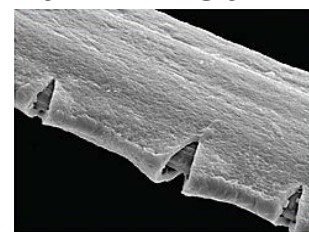
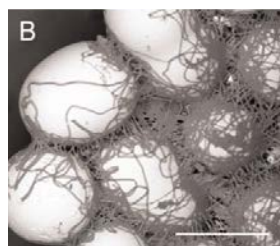
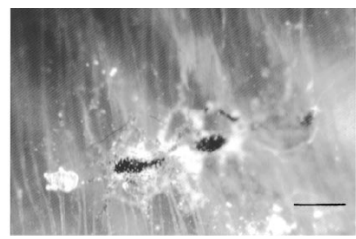
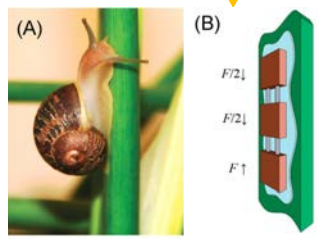


More inspiration.....



underwater sealants

self-healing fibers



reversible adhesives

underwater adhesives

light-weight high hardness materials

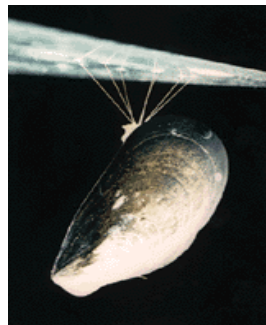
More inspiration.....



Visco-elastic fluids

Hard solids

More inspiration.....



REPORTS

MATERIALS SCIENCE

Toughening elastomers using mussel-inspired iron-catechol complexes

Emmanouela Filippidi,^{1,2*} Thomas R. Cristiani,^{1,3*} Claus D. Eisenbach,^{1,4} J. Herbert Waite,^{1,5} Jacob N. Israelachvili,^{1,3,6} B. Kollbe Ahn,⁷ Megan T. Valentine^{1,2†}

Materials often exhibit a trade-off between stiffness and extensibility; for example, strengthening elastomers by increasing their cross-link density leads to embrittlement and decreased toughness. Inspired by cuticles of marine mussel byssi, we circumvent this inherent trade-off by incorporating sacrificial, reversible iron-catechol cross-links into a dry, loosely cross-linked epoxy network. The iron-containing network exhibits two to three orders of magnitude increases in stiffness, tensile strength, and tensile toughness compared to its iron-free precursor while gaining recoverable hysteretic energy dissipation and maintaining its original extensibility. Compared to previous realizations of this chemistry in hydrogels, the dry nature of the network enables larger property enhancement owing to the cooperative effects of both the increased cross-link density given by the reversible iron-catecholate complexes and the chain-restricting ionic nanodomains that they form.

Visco-elastic fluids

Hard solids



THANK YOU

Collaborators:

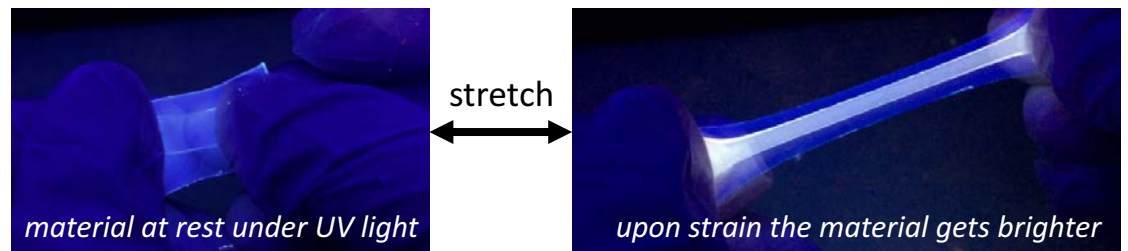
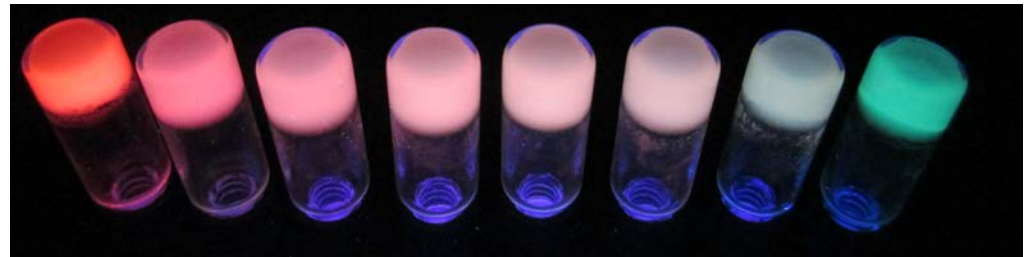
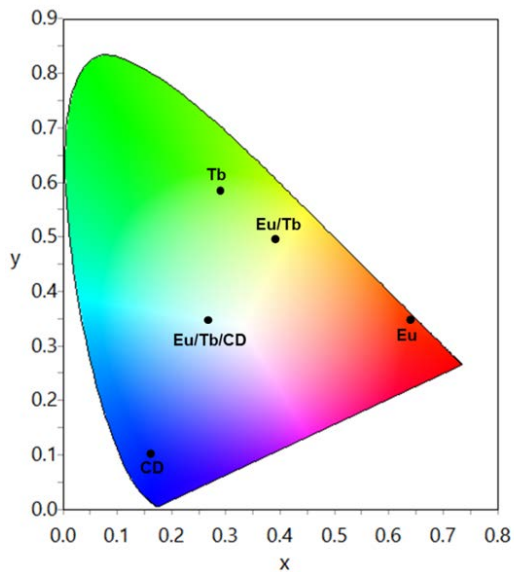
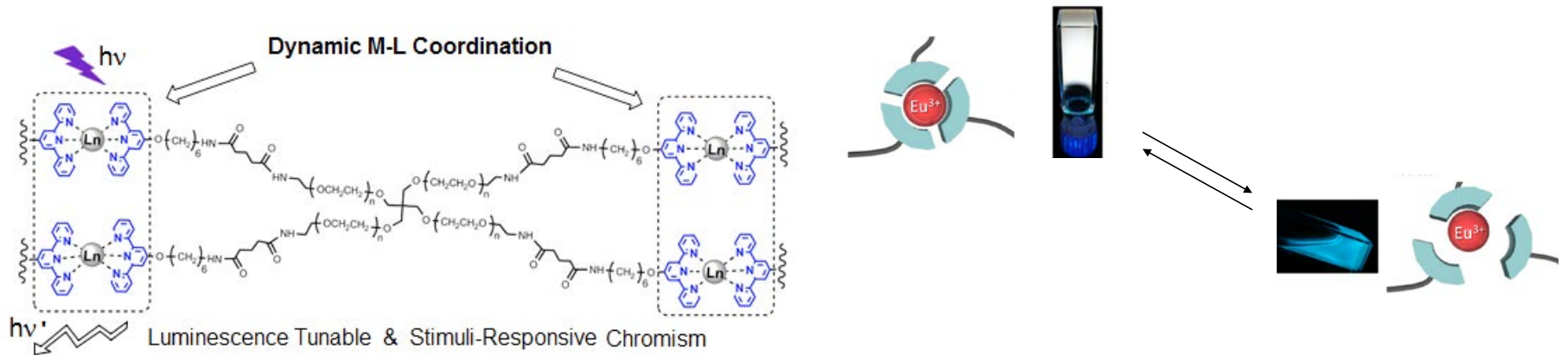
Gareth McKinley
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Grindy *et al*, Nature Materials (2015)
Chen *et al*, Adv. Opt. Mat. (2015)
Chen *et al*, JACS (2015)
Li *et al*, ACS Nano (2016)
Grindy *et al*, Macromolecules (2016)
Grindy *et al*, Soft Matter (2017)

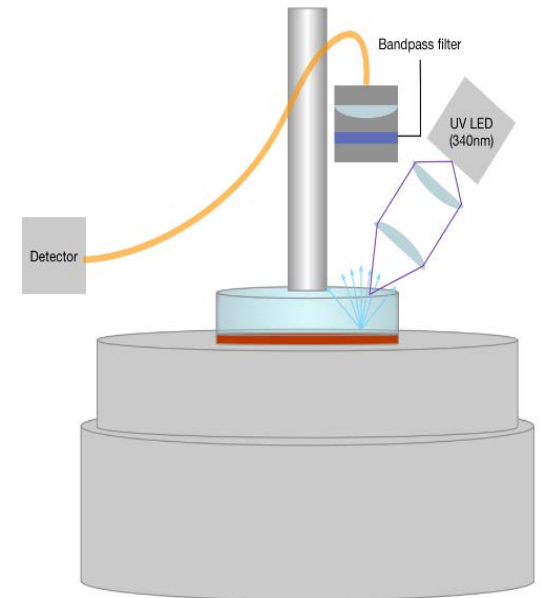
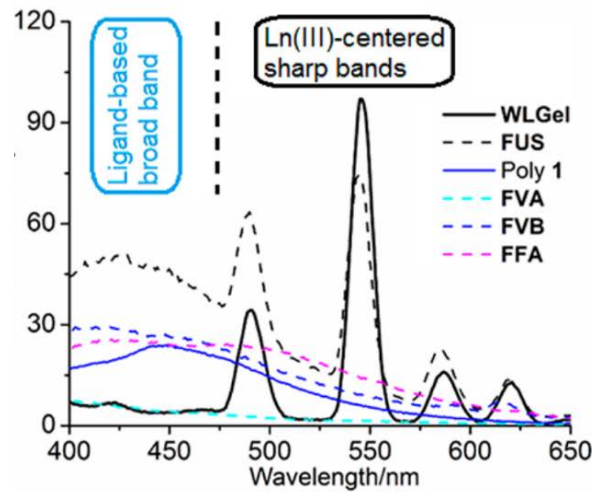
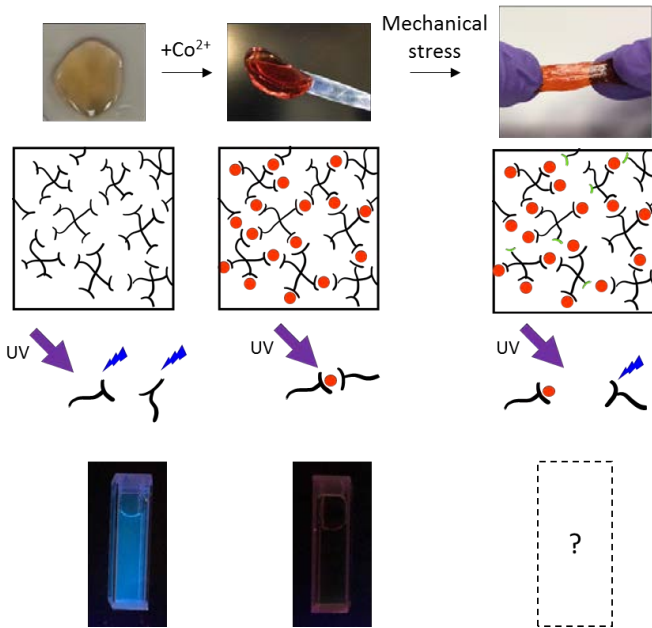
Energy dissipative crosslink engineering

To engineer self-reporting polymer materials with energy-dissipation and material failure sensing capacity: **on a macroscopic scale**



Energy dissipative crosslink engineering

To engineer self-reporting polymer materials with energy-dissipation and material failure sensing capacity: *on a microscopic scale*



Metal-coordinate networks: Ions vs particles

$$G(t) = G_0 \exp\left[-(t/\tau)^a\right], 0 < a < 1$$

$$\ln[\tau(T)] = \ln \tau_0 + \frac{E_a}{kT}$$

(pH=4)

NP gel:

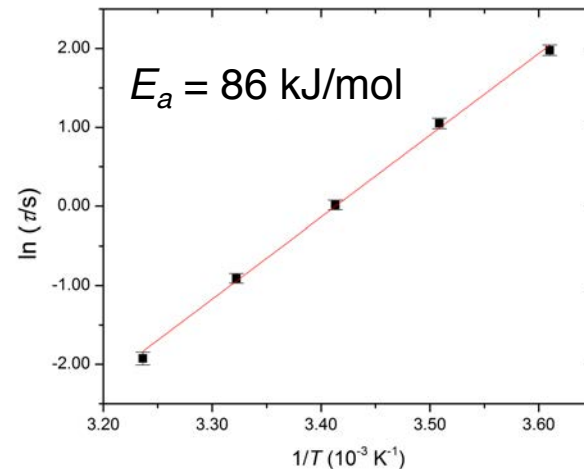
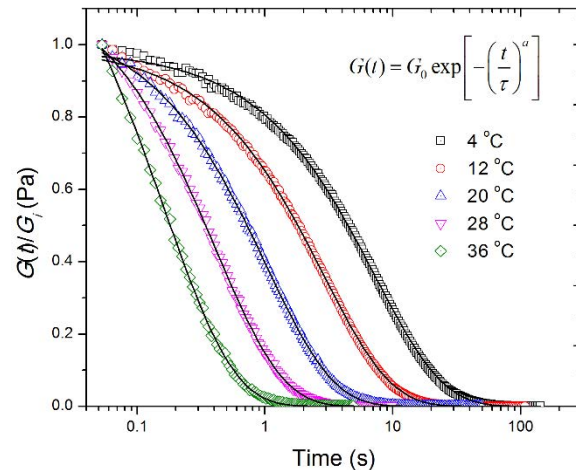
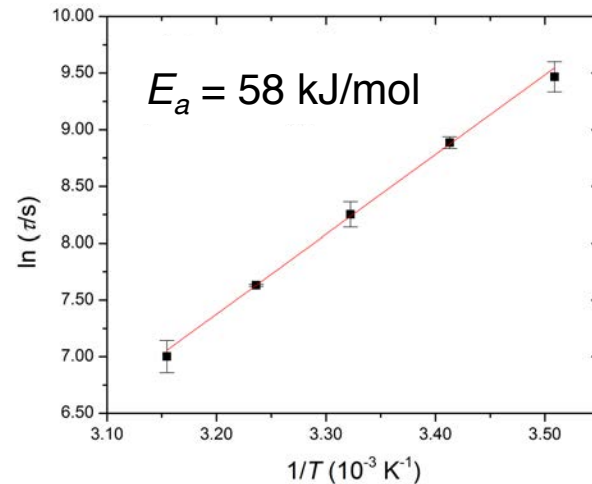
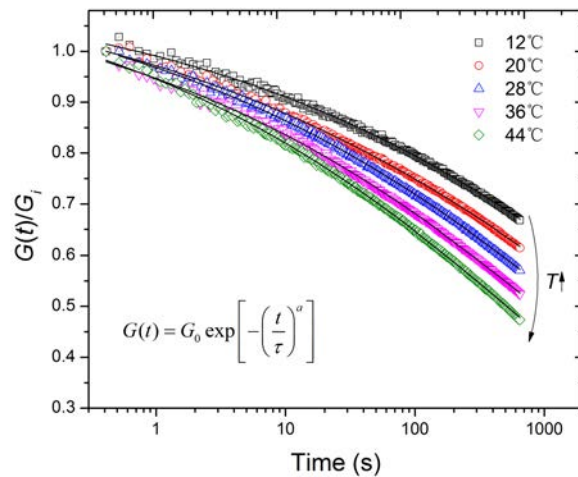


Chemical environment

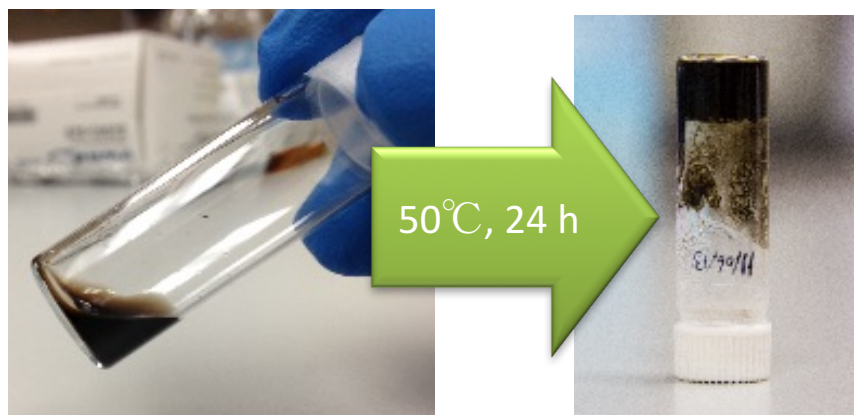
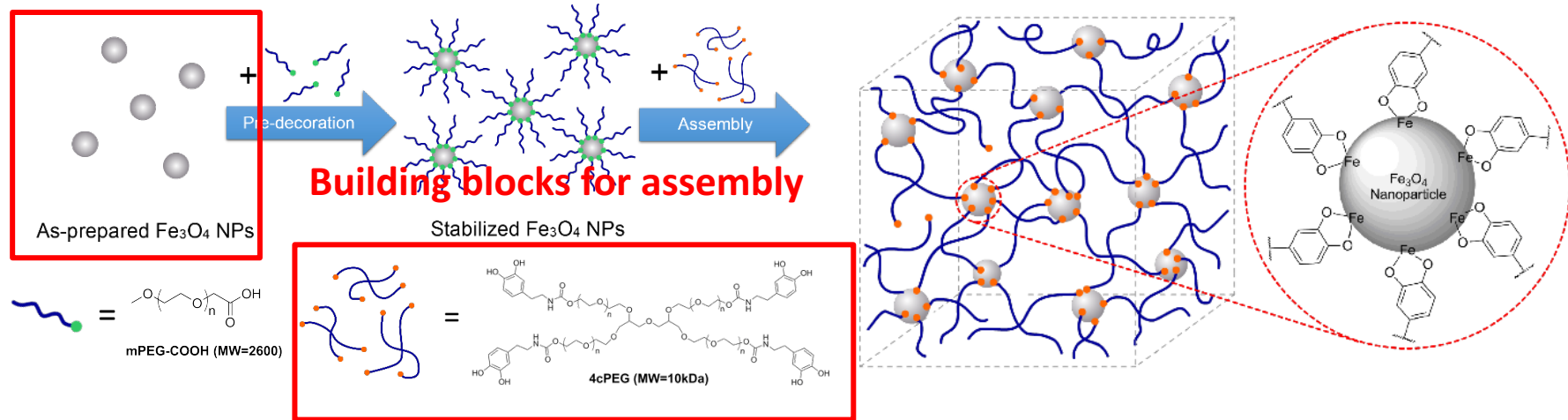


Fe³⁺ gel:

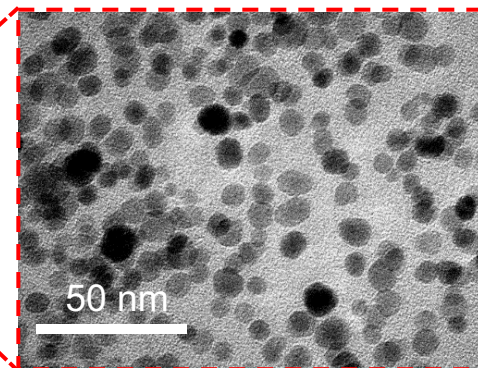
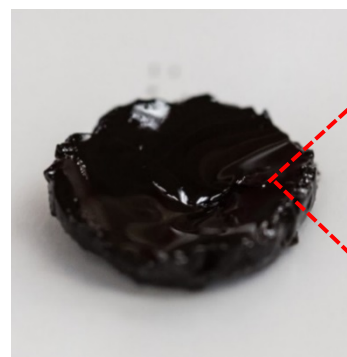
(pH=12)



Metal-coordinate networks: particles



Sol-gel transition



As-prepared NP gel