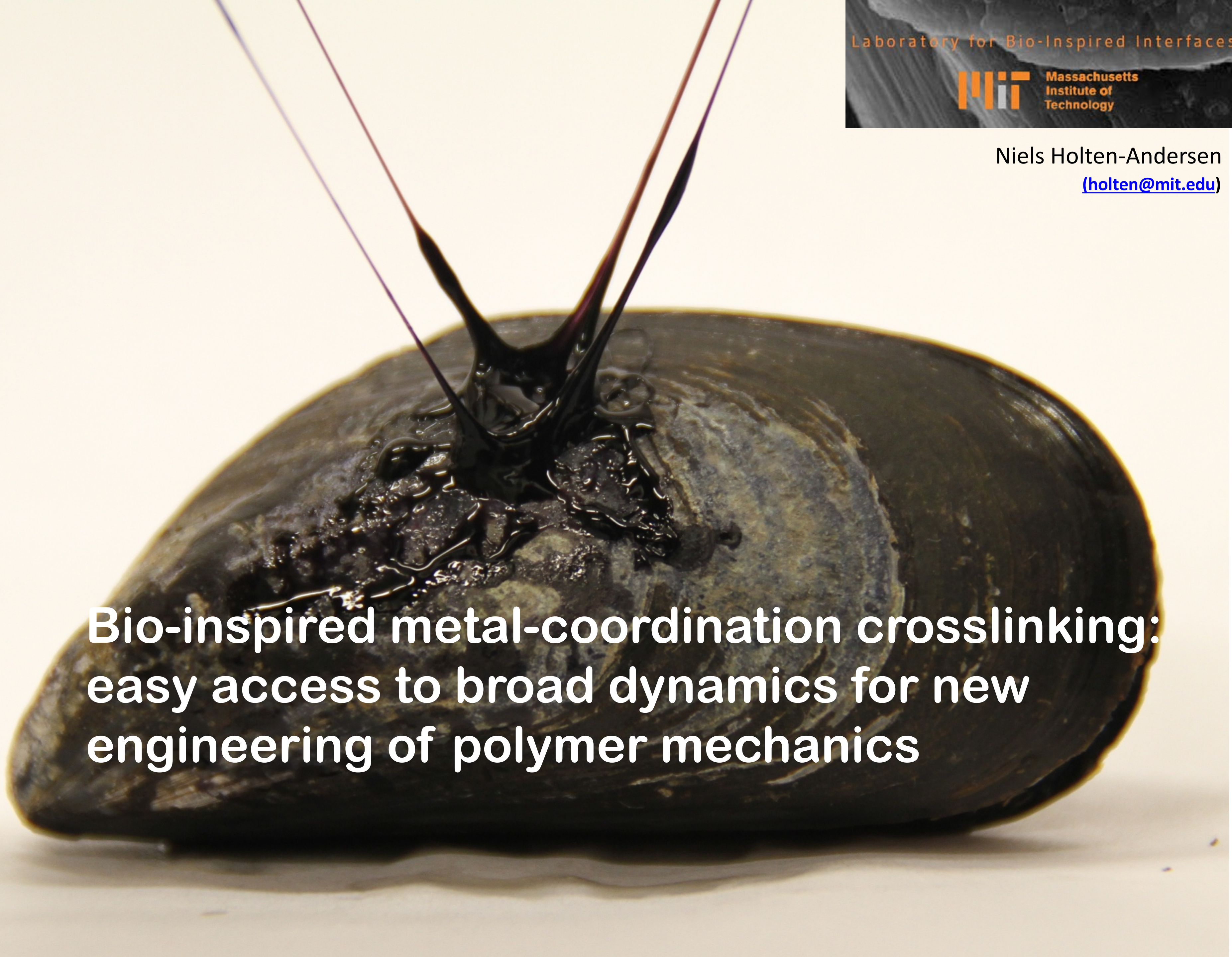
Laboratory for Bio-Inspired Interfaces
Massachusetts Institute of Technology

Niels Holten-Andersen
(holten@mit.edu)



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

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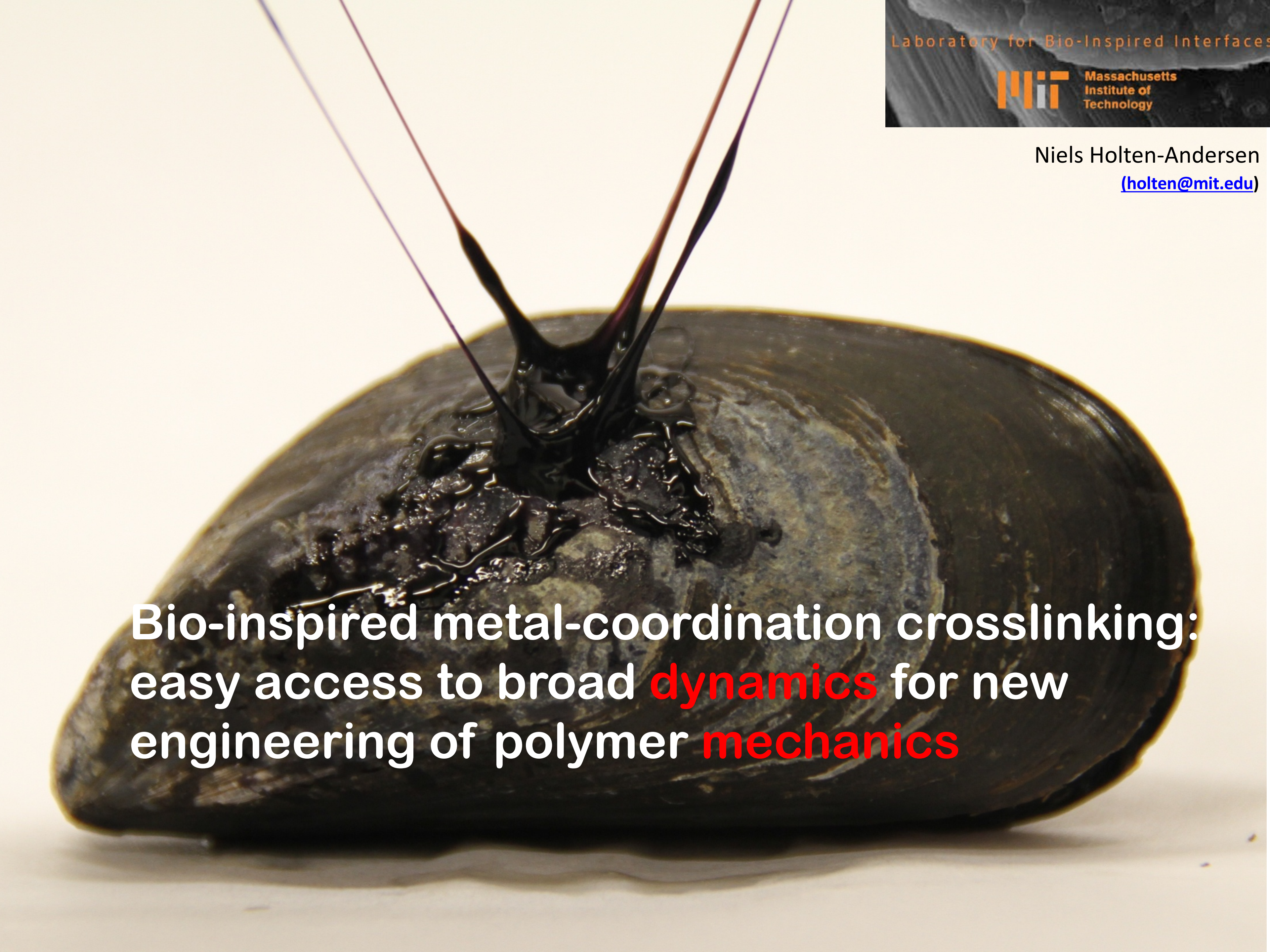
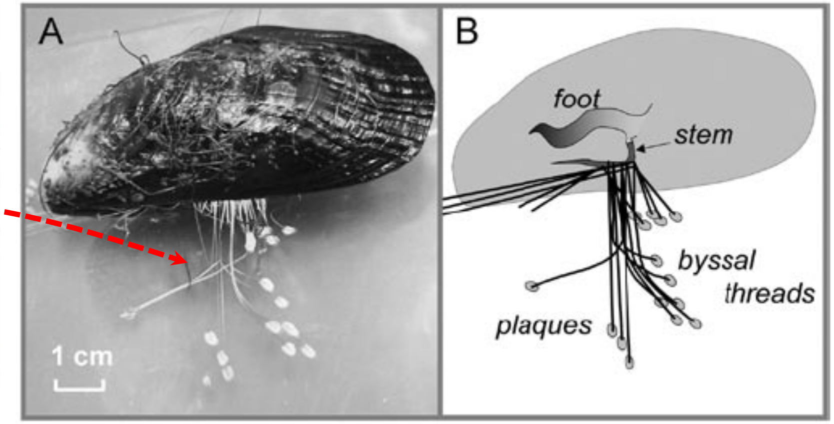


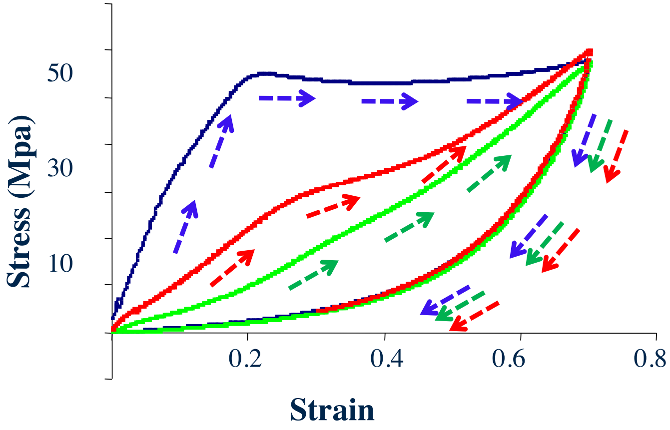
Bio-inspired metal-coordination crosslinking: easy access to broad dynamics for new engineering of polymer mechanics

Mechanical energy dissipation in mussel threads



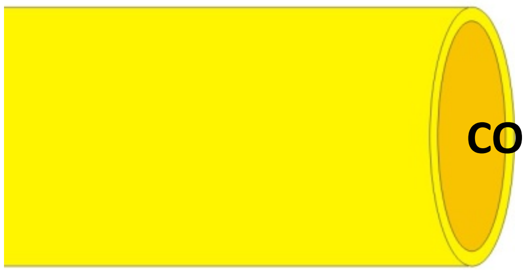
Holten-Andersen & Waite, *J. Dental Research.* **87**, 701-709, (2008)

Repeated stress-strain cycles



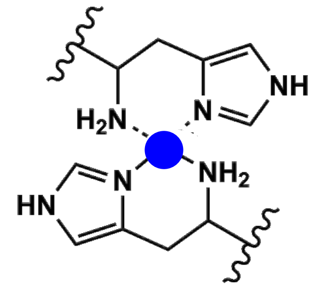
Toughness
Self-healing

Metal-ion coordinate crosslinking in mussel threads

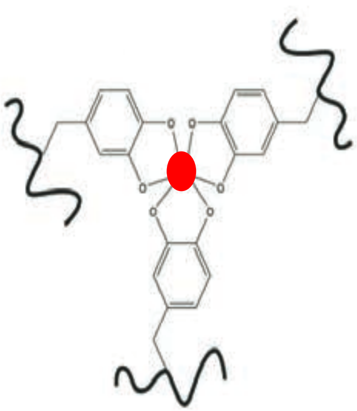


COATING

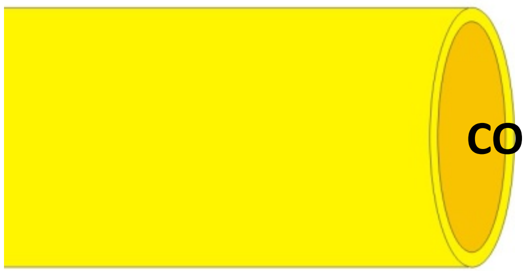
Histidine-metal ion coordination complexes



Dopa-metal ion coordination complexes

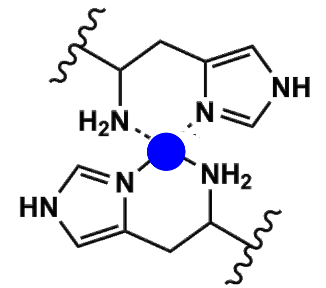


Metal-ion coordinate crosslinking in mussel threads

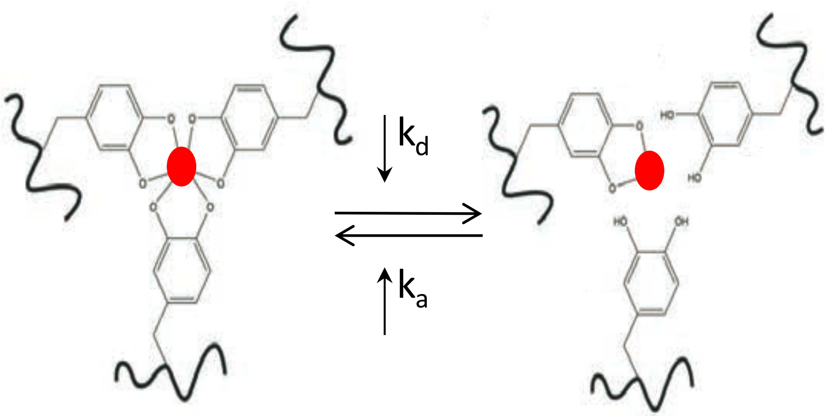


COATING

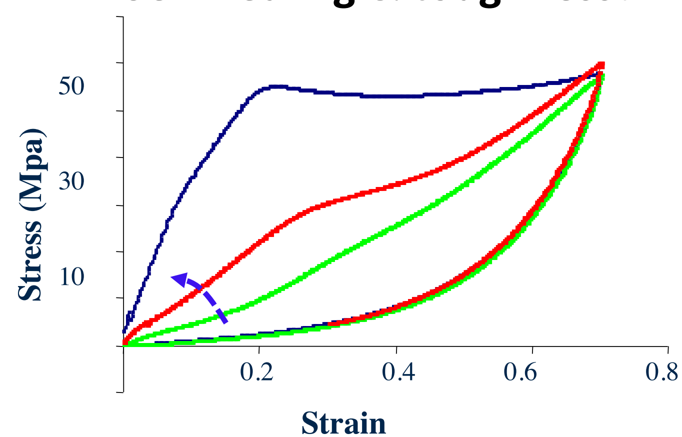
Histidine-metal ion coordination complexes



Dopa-metal ion coordination complexes



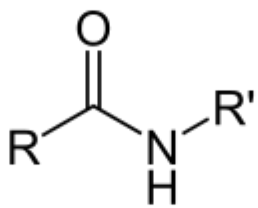
Self-healing & toughness?



Harrington et al. *Science* **328,** 216-220 (2010)

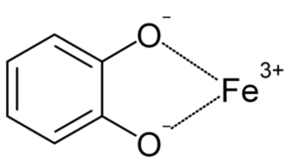
Metal-coordination in Nature

Covalent bonds



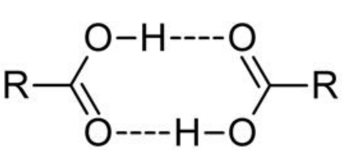
~100-1000 kJ/mol

Coordination bonds



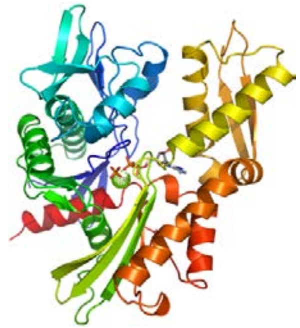
~10-100 kJ/mol

Non-covalent bonds



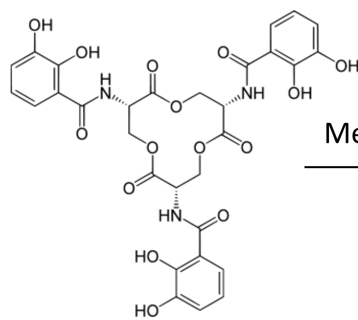
~1-10 kJ/mol

Metallo-proteins

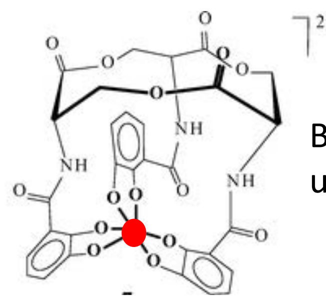


Enzymes
Fe-transport
O_2-transport
Heat shock proteins

Siderophores

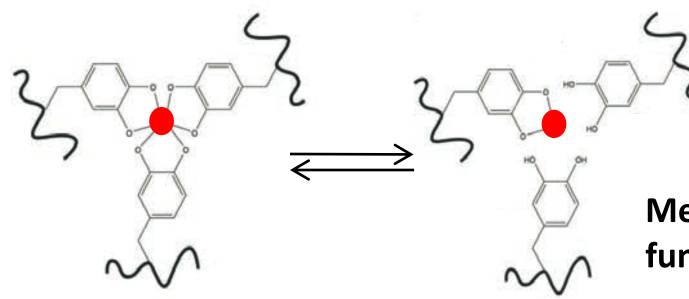


Metal



Bacterial metal-uptake

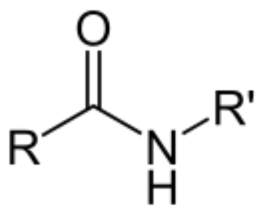
Bio-materials



Mechanical function?

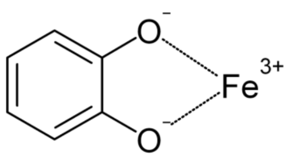
Metal-coordination in Nature

Covalent bonds



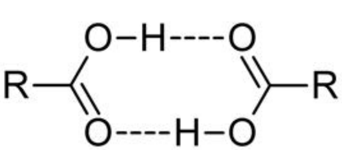
~100-1000 kJ/mol

Coordination bonds



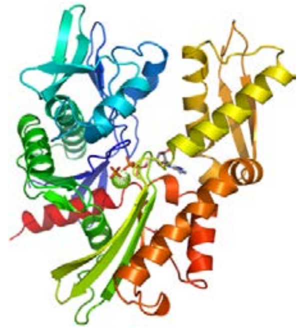
~10-100 kJ/mol
(~4-40 kT/bond)

Non-covalent bonds



~1-10 kJ/mol

Metallo-proteins



Enzymes
Fe-transport
O_2-transport
Heat shock proteins

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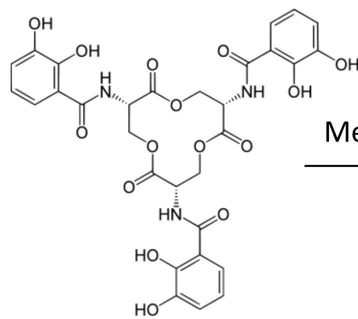
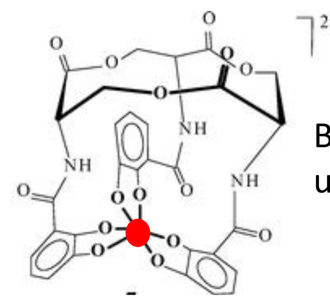
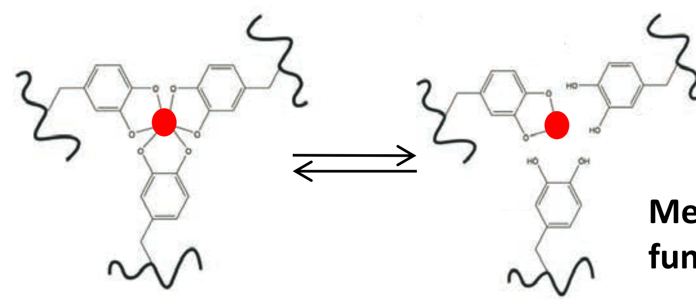


Metal



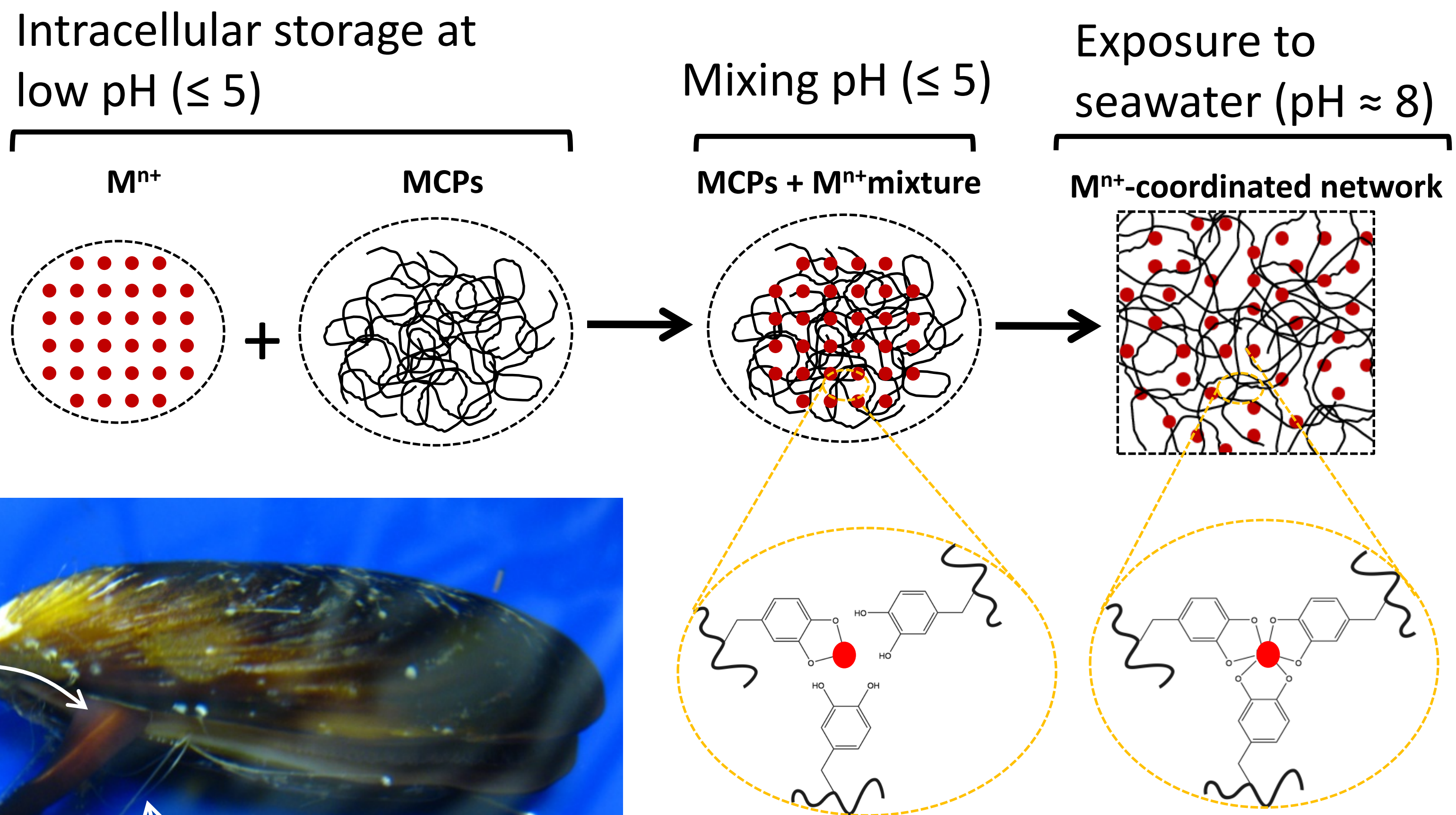
Bacterial metal-uptake

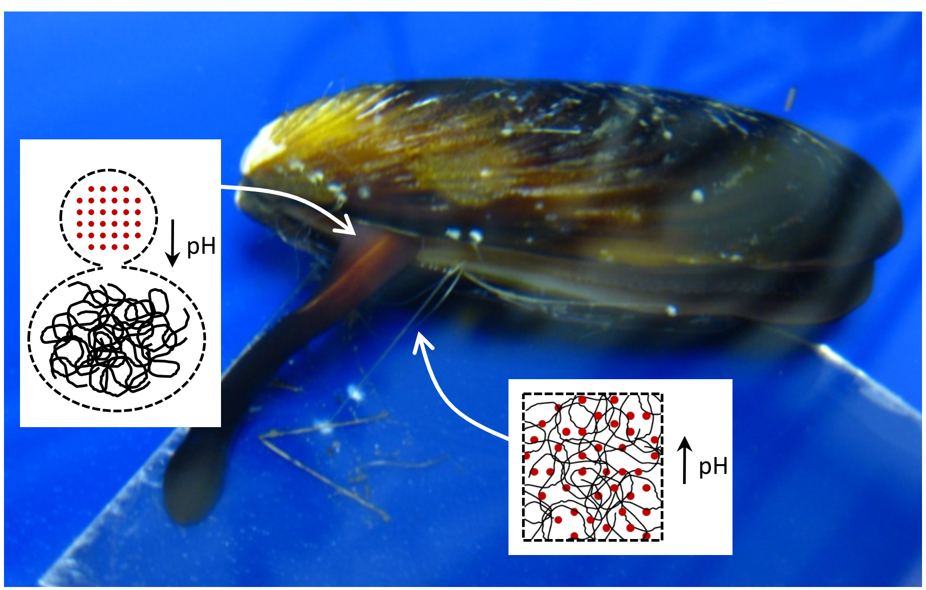
Bio-materials



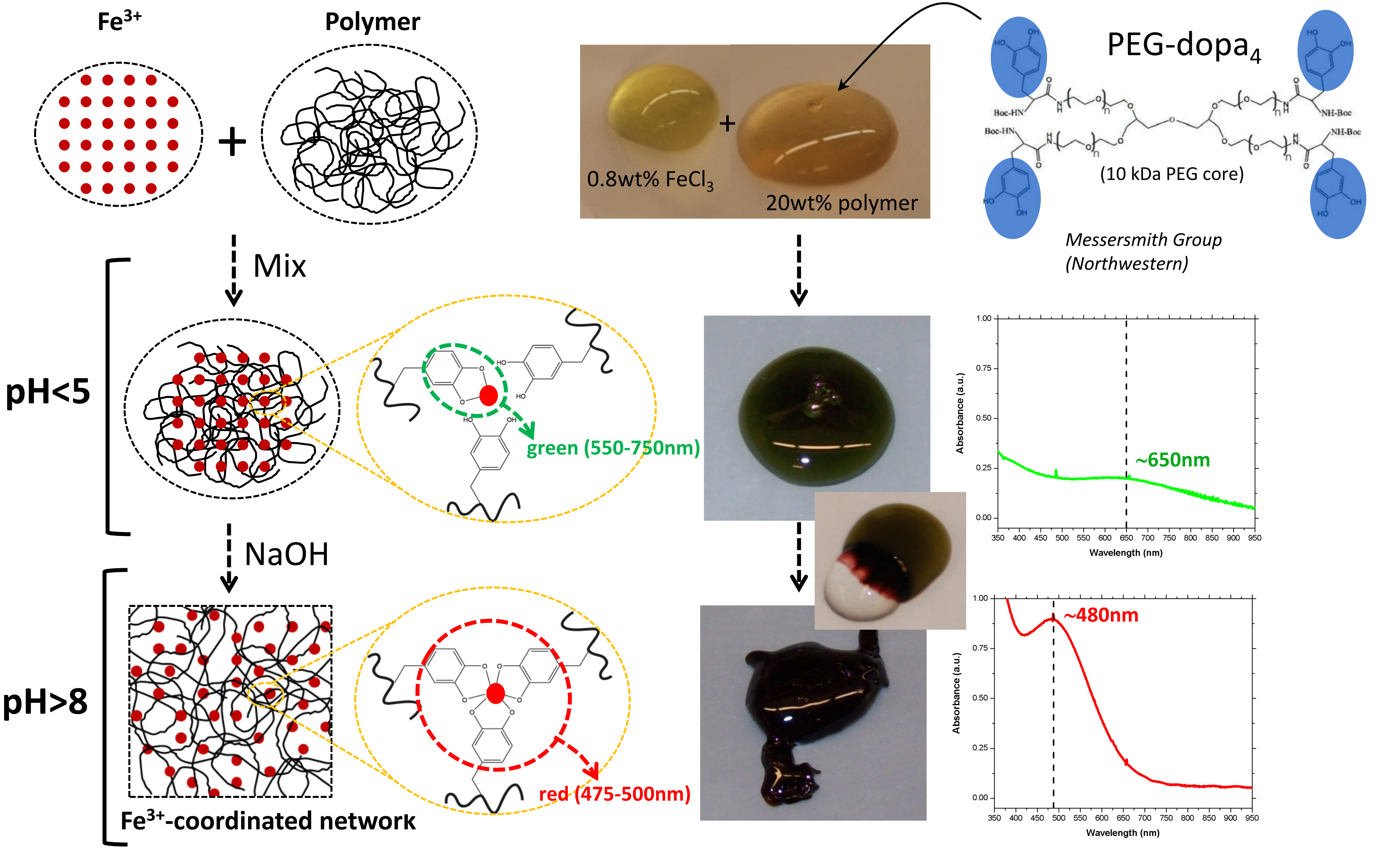
Mechanical function?

Metal-coordinated mussel thread assembly?



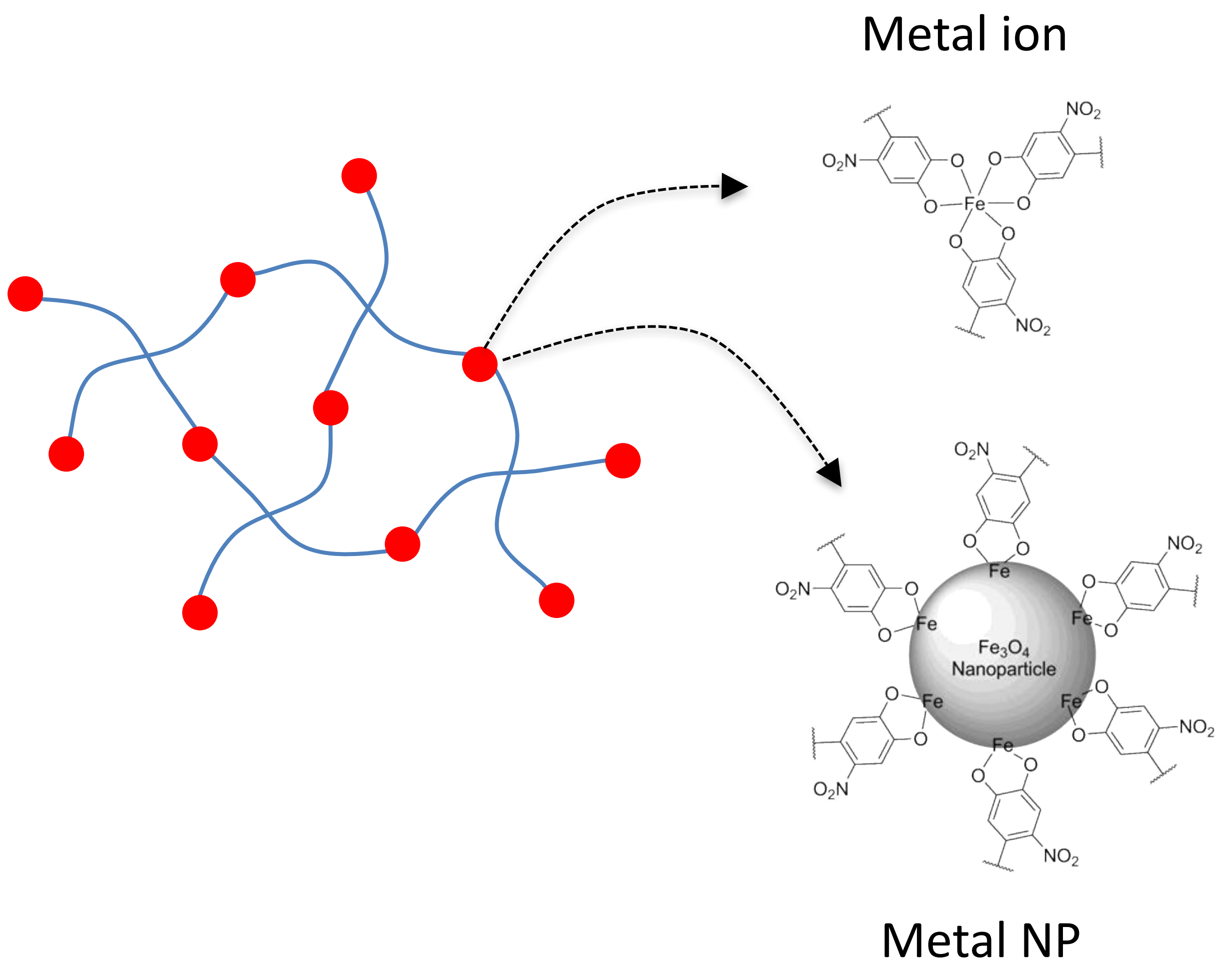


Metal-coordinated polymer network assembly

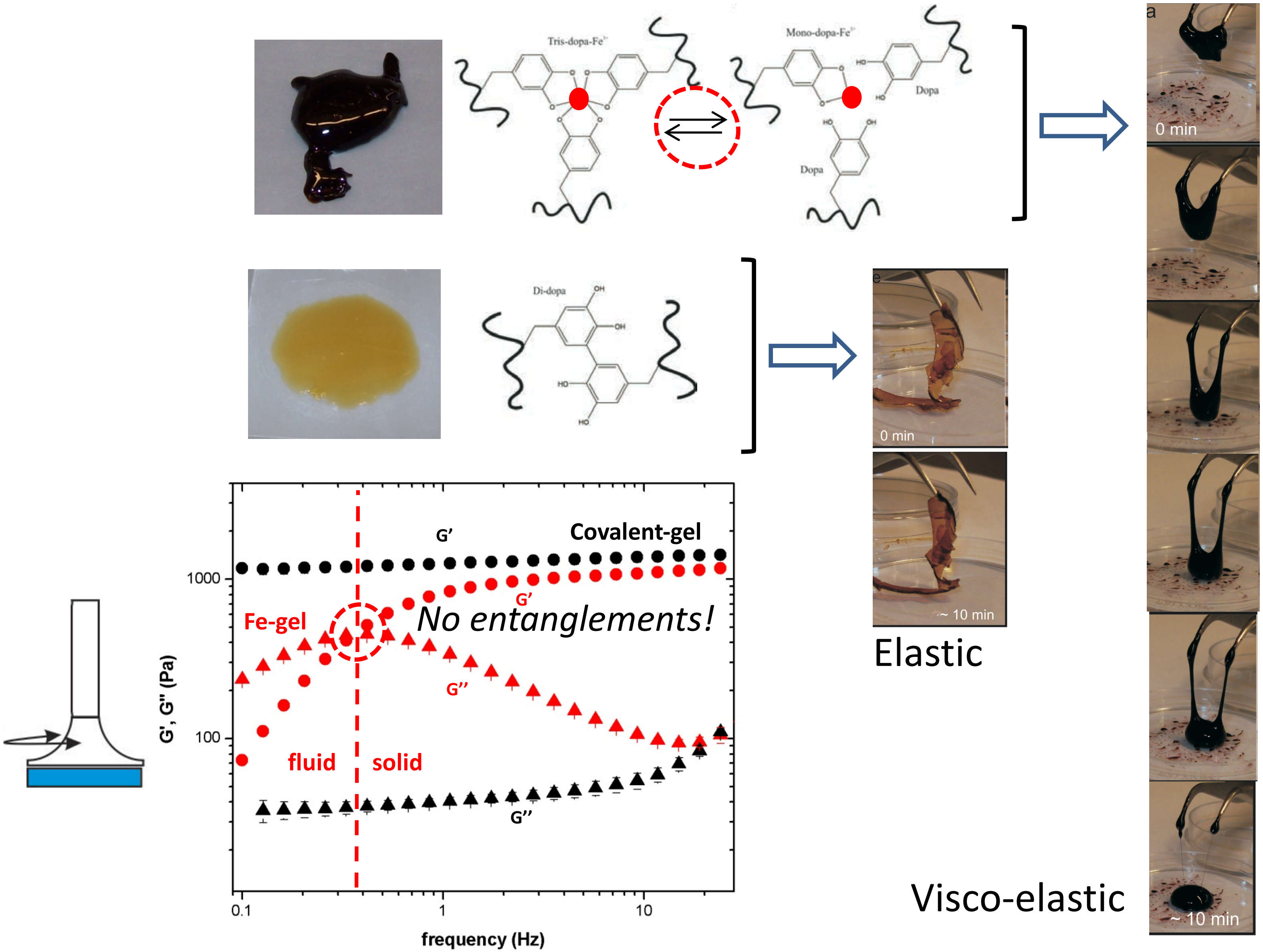


Holten-Andersen, Harrington, Birkedal, Lee, Messersmith, Lee, & Waite. *PNAS.* **108**, 2551-2655, (2011)

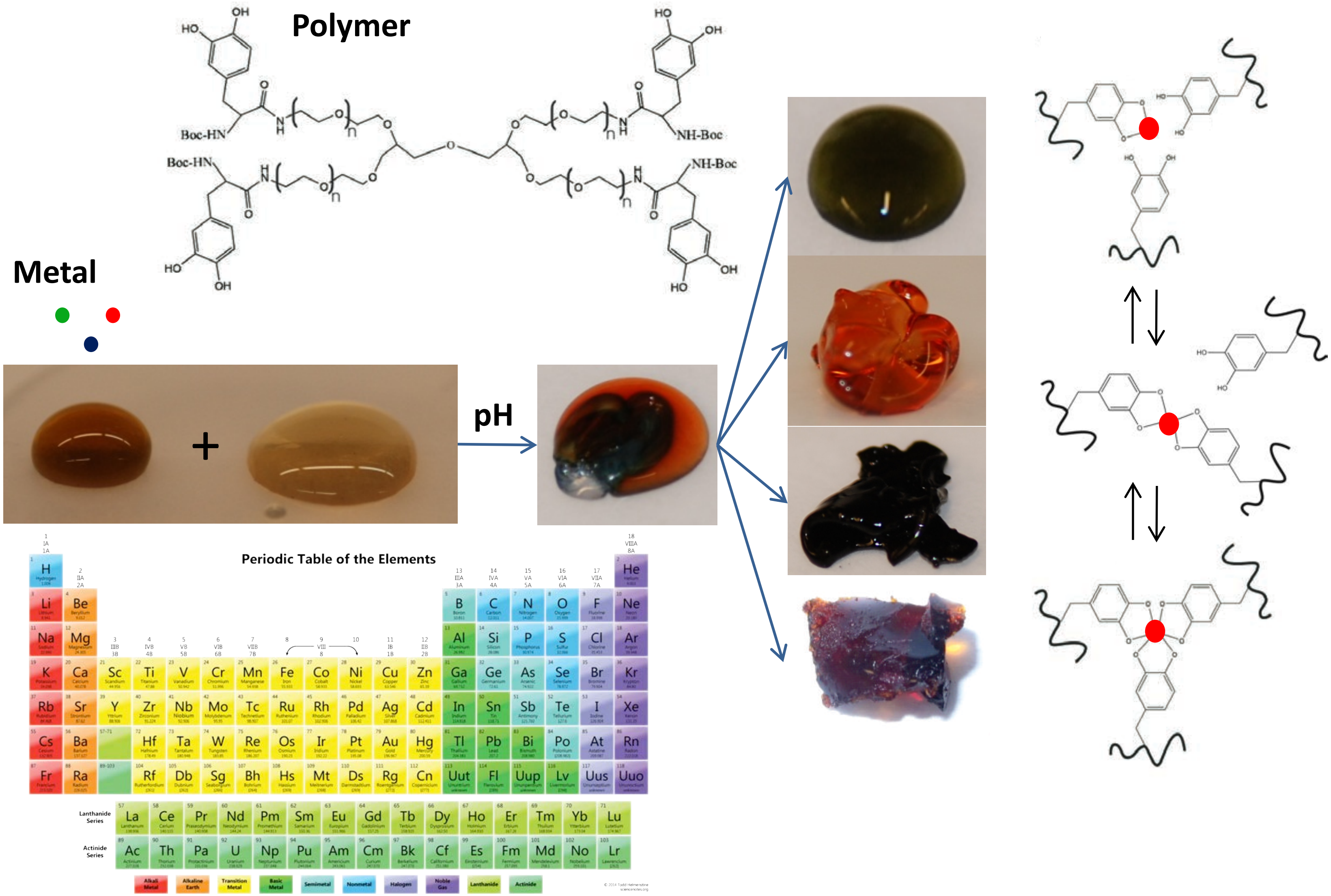
Bio-inspired metal-coordinate crosslinked networks



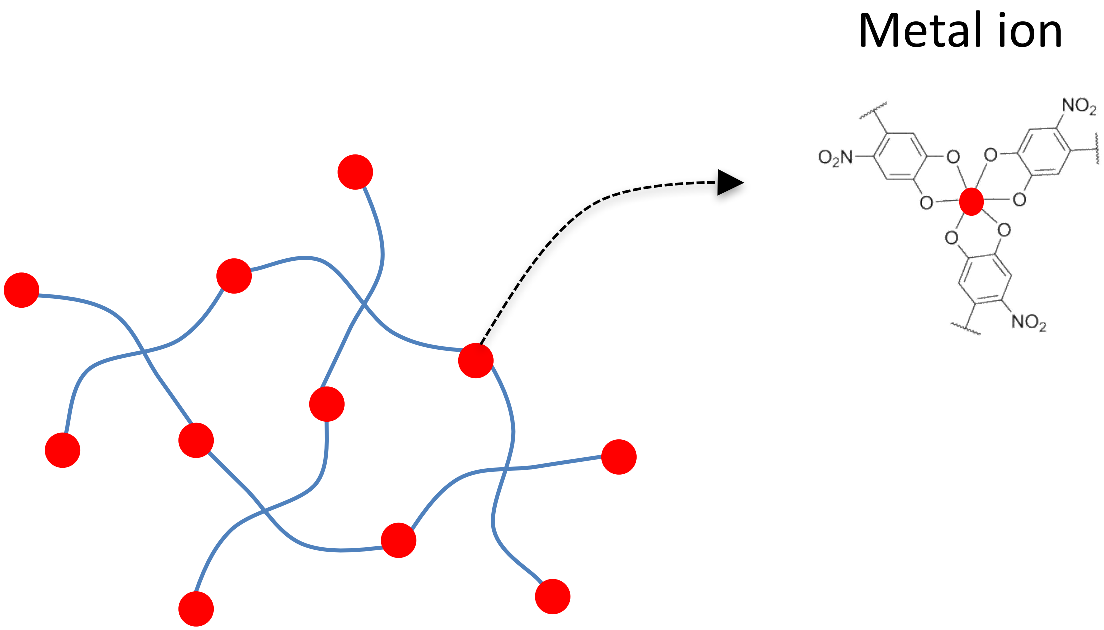
Metal ion-coordinate dynamics set gel mechanics



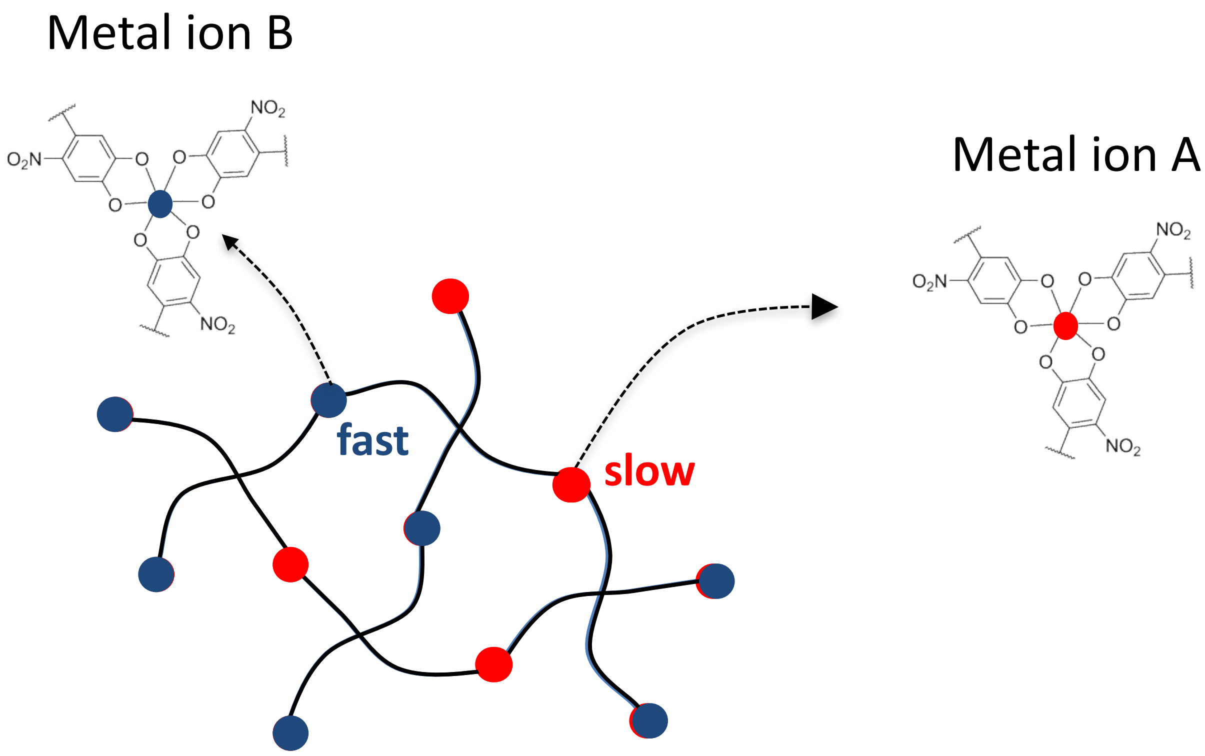
Metal ion-coordinate dynamics set gel mechanics



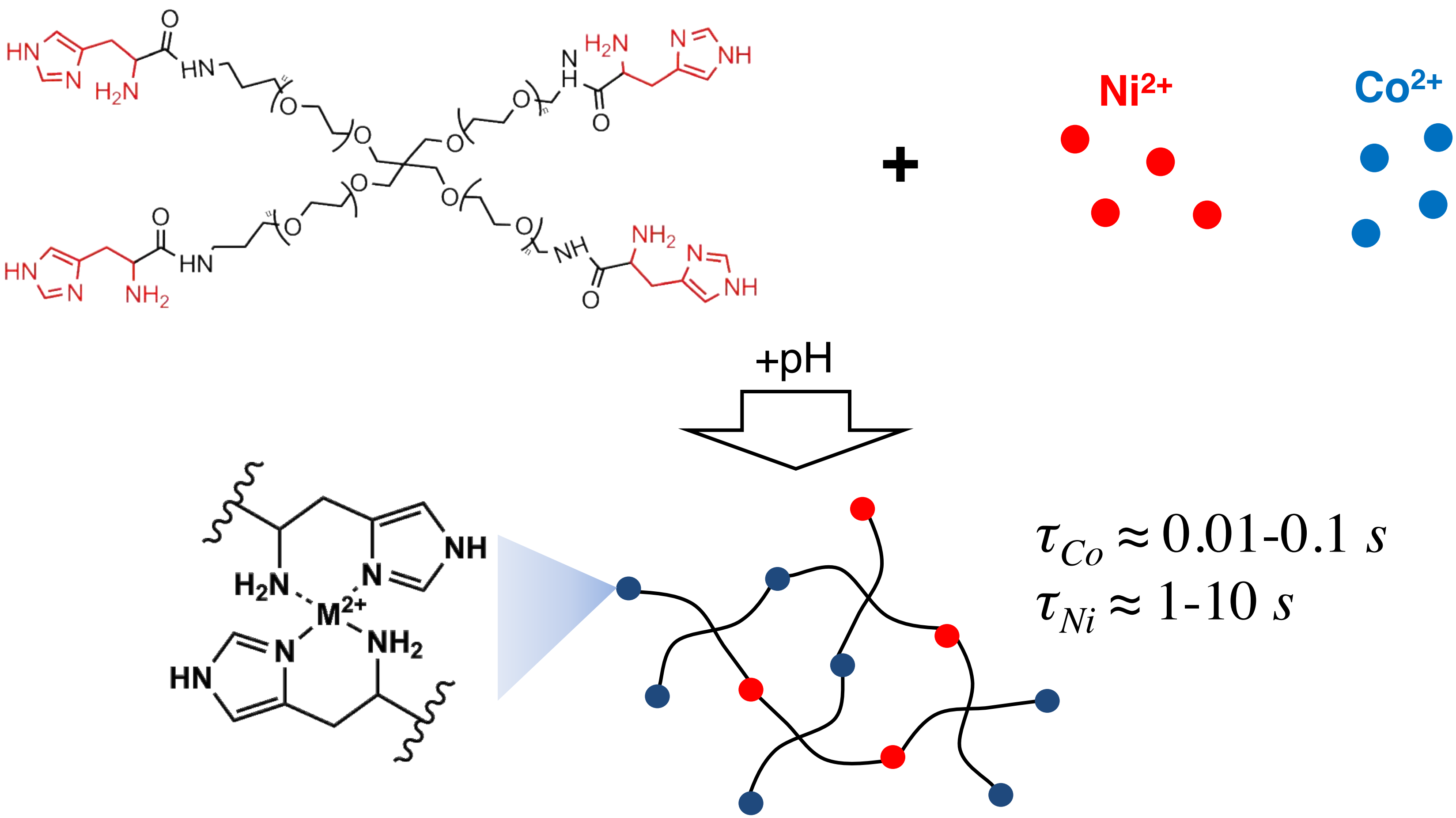
Metal ion-coordinate dynamics set gel mechanics



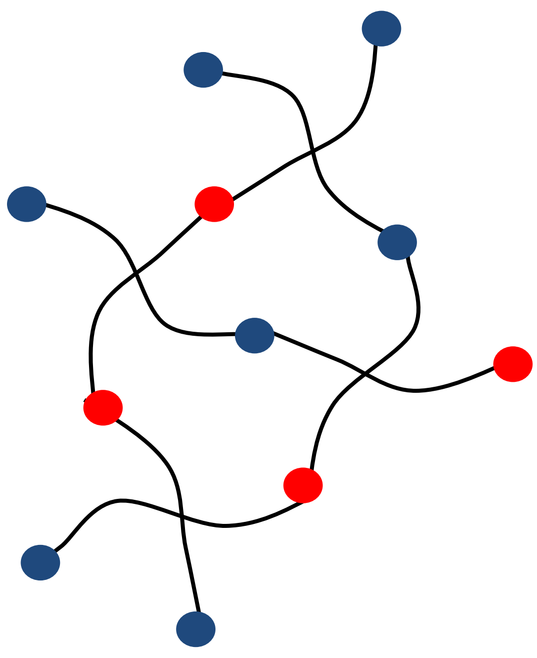
Metal ion-coordinate dynamics set gel mechanics

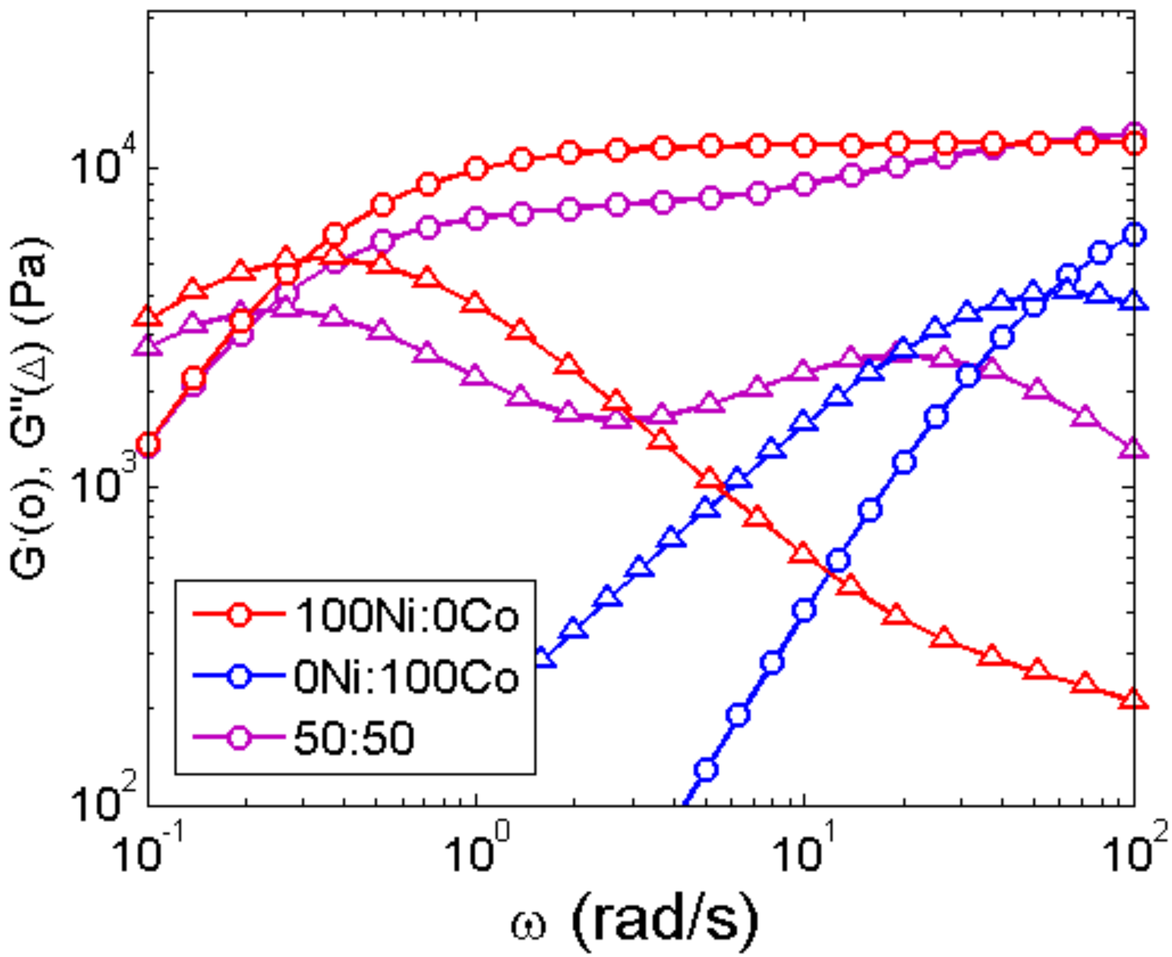


Metal ion-coordinate dynamics set gel mechanics



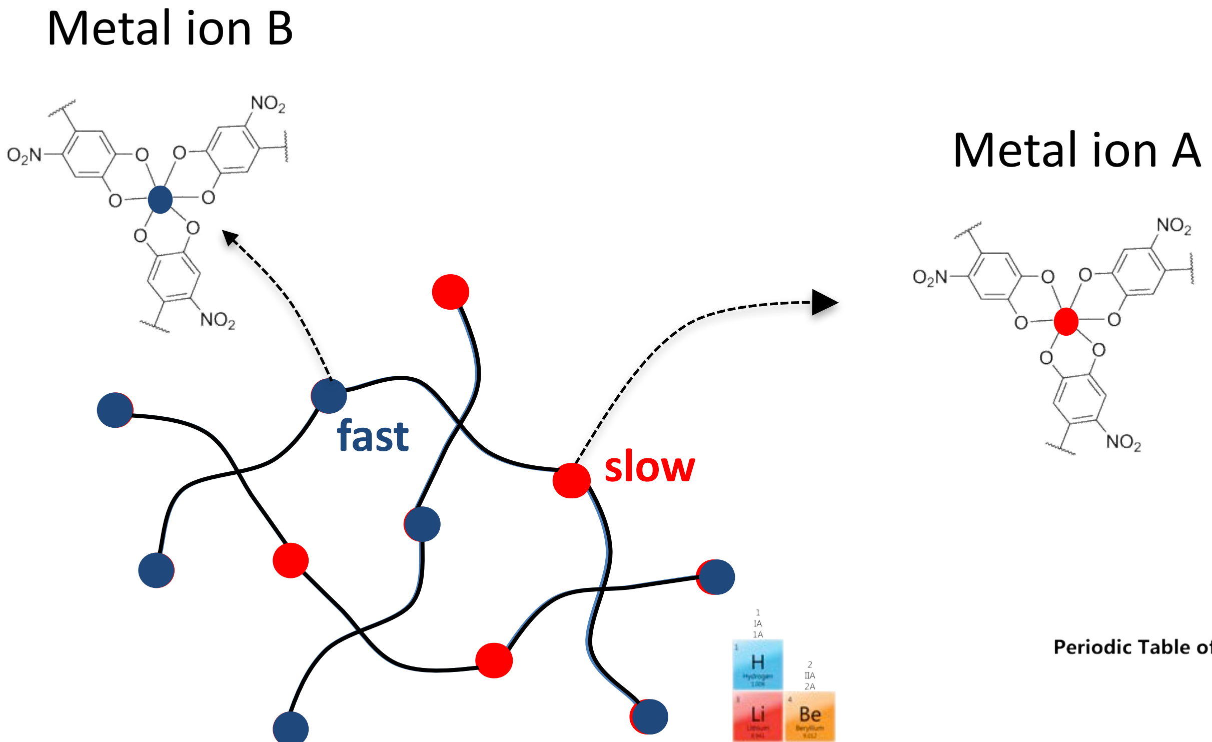
Metal ion-coordinate dynamics set gel mechanics

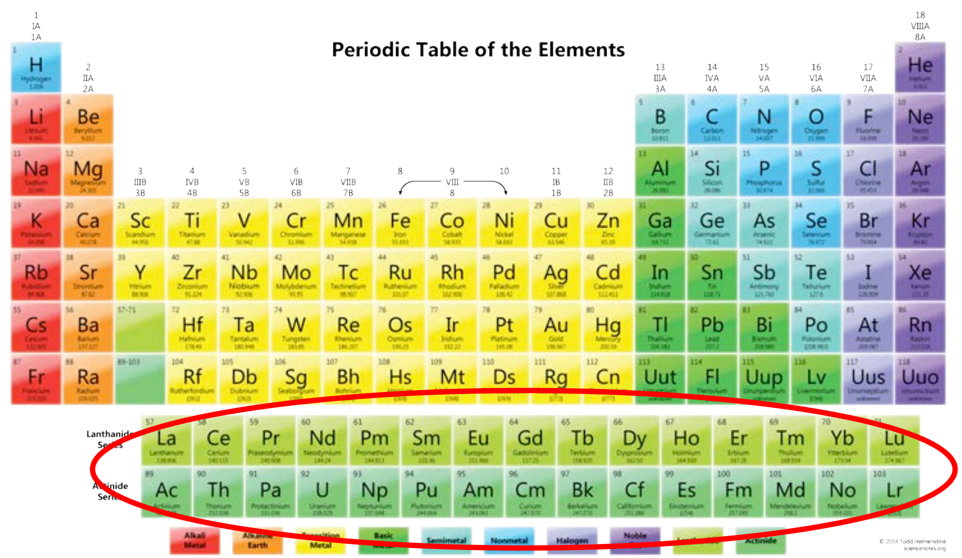




Grindy *et al*, Nature Materials (2015)

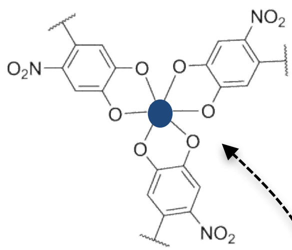
Metal ion-coordinate dynamics set gel mechanics

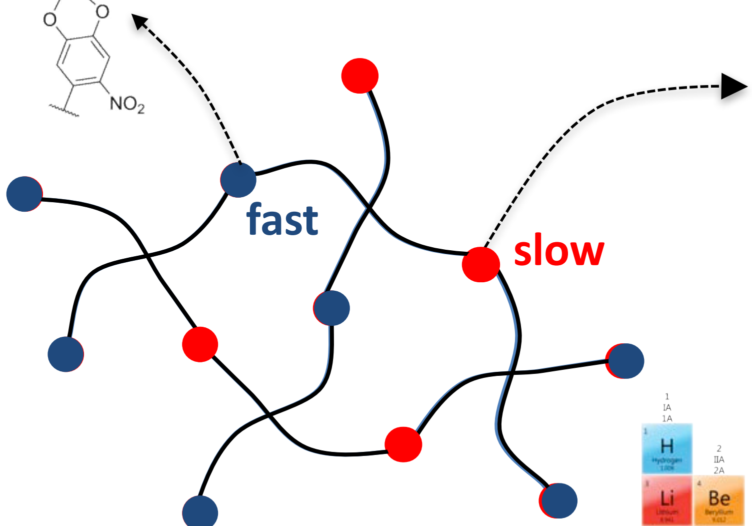




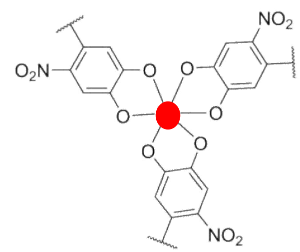
Metal ion-coordinate dynamics set gel mechanics

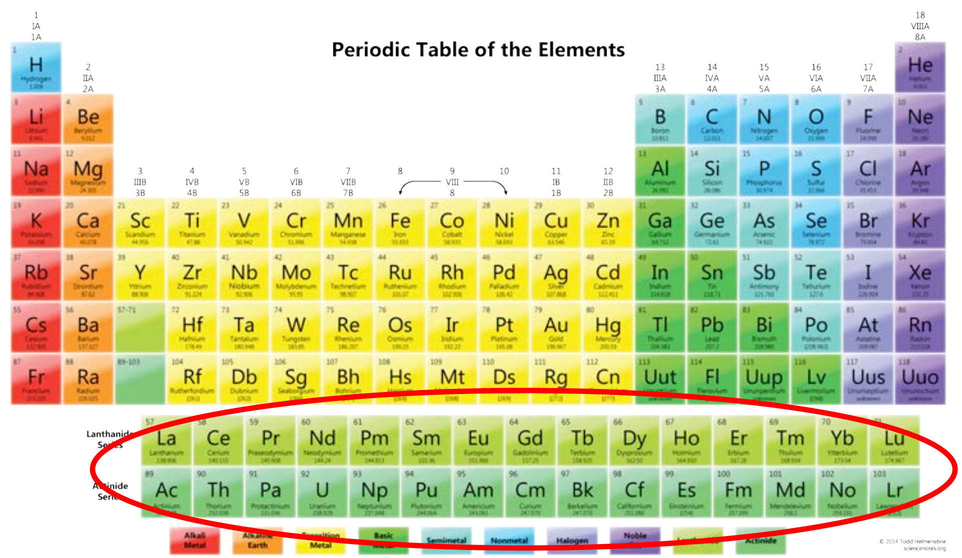
Lanthanide Metal ion B





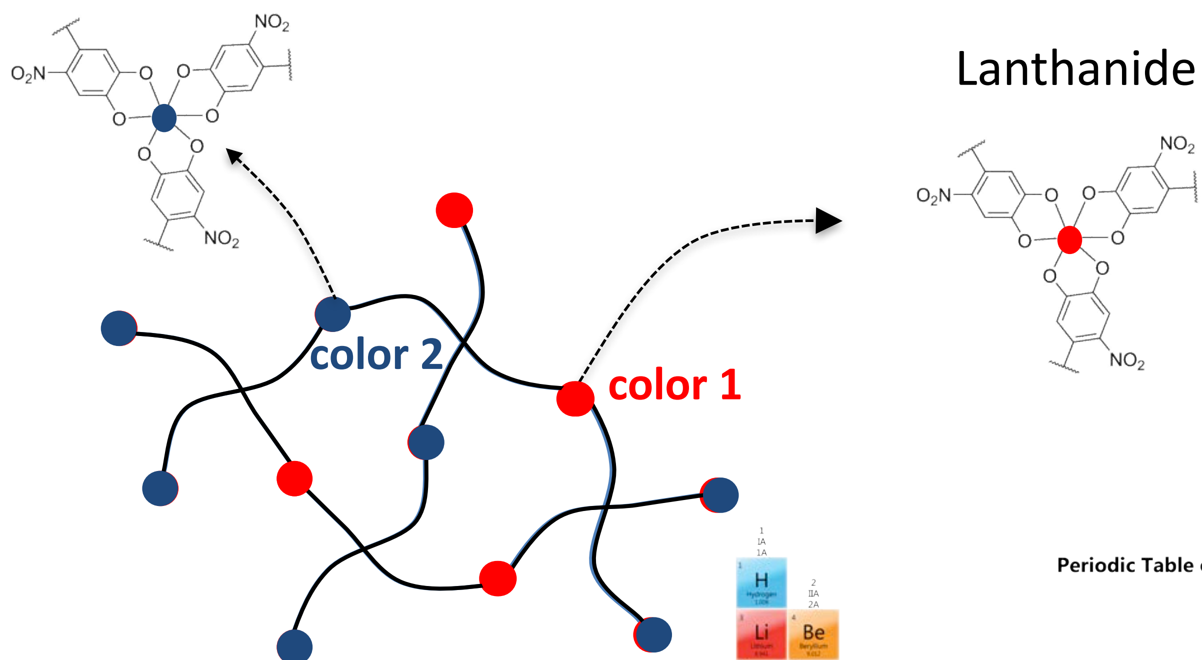
Lanthanide metal ion A

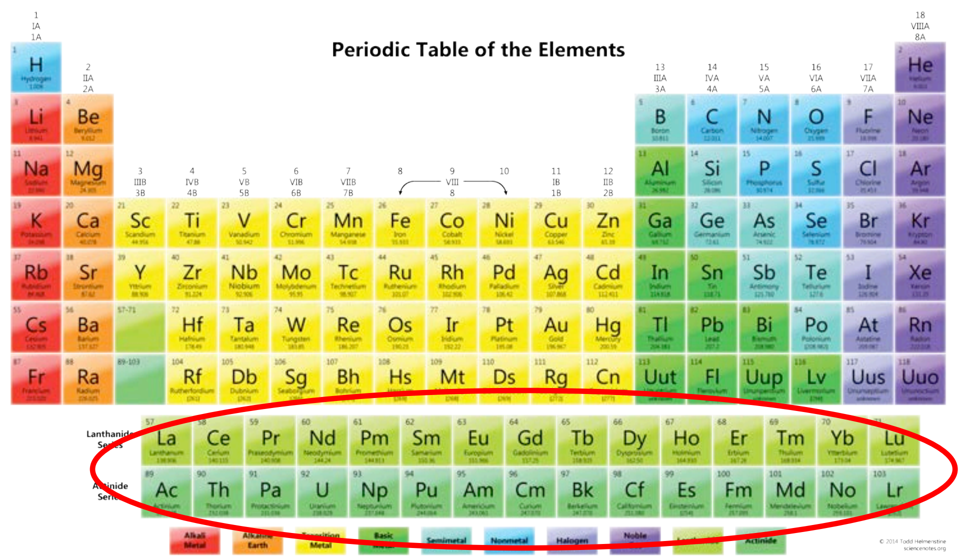




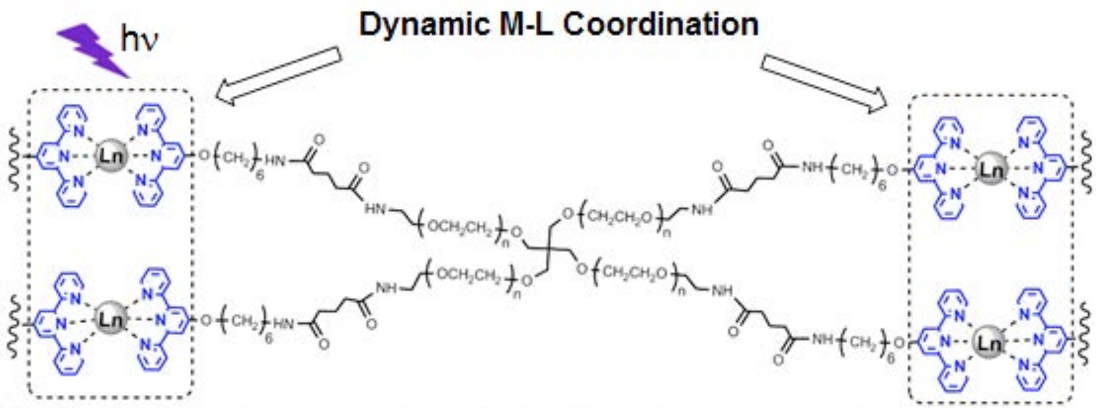
Metal ion-coordinate dynamics set gel mechanics

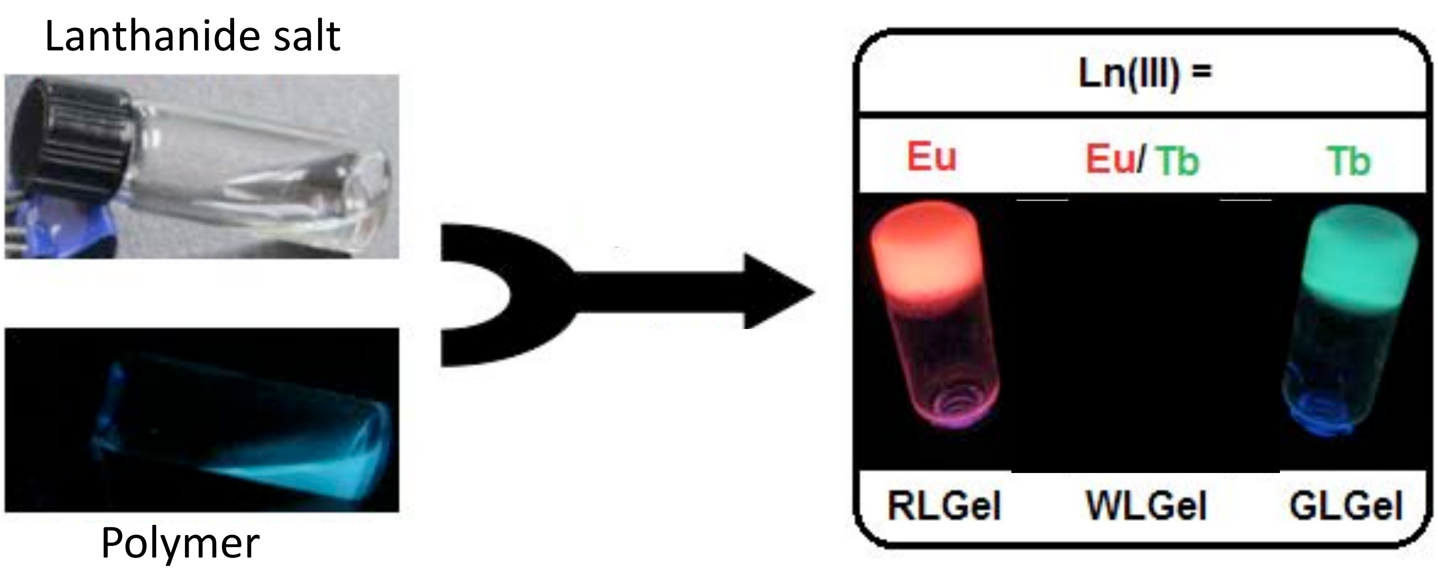
Lanthanide Metal ion B





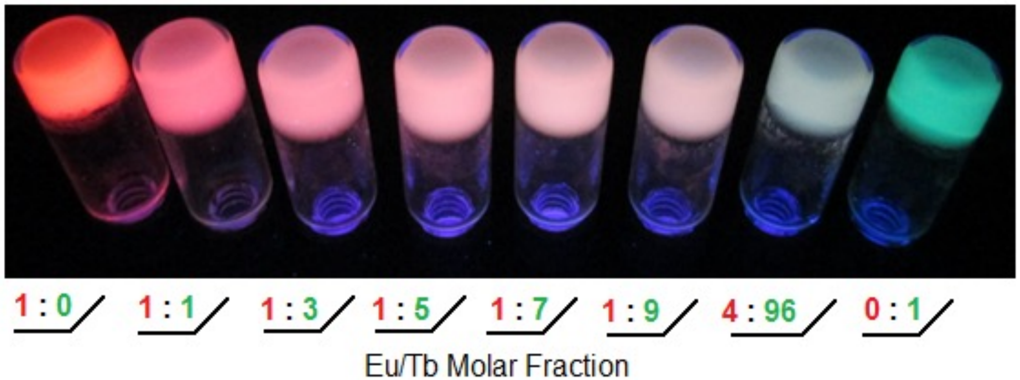
Light-emitting stimuli-responsive polymer networks

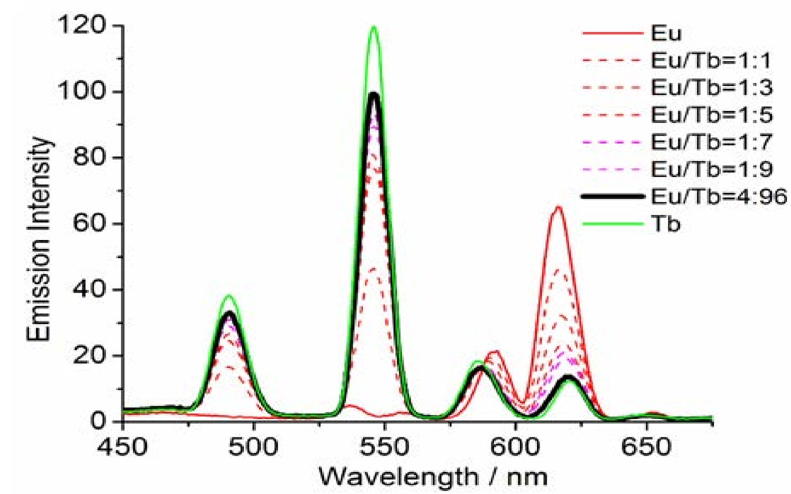


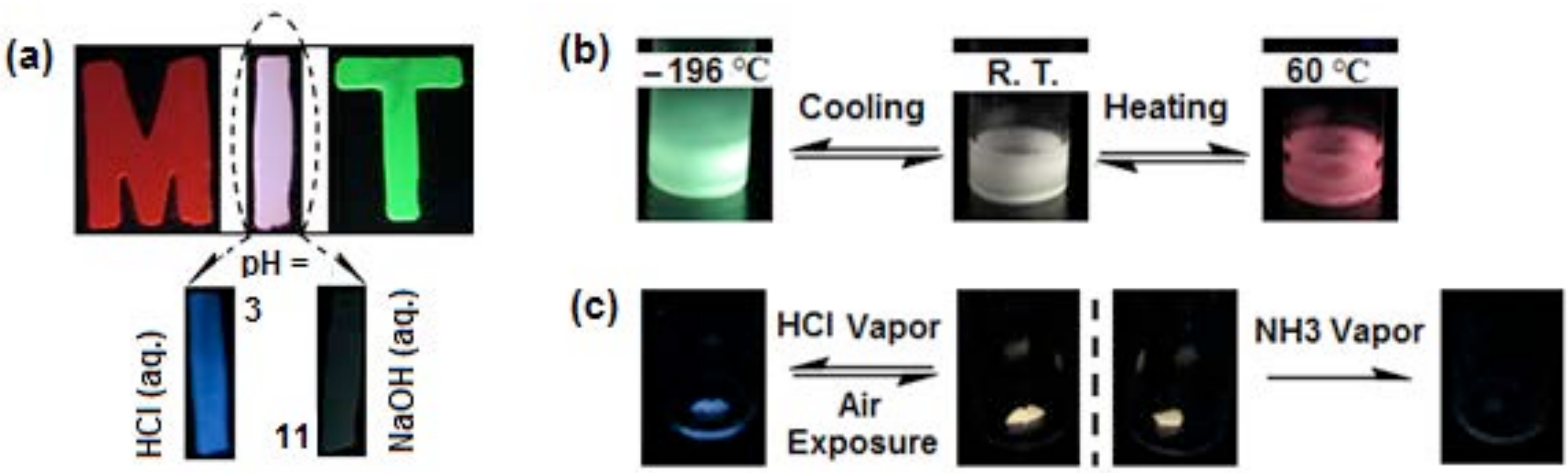


Chen *et al*, JACS, 2015

Light-emitting stimuli-responsive polymer networks

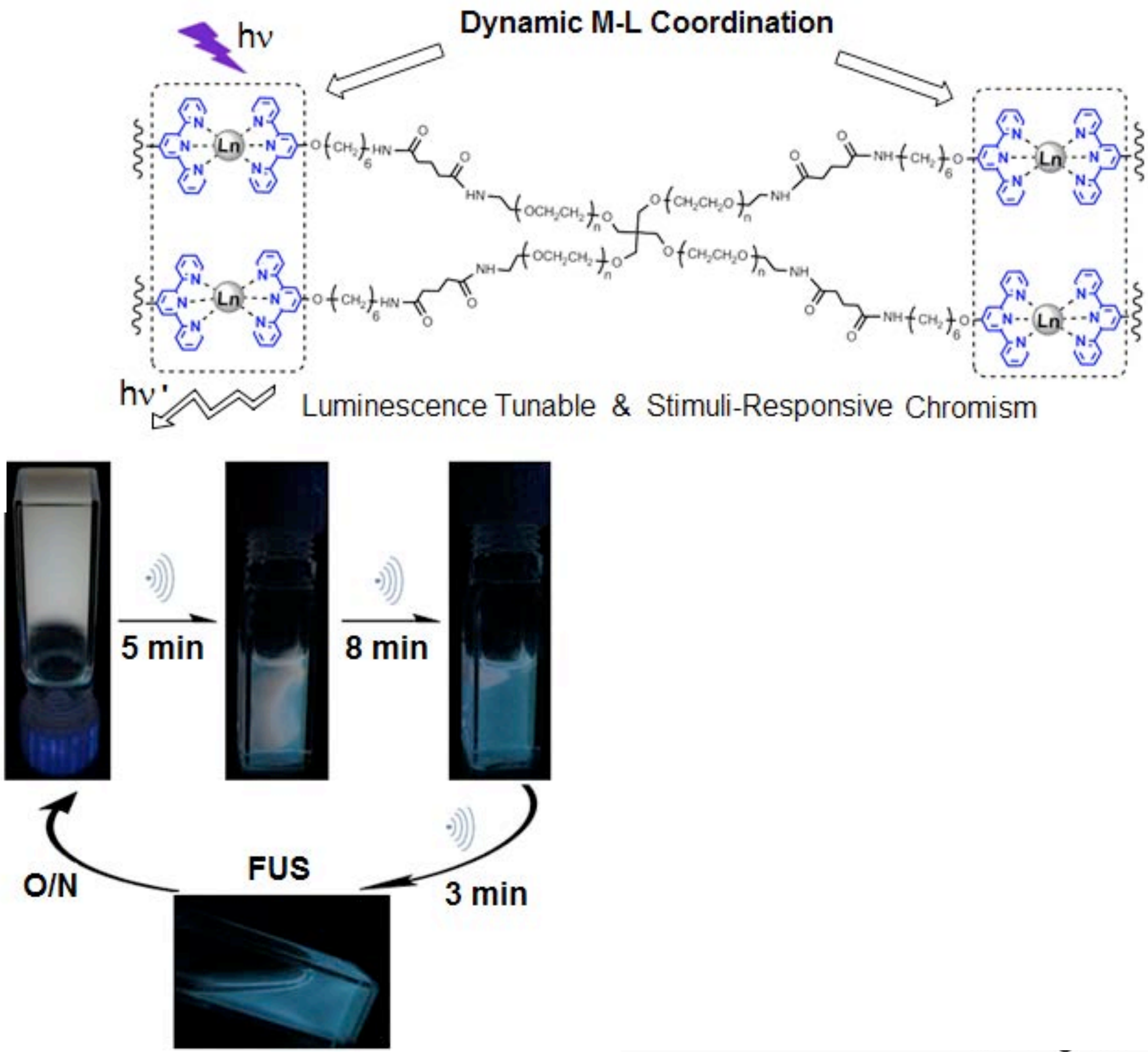






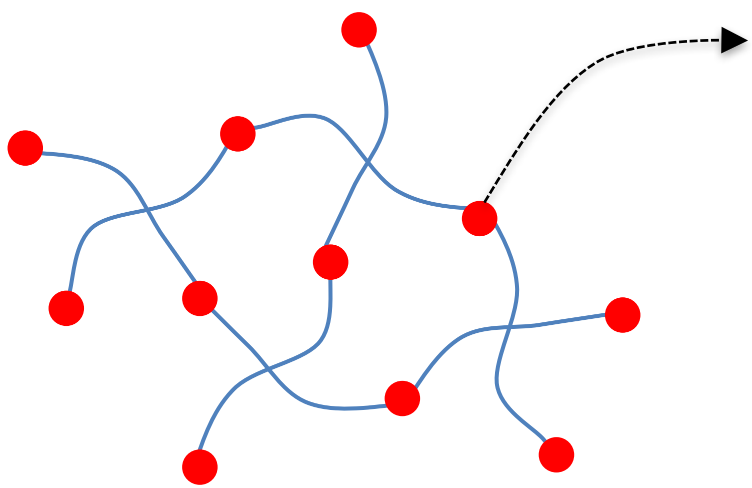
Chen *et al*, JACS, 2015

Light-emitting stimuli-responsive polymer networks

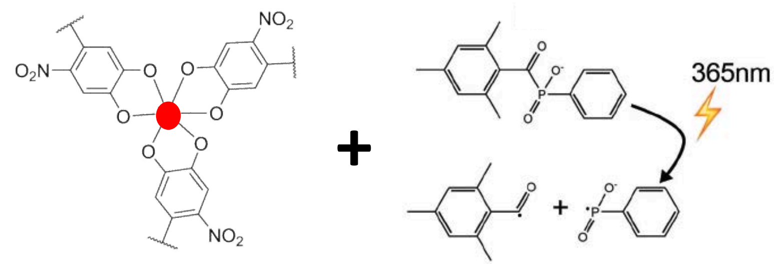


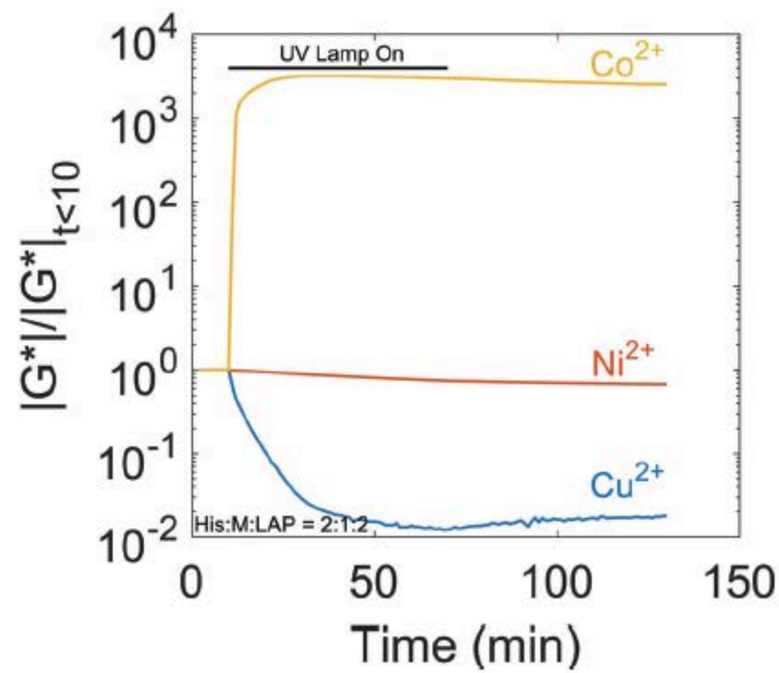
Chen *et al*, JACS, 2015

Metal ion-coordinate dynamics set gel mechanics



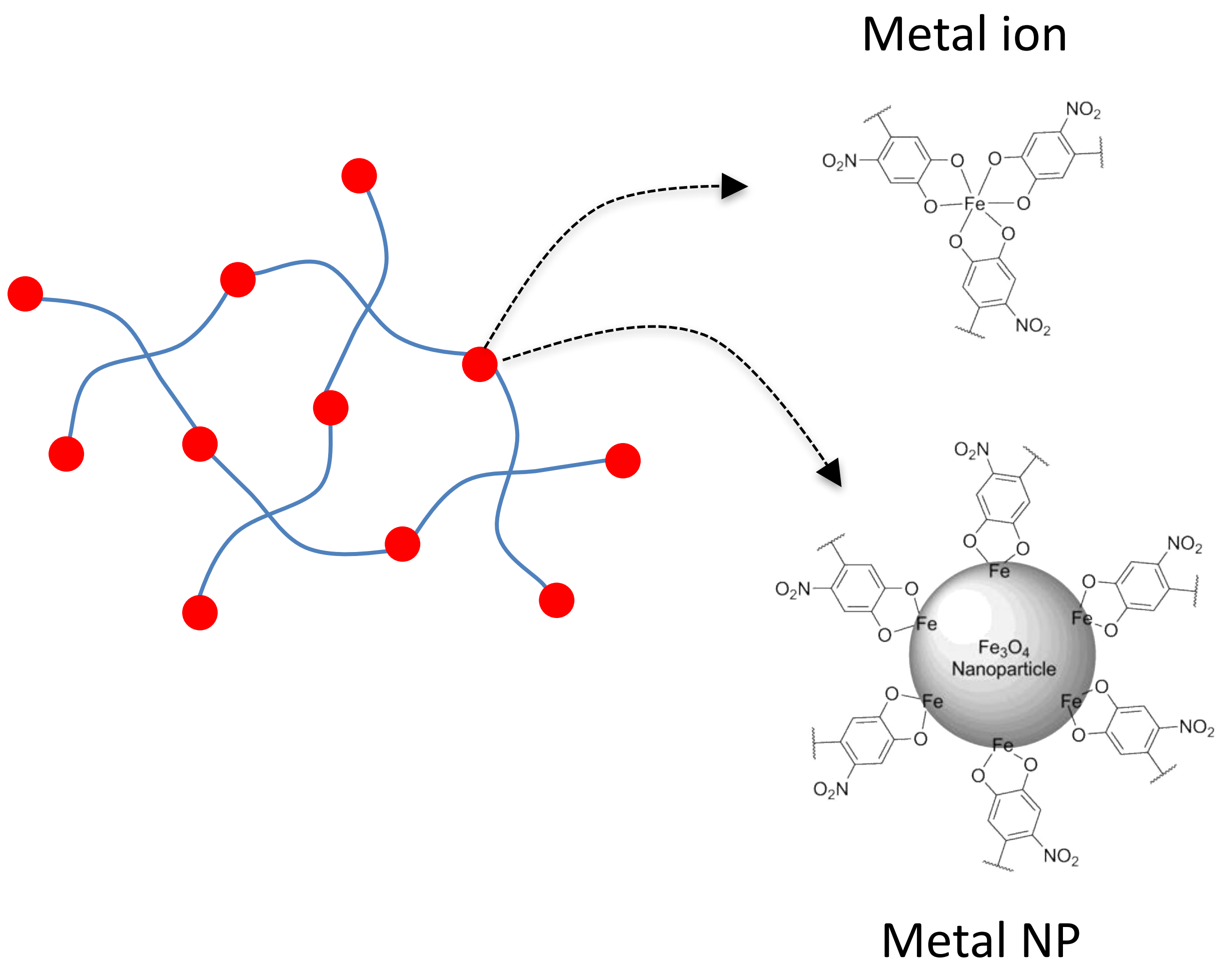
Metal ion





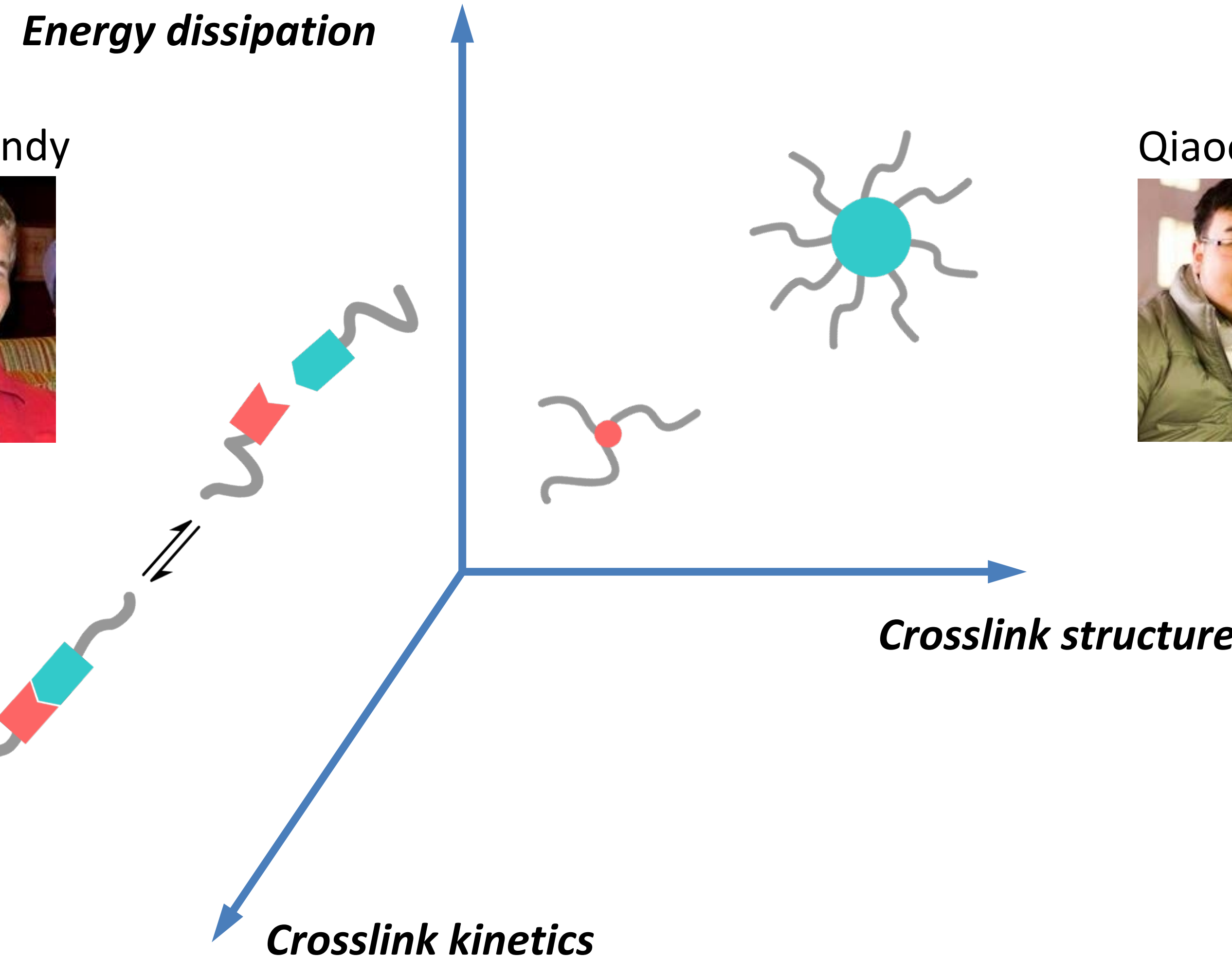
Grindy *et al*, Soft Matter (2017)

Bio-inspired metal-coordinate crosslinked networks



Energy dissipative crosslink engineering

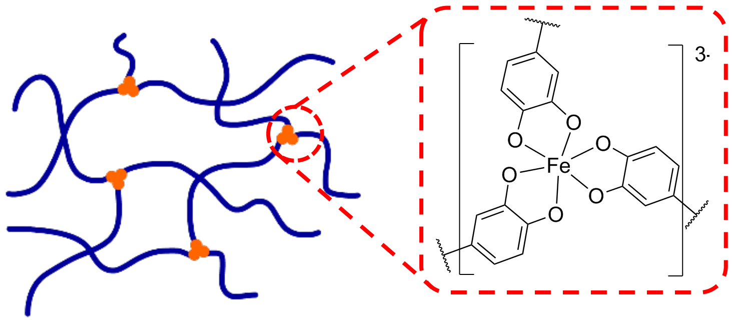
Scott Grindy



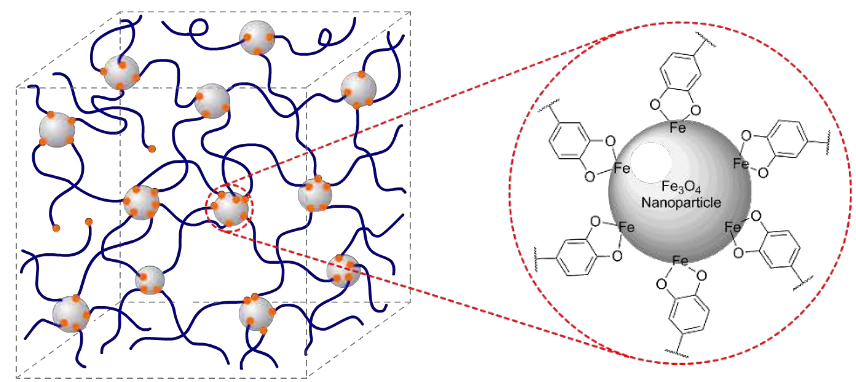
Qiaochu Li

Energy dissipative crosslinks: Ions vs Nano-particles

f **: number of ligands at each crosslink**

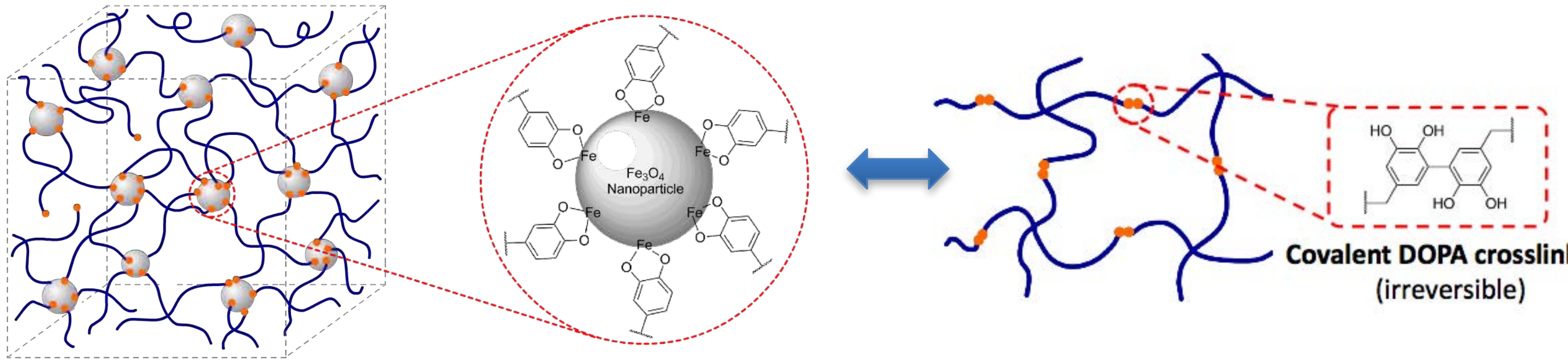


$$f = 3$$

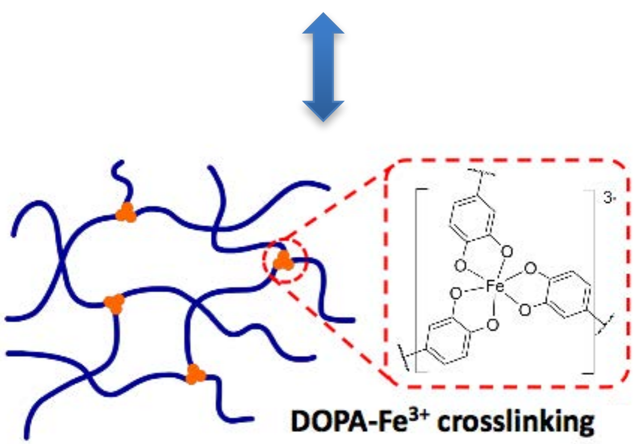


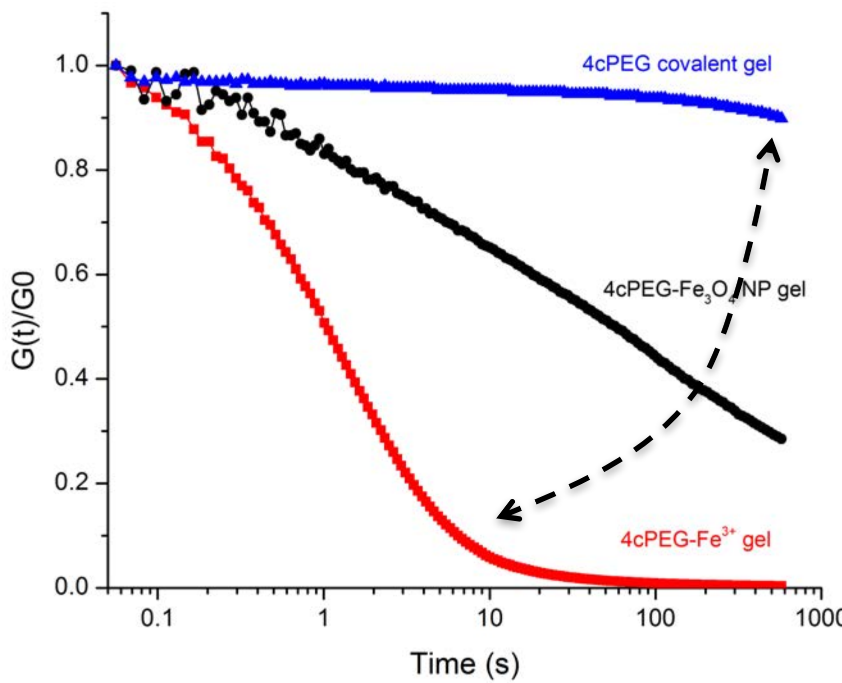
$$f \sim 10^2$$

Energy dissipative crosslinks: Ions vs Nano-particles



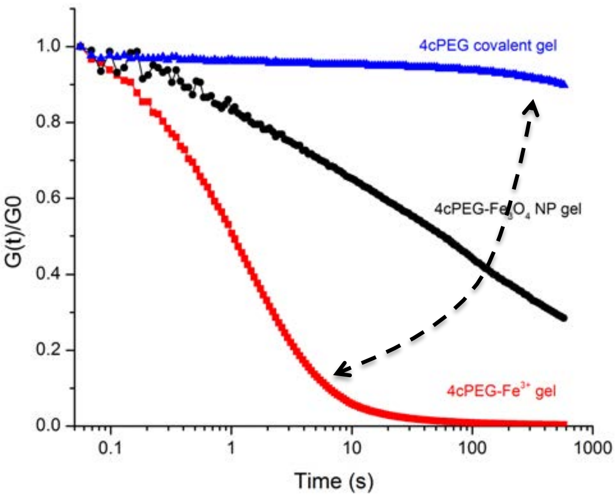
Self-assembled Hydrogel Network



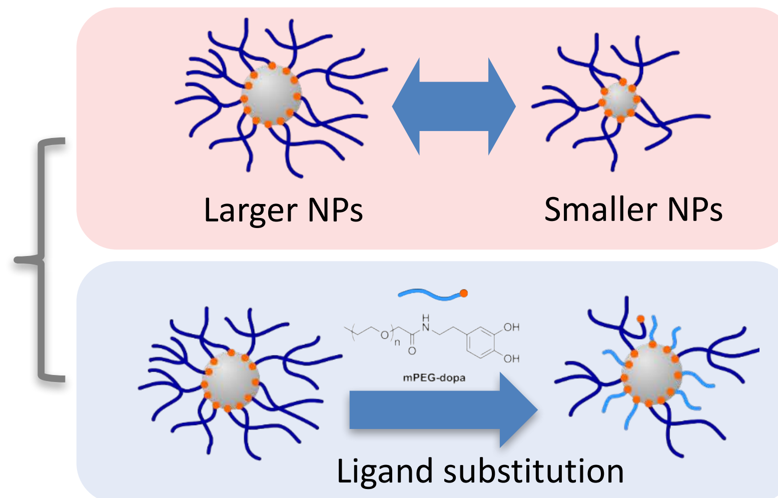


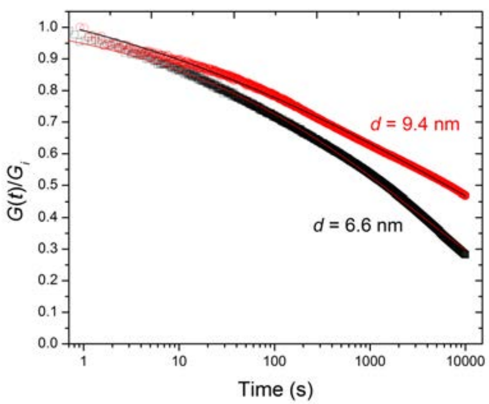
role of f in controlling relaxation time τ?

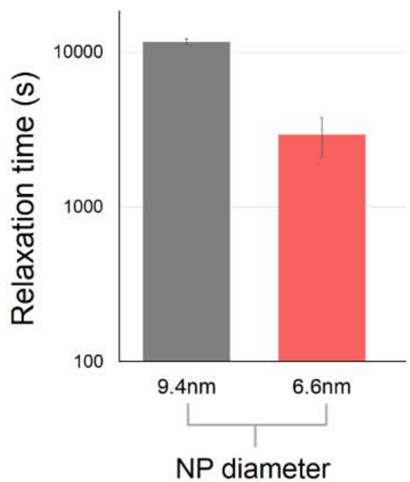
Energy dissipative crosslinks: $\tau \propto f$

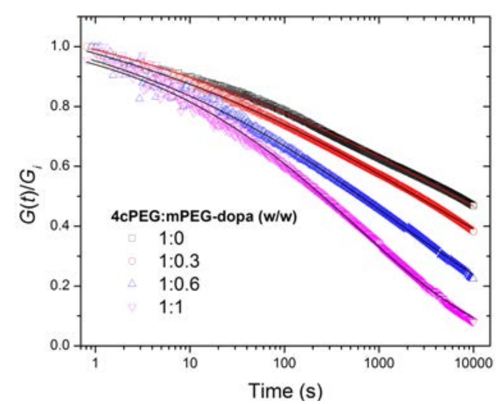


$$\tau \propto f$$



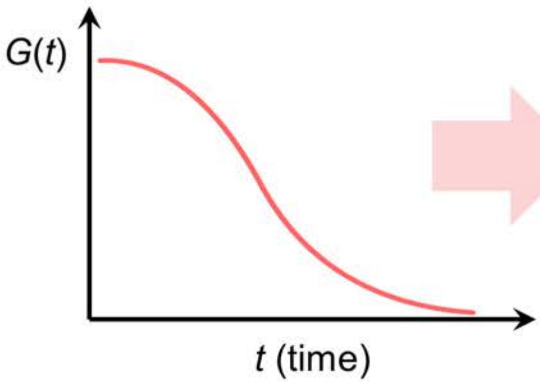






Li *et al*, ACS Nano (2016

Energy dissipative crosslinks: $\tau \propto f$

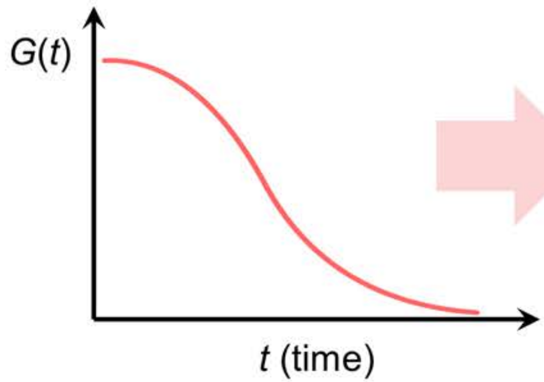


$$G(t) = G_0 e^{-\left(\frac{t}{\tau}\right)}$$

$\boldsymbol{\tau}$: Characteristic relaxation time

Kohlrausch’ s stretched exponential relaxation equation

Energy dissipative crosslinks: α

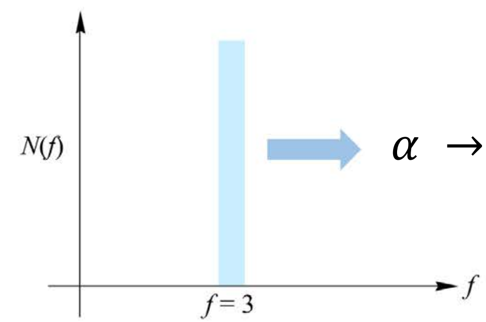


$$G(t) = G_0 e^{-\left(\frac{t}{\tau}\right)^{\alpha}}$$

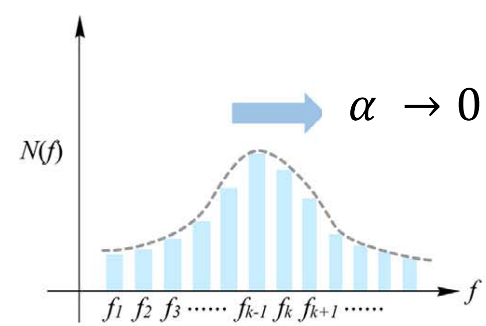
Kohlrausch' s stretched exponential relaxation equation

$\boldsymbol{\alpha}$: Kohlrausch's exponent

$\boldsymbol{\tau}$: Characteristic relaxation time

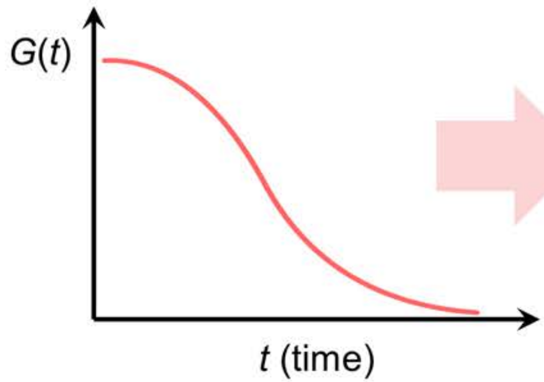


$\alpha \rightarrow 1$



$\alpha \rightarrow 0$

Energy dissipative crosslinks: α

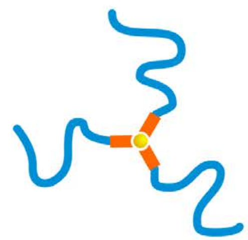


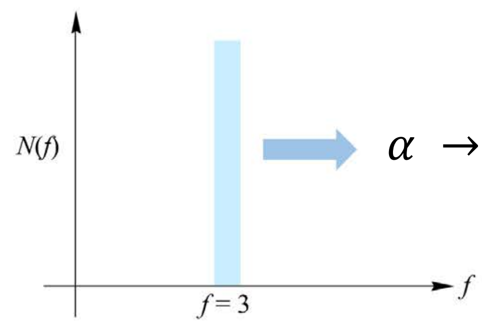
$$G(t) = G_0 e^{-\left(\frac{t}{\tau}\right)^{\alpha}}$$

α: Kohlrausch's exponent

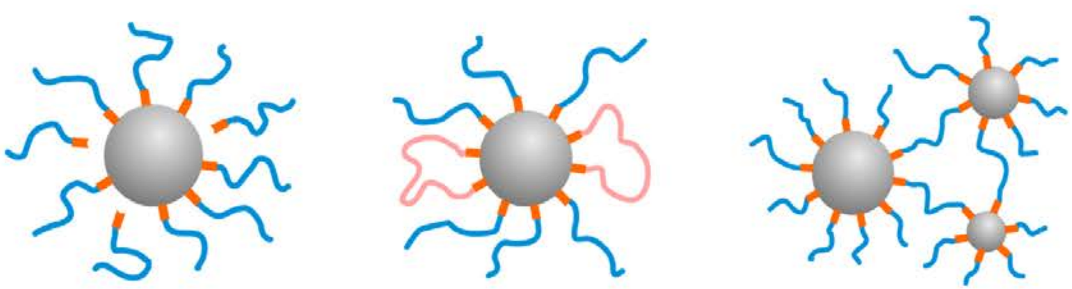
τ: Characteristic relaxation time

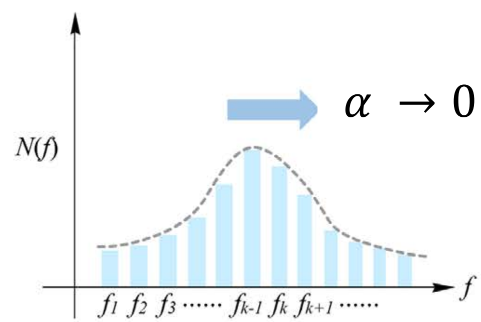
Kohlrausch' s stretched exponential relaxation equation





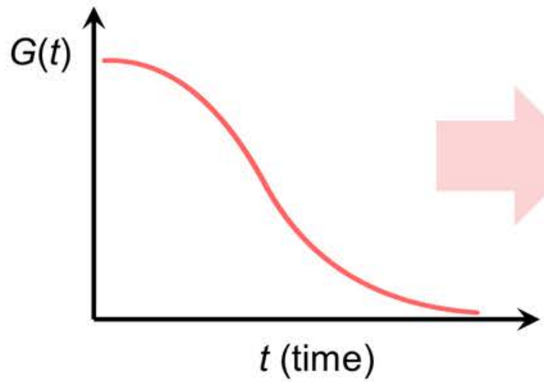
$\alpha \rightarrow 1$





$\alpha \rightarrow 0$

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



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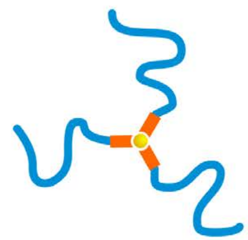
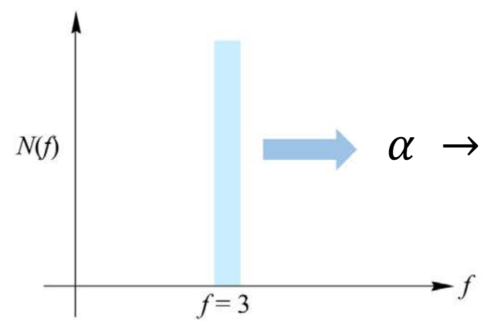
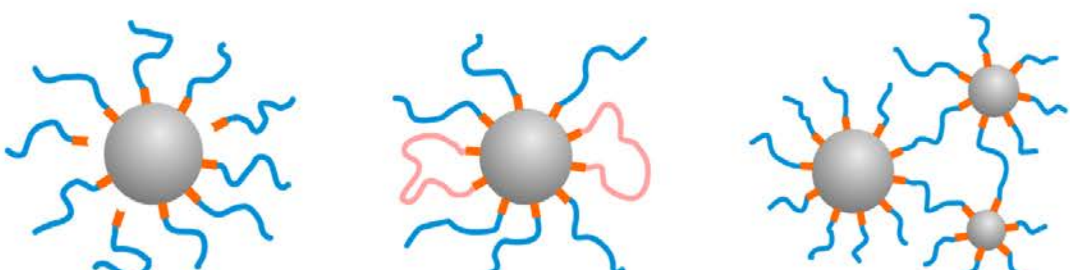
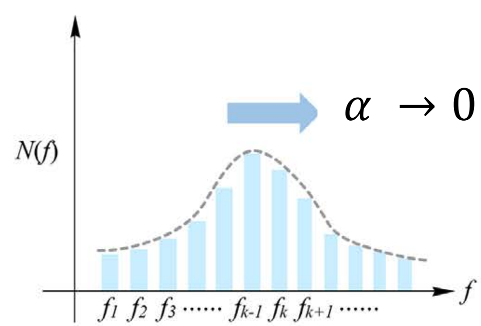




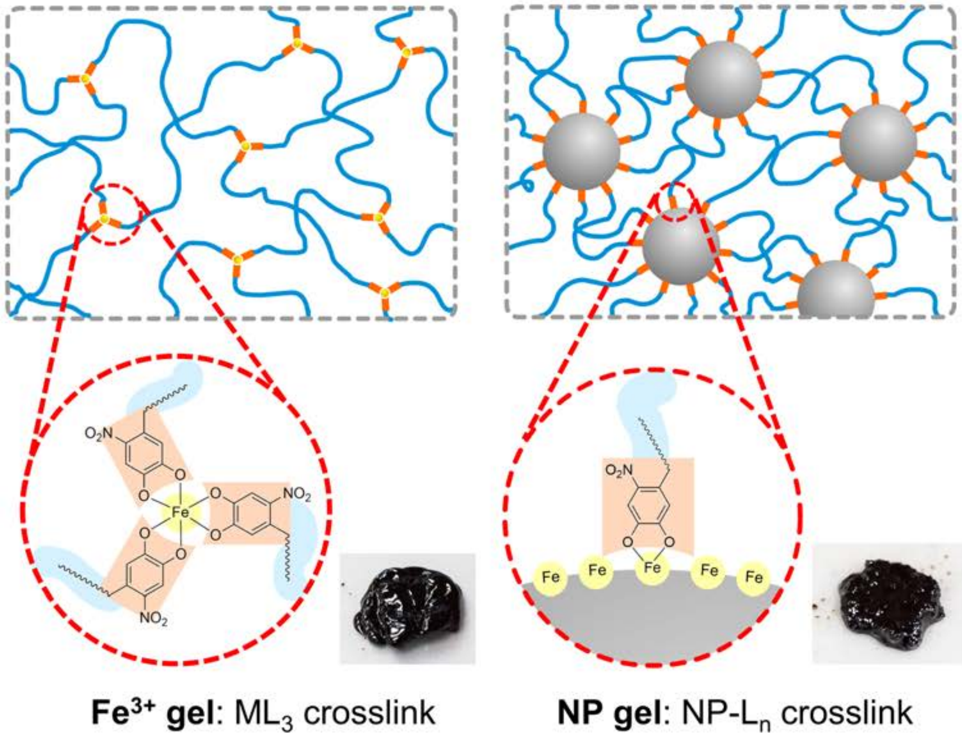
$\alpha \rightarrow 1$

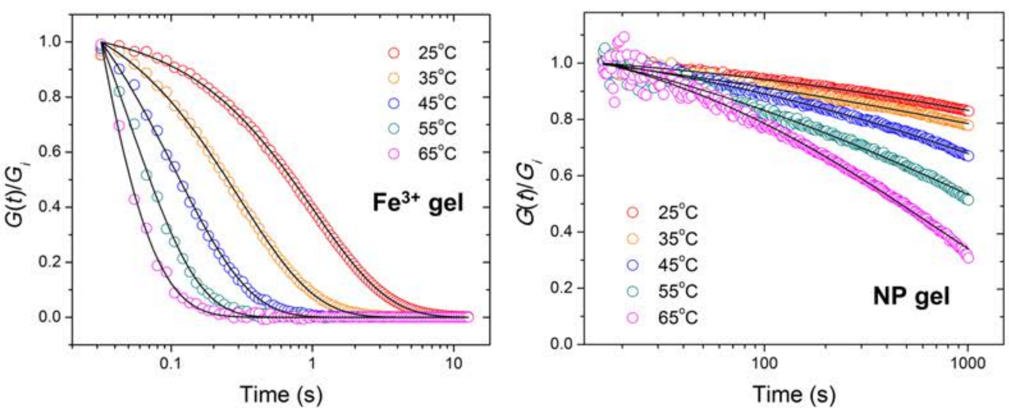




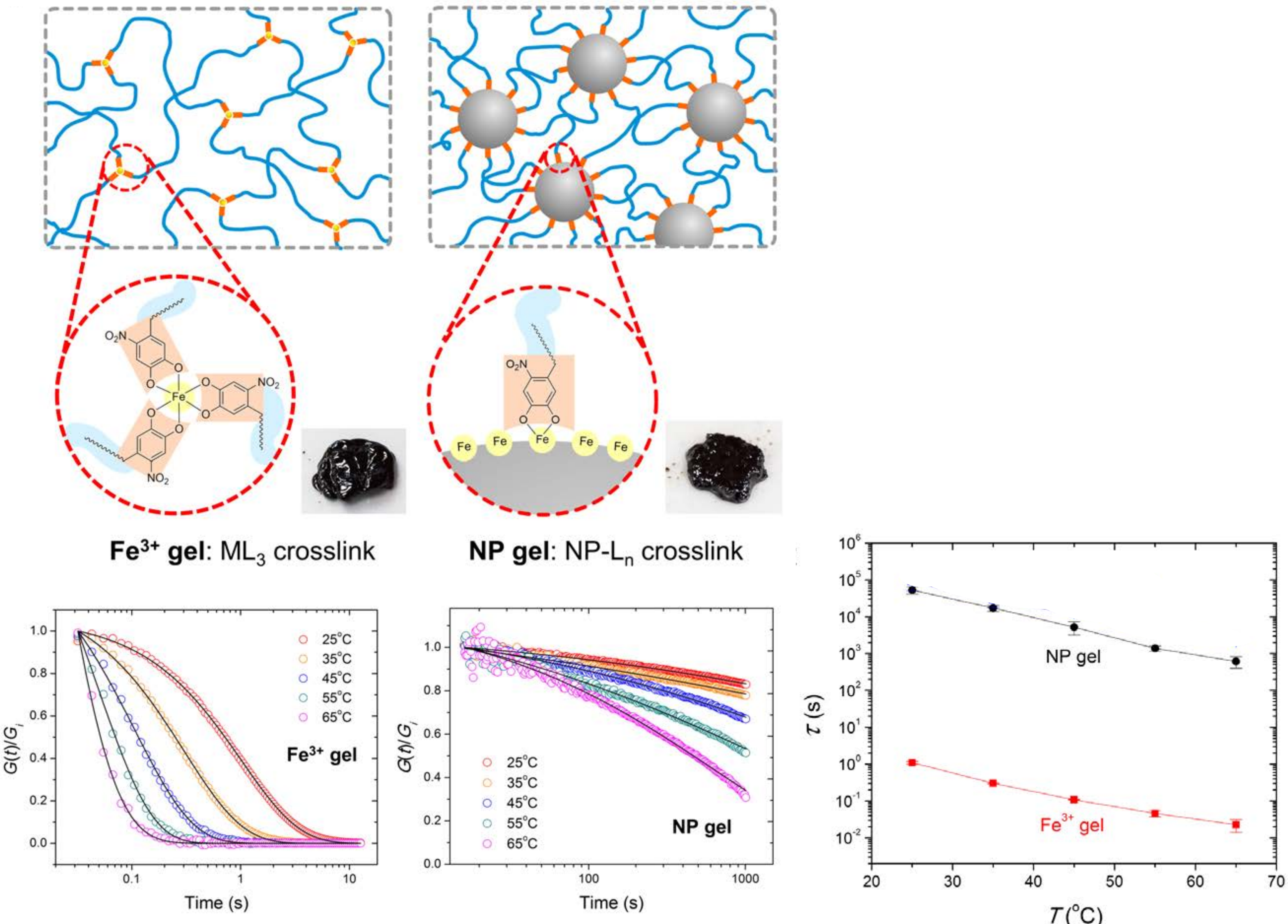
$\alpha \rightarrow 0$

Energy dissipative crosslinks : tau vs alpha

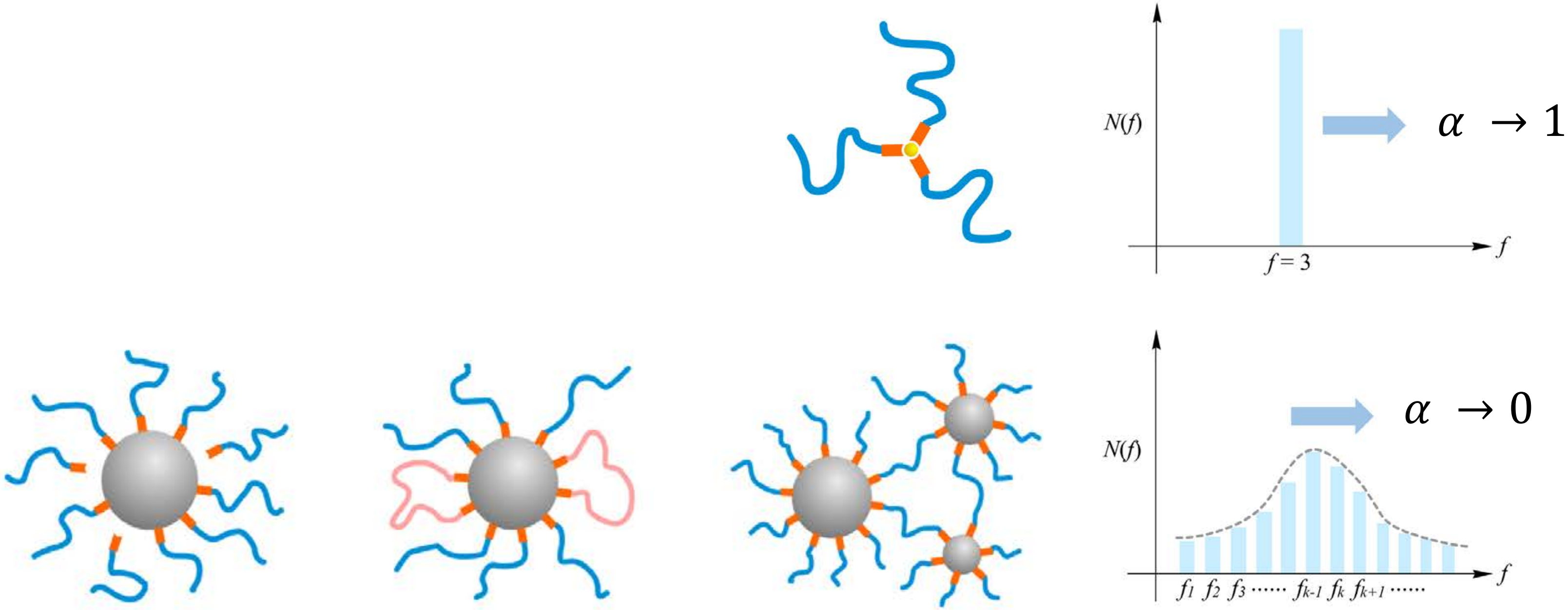


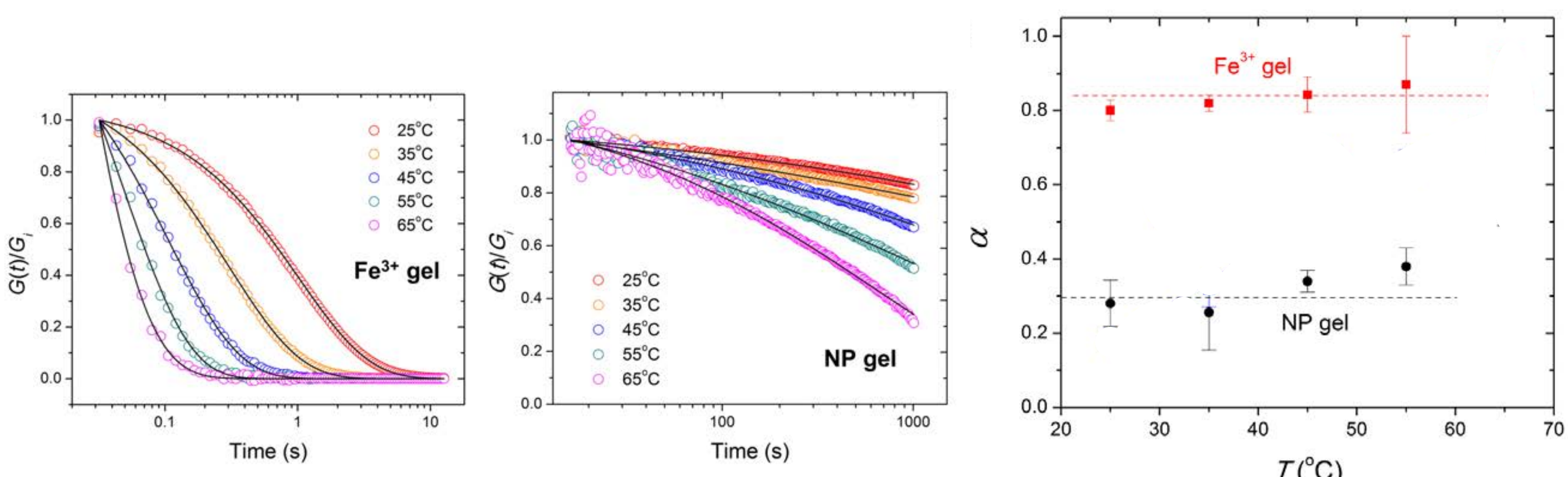


Energy dissipative crosslinks : tau vs alpha

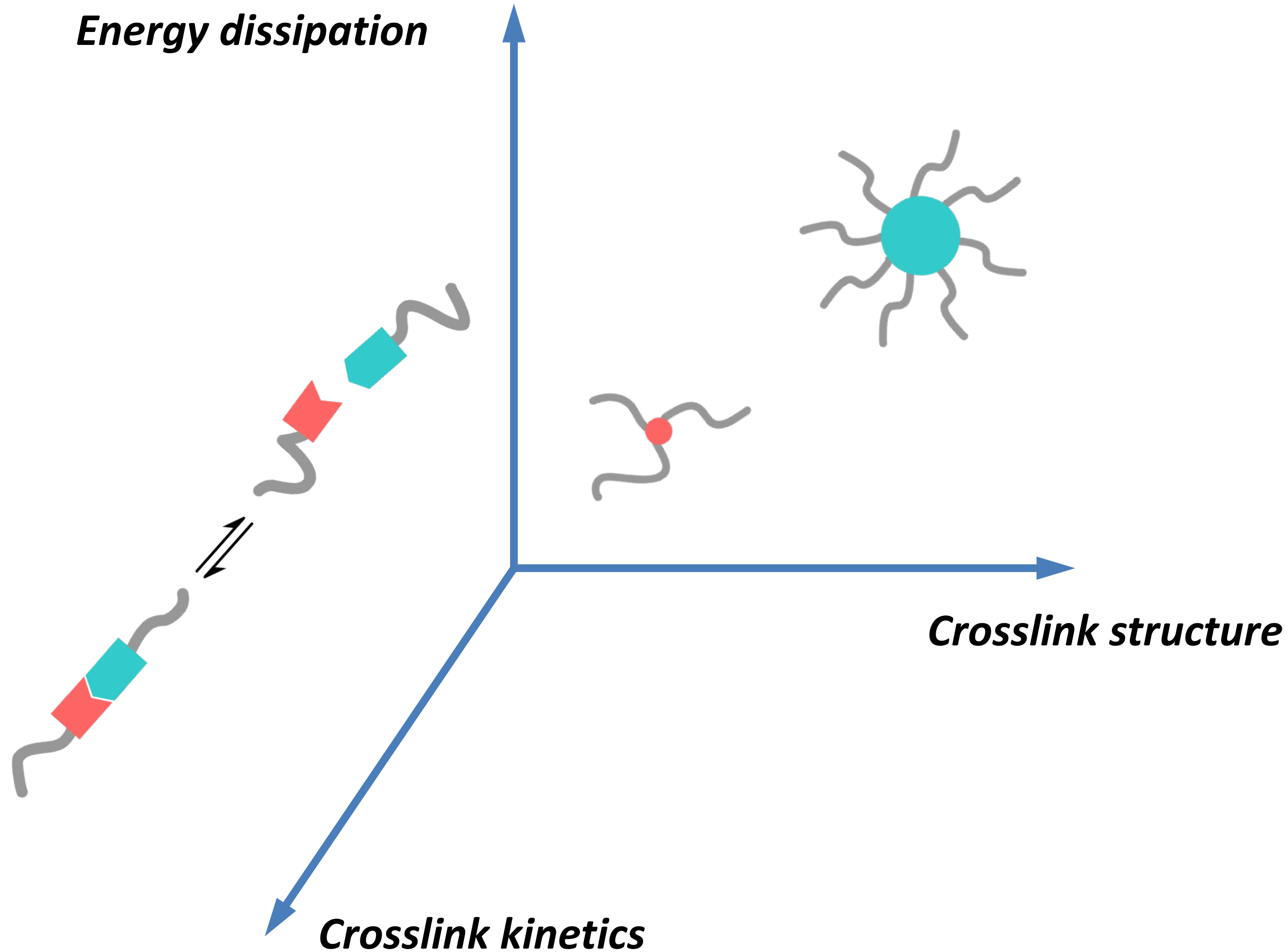


Energy dissipative crosslinks : tau vs alpha

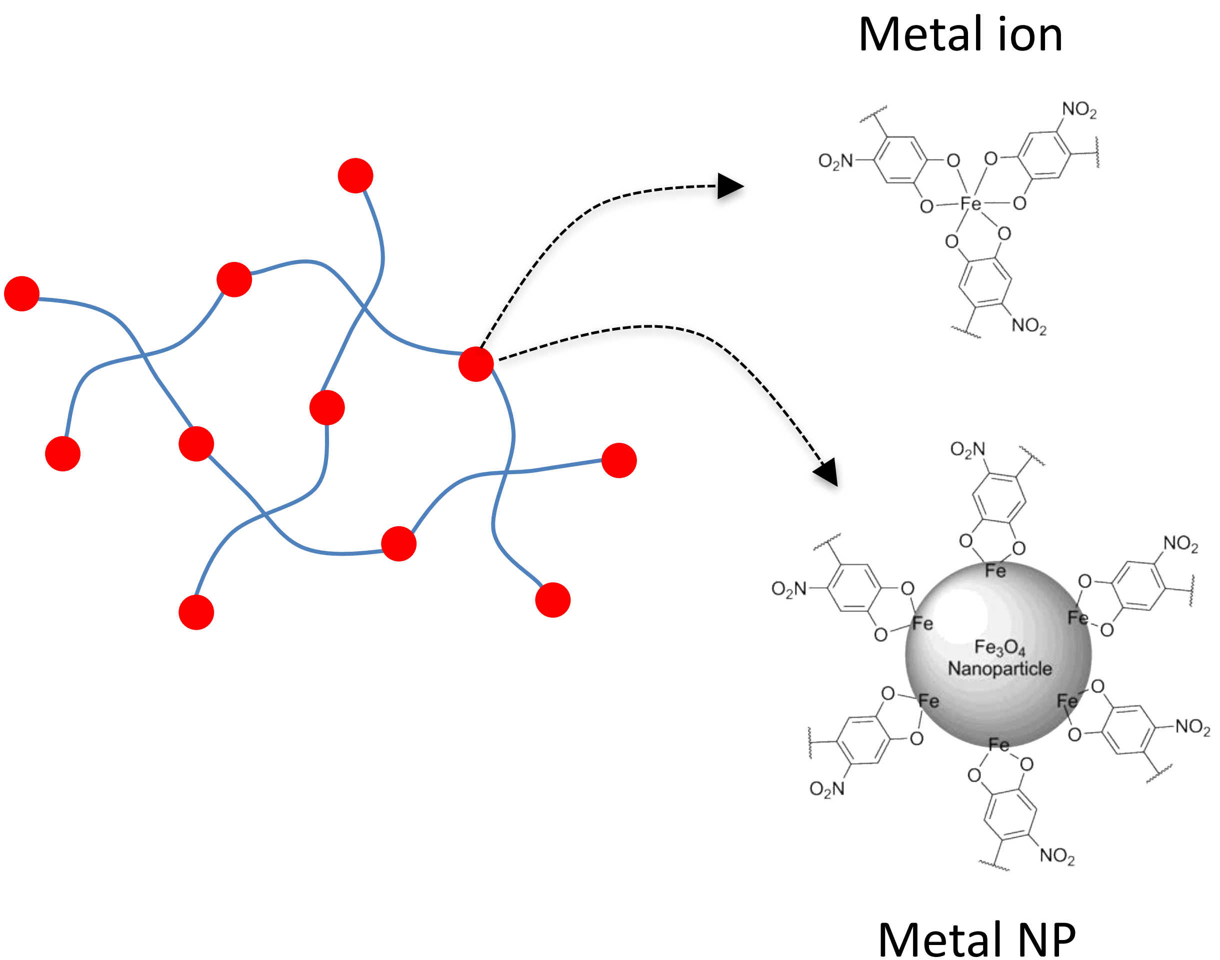




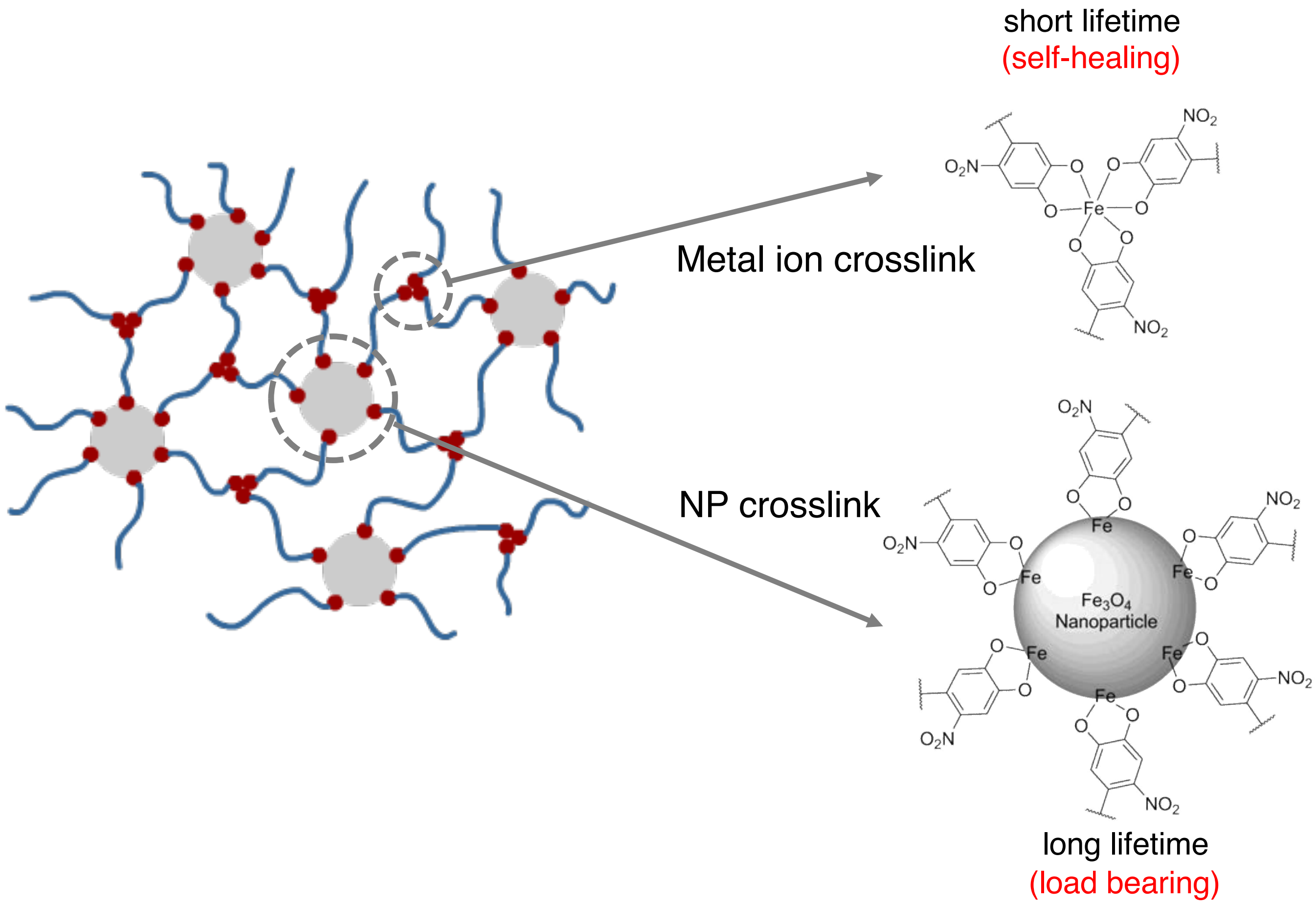
Energy dissipative crosslink engineering



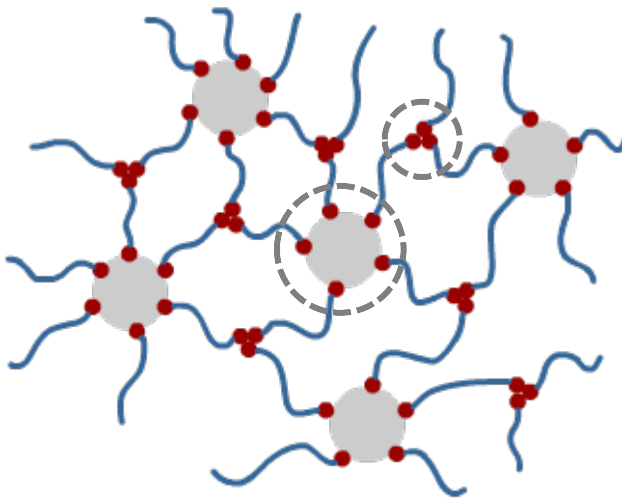
Energy dissipative crosslink engineering

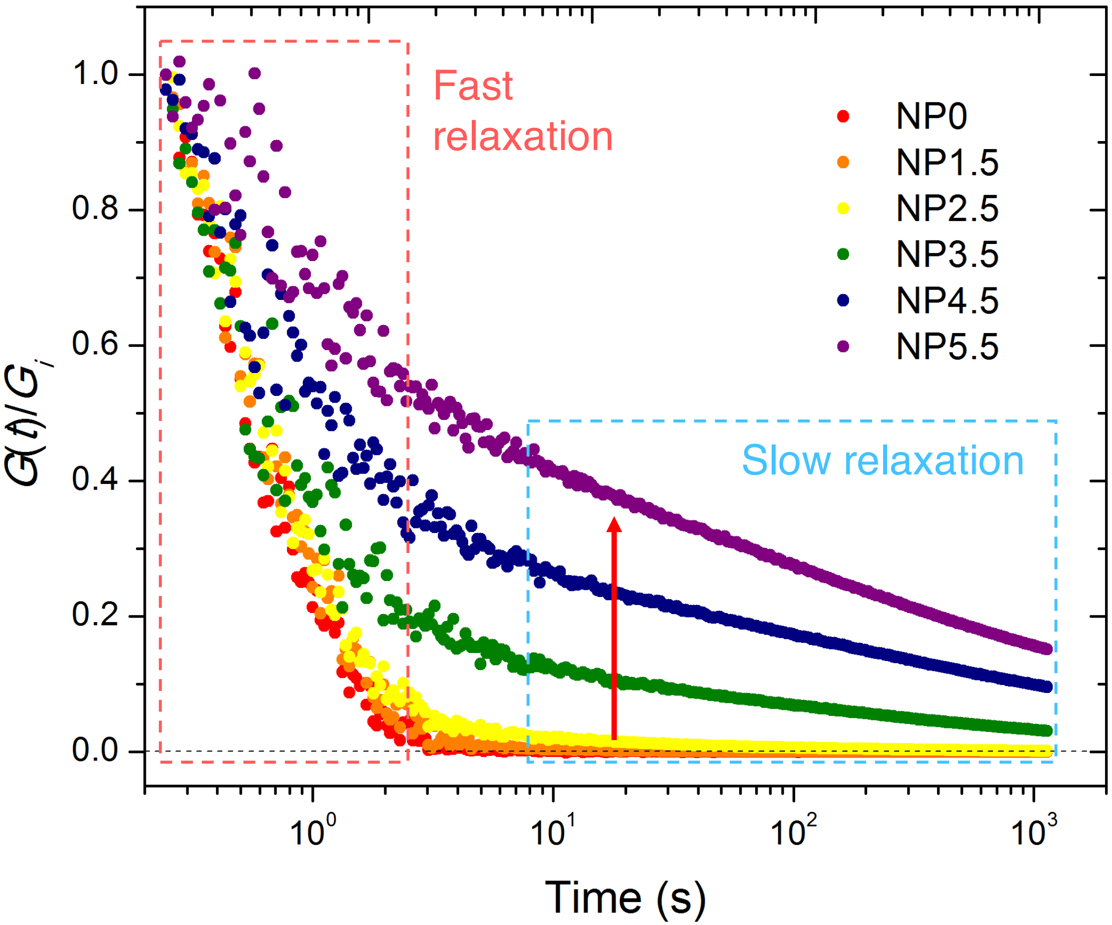


Energy dissipative crosslink engineering

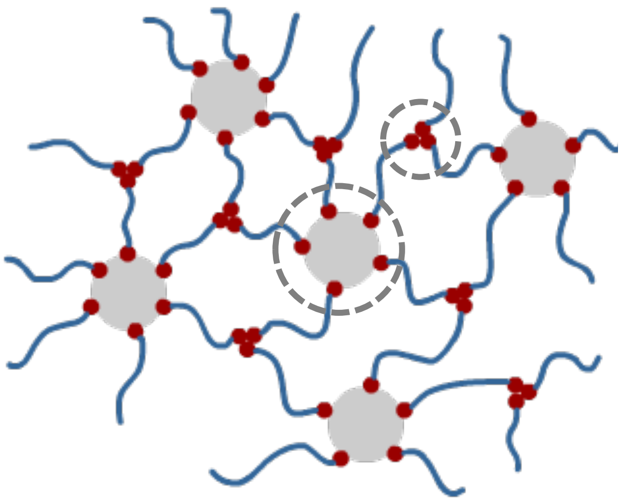


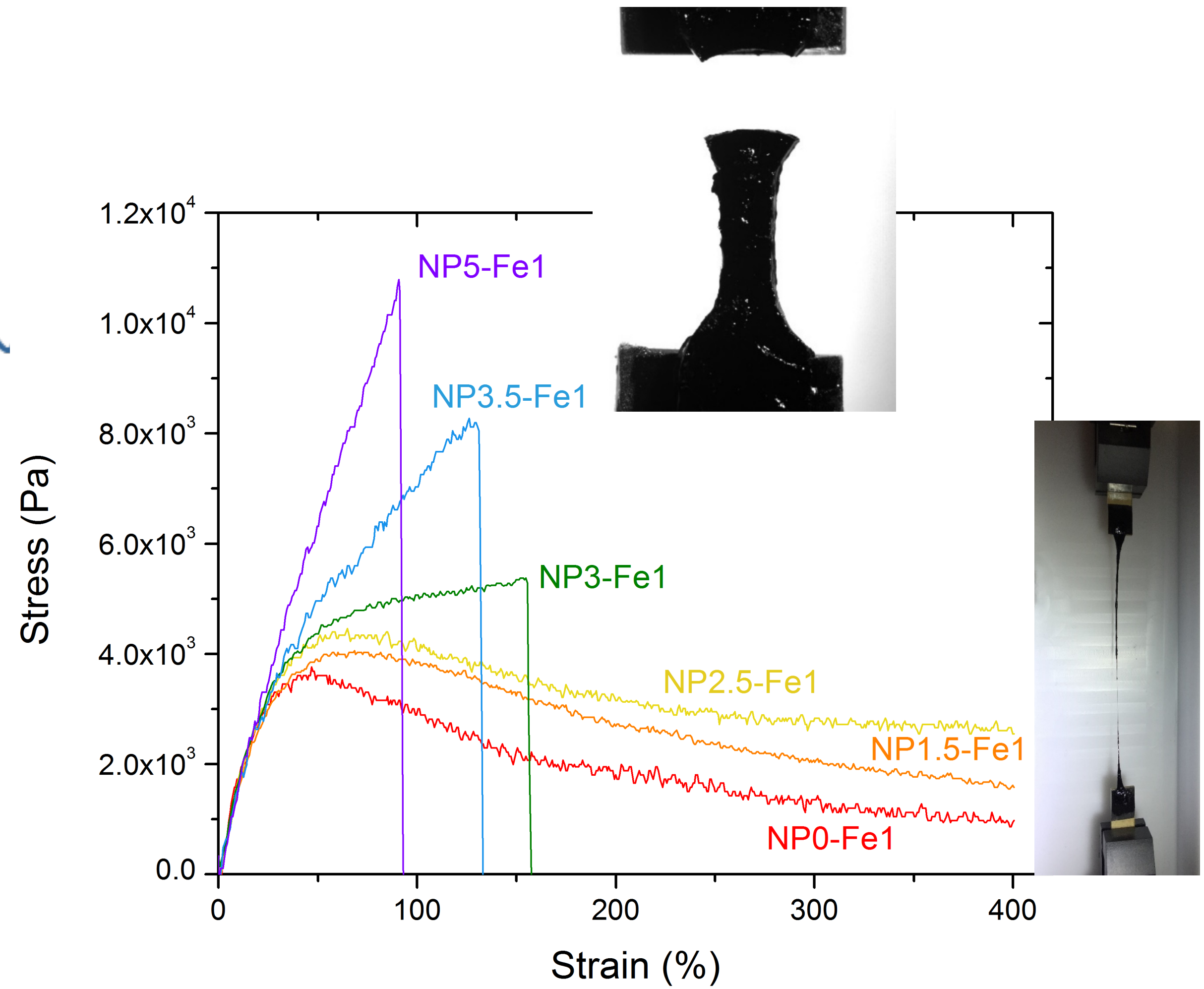
Energy dissipative crosslink engineering

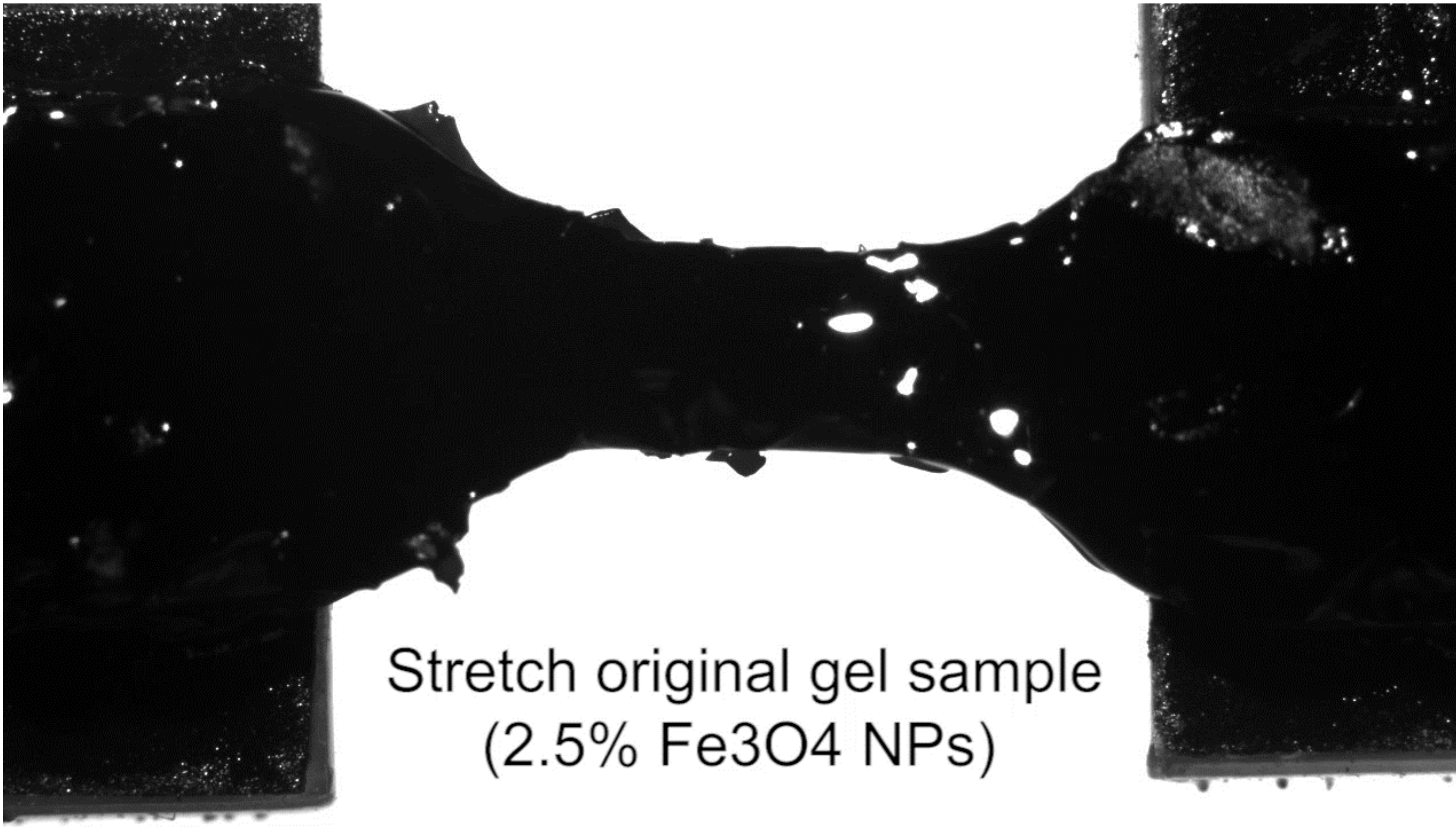




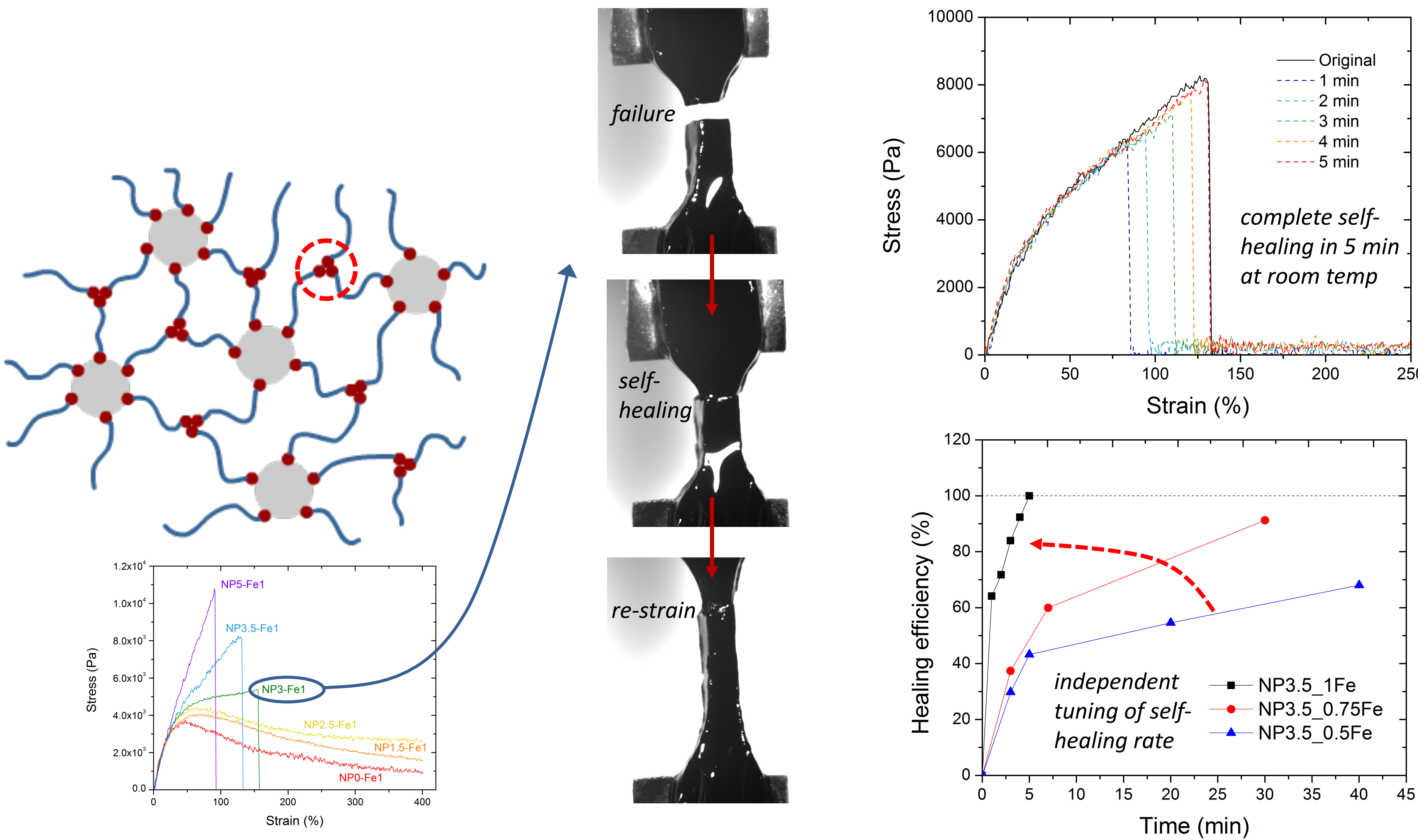
Energy dissipative crosslink engineering



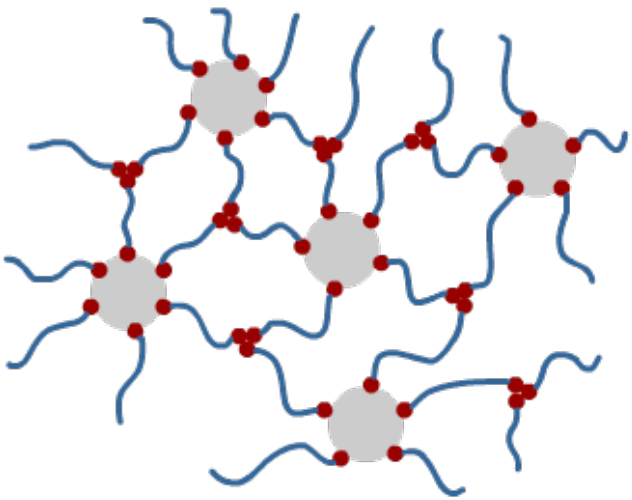


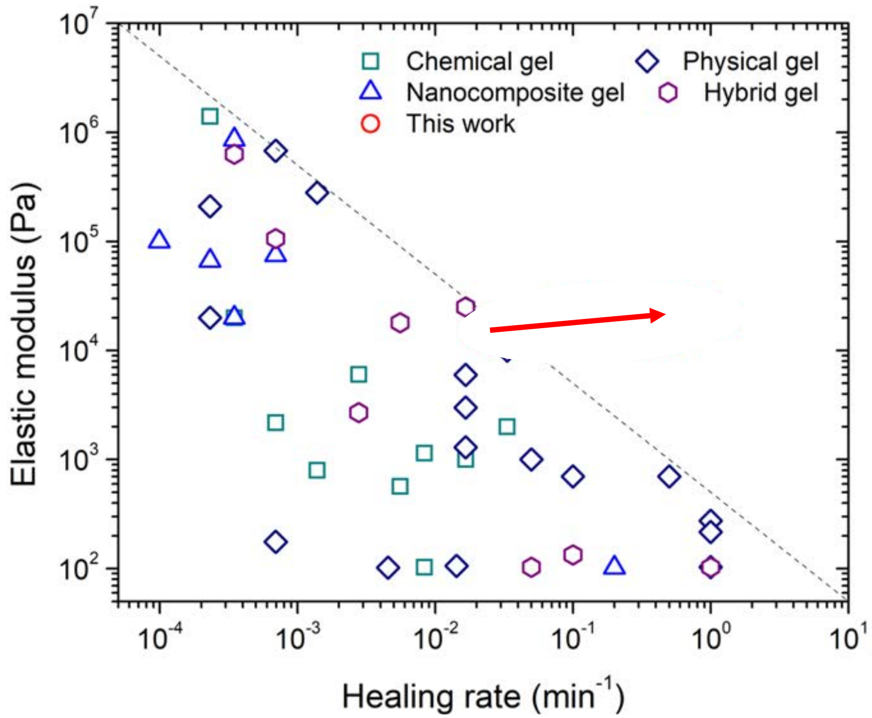

Stretch original gel sample
(2.5% Fe3O4 NPs)

Energy dissipative crosslink engineering

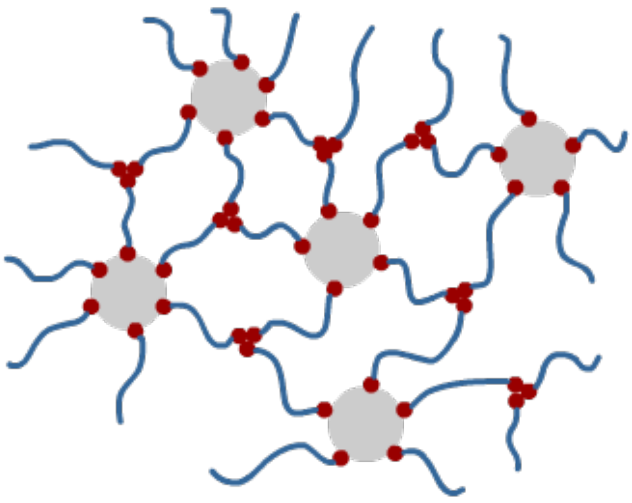


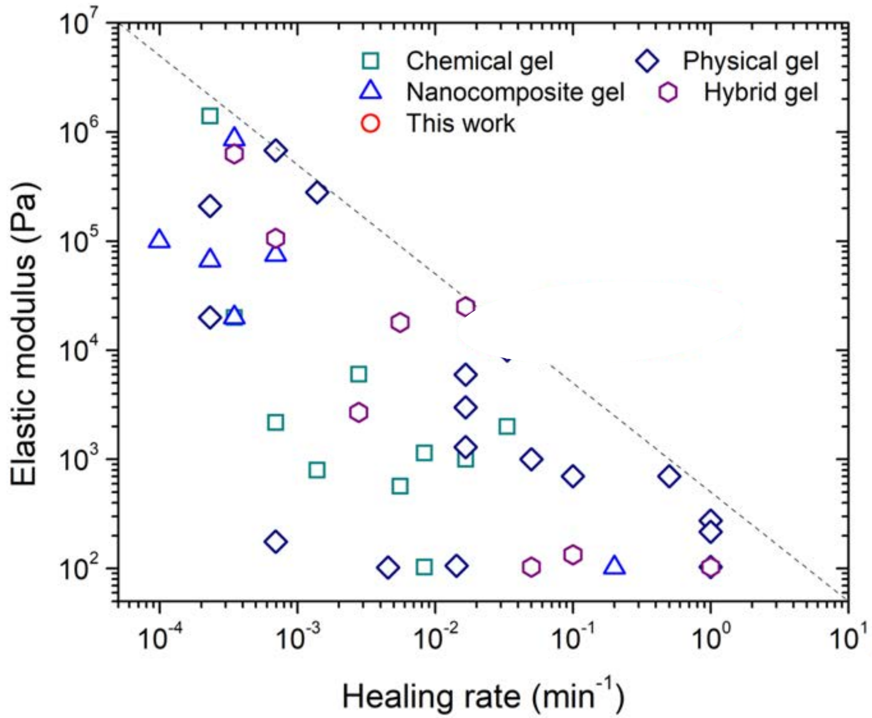
Energy dissipative crosslink engineering





Energy dissipative crosslink engineering

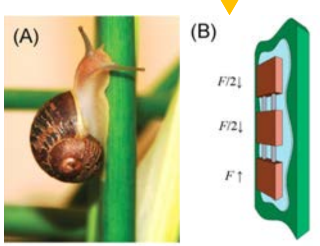


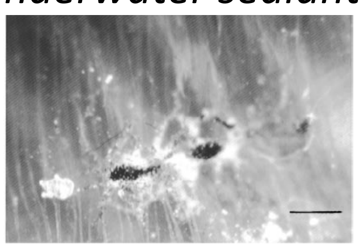


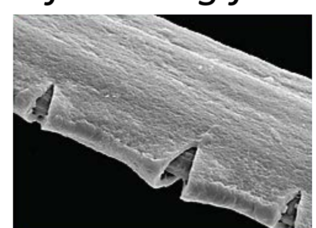
More inspiration……

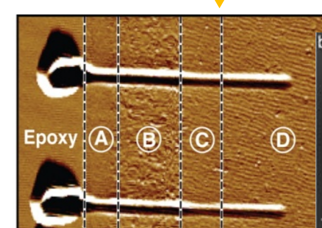
underwater sealants

self-healing fibers









reversible adhesives

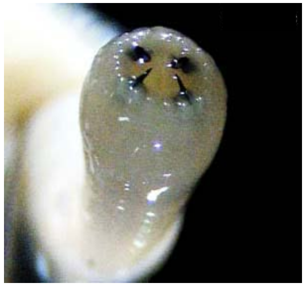
underwater adhesives

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 ionomeric nanodomains that they form.

Visco-elastic fluids

Hard solids

3M | ONR Department of the Navy Science & Technology | ExxonMobil | MITei MIT Energy Initiative | NSF

Collaborators:

Gareth McKinley (*MIT)*

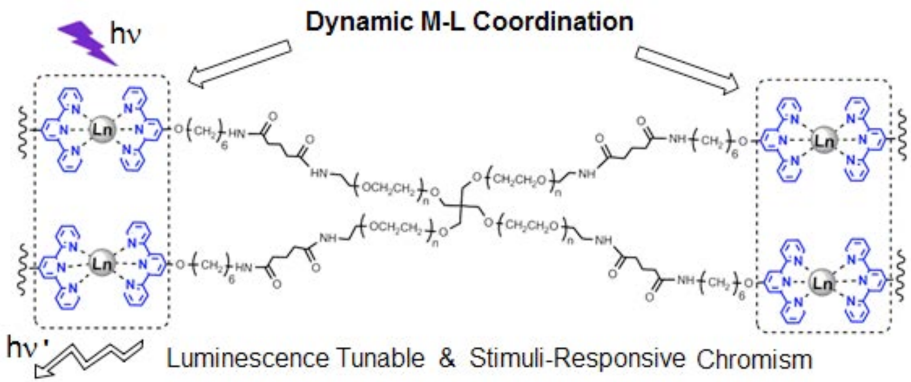
Joe Tracy

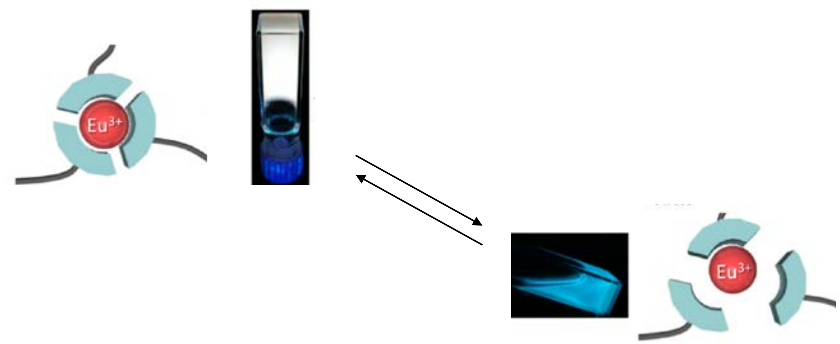
(NCSU)

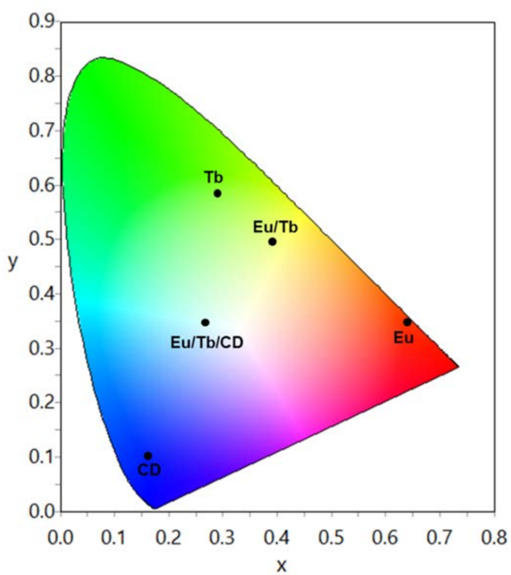
Grindy *et al*, Nature Materials (2015)
Chen *et al*, Adv. Opt. Mat. (2015)
Chen *et al*, JACS (2015)
Li *et al*, ACS Nano (2016)
Grindy *et al*, Macromolecules (2016)
Grindy *et al*, Soft Matter (2017)

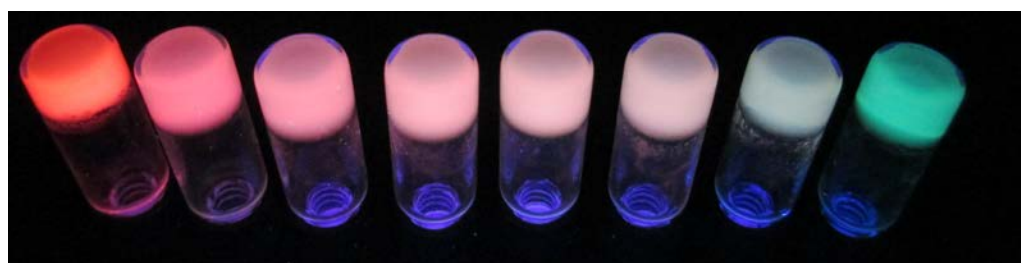
Energy dissipative crosslink engineering

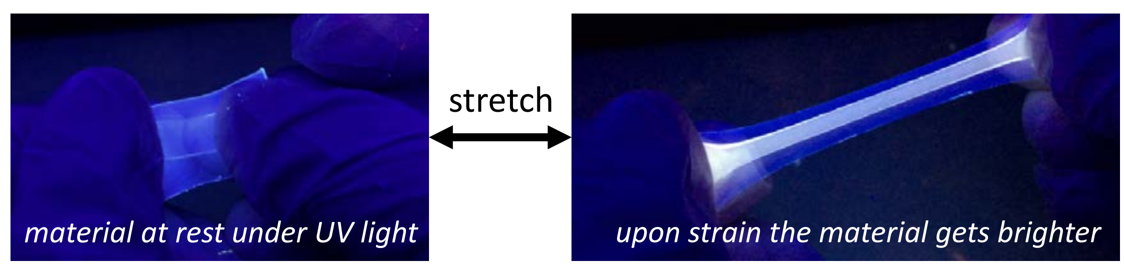
To engineer self-reporting polymer materials with energy-dissipation and material failure sensing capacity: ***on a macroscopic scale***





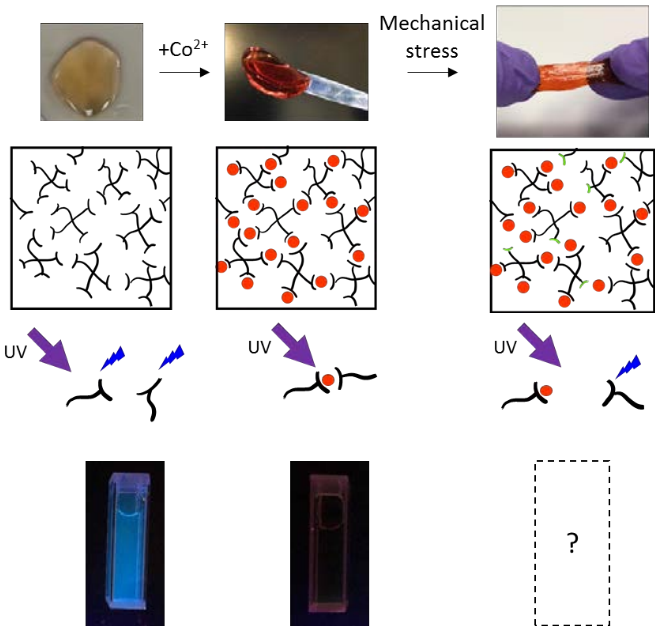


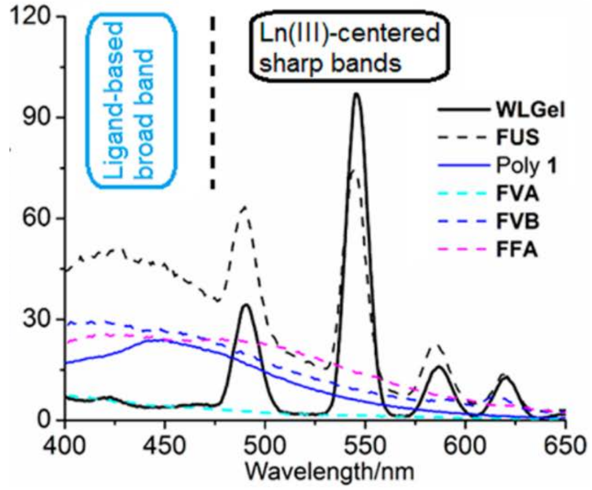


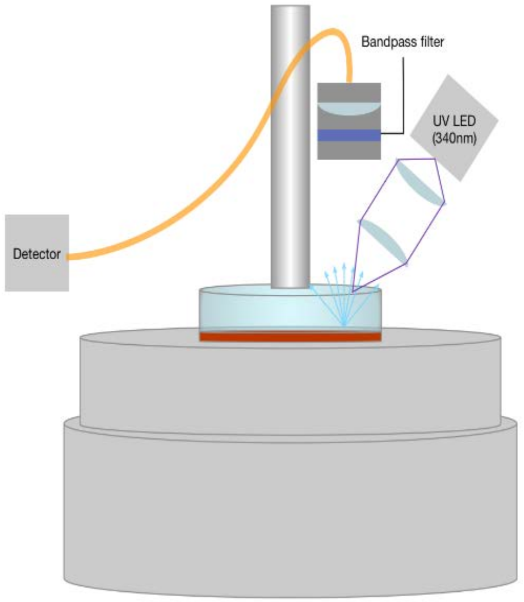


Energy dissipative crosslink engineering

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







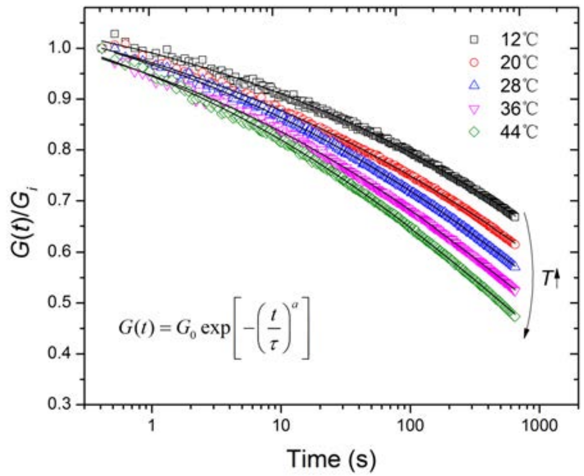
Metal-coordinate networks: Ions vs particles

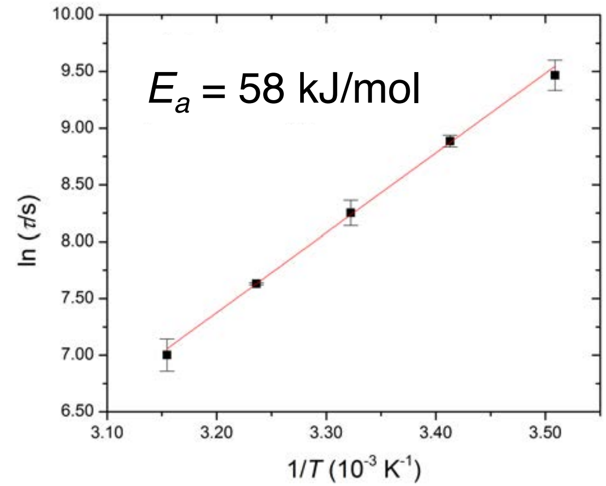
$$G(t) = G_0 \exp\left[-(t/\tau)^a\right], 0 < a < 1$$

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

(pH=4)

NP gel:

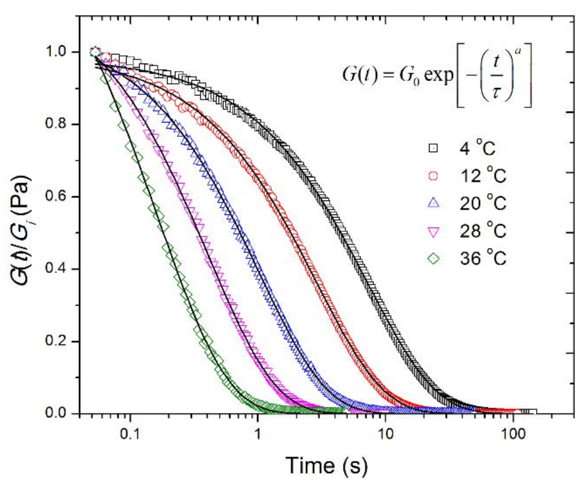


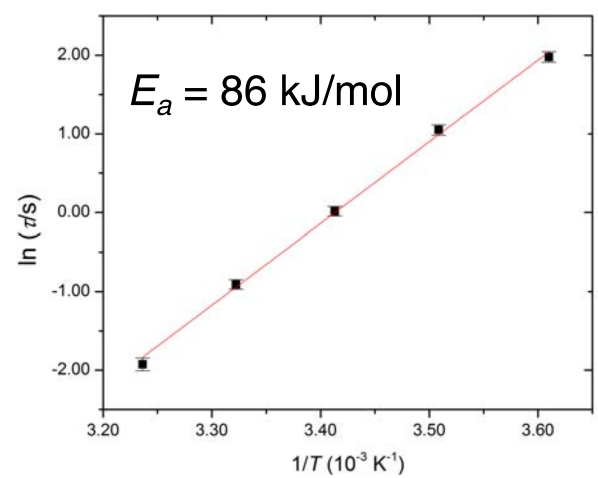


Chemical environment

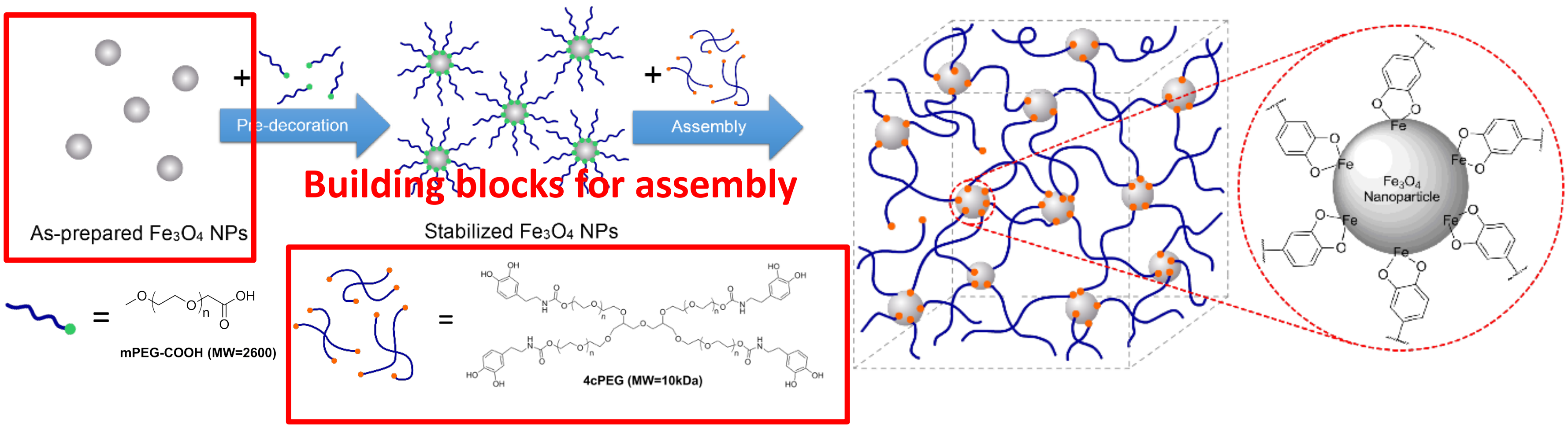
Fe^3+ gel:

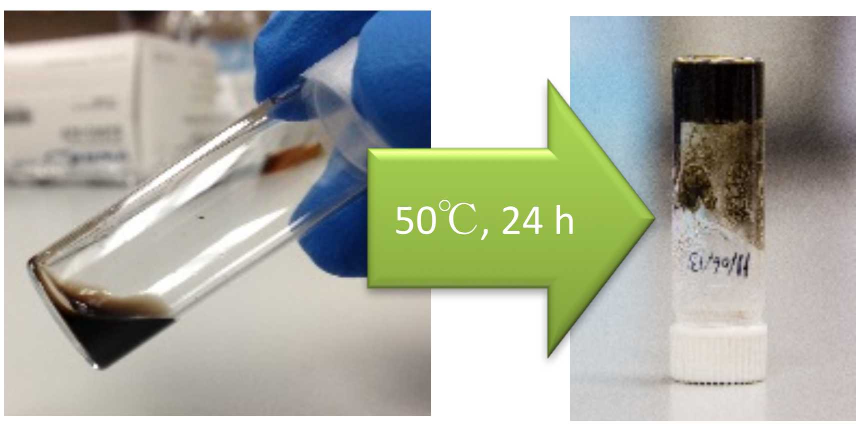
(pH=12)



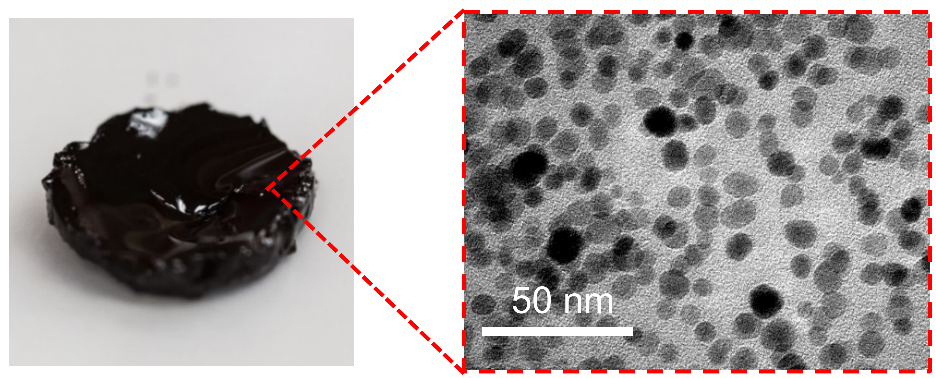


Metal-coordinate networks: particles





Sol-gel transition



As-prepared NP gel

Qiaochu Li *et al*, **ACS Nano** (2015)