university of groningen / faculty of science and engineering / zernike institute for advanced materials

Smart Emulsions using Responsive Pickering Emulsifiers

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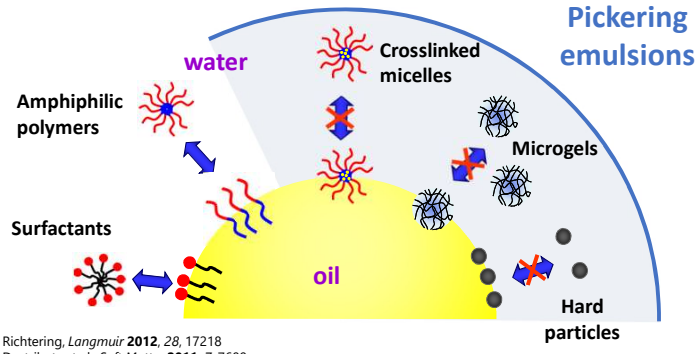
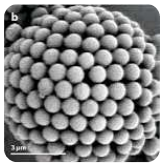
Emulsions

Metastable multiphasic mixture of two or more immiscible liquids
- Food, cosmetic, oil recovery, pharmaceutical industries …

Requirement: Stabilization of oil-water interfaces into spherical drops to avoid dramatic phase separation
- Use of amphiphilic molecules to decrease the interfacial tension



Richtering, *Langmuir* **2012**, *28*, 17218
Destribats et al., *Soft Matter* **2011**, *7*, 7689
Pickering, S. U., Pickering : Emulsions. In Emulsions, **1907**
Wang et al., *Mater. Chem. Front.* **2019**, 3, 356



Irreversible particles adsorption
- Limited coalescence
- Kinetically stable emulsions
- Chemical stability of the internal phase
  - ➢ Favorable for long-term storage

But detrimental when it comes to on-demand demulsification (catalytic reactions, release of active principle …)

Responsive Pickering Emulsions

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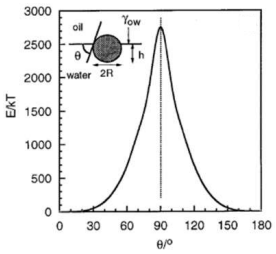
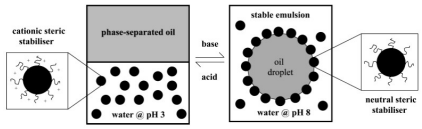
- Energy of adsorption of a hard particle



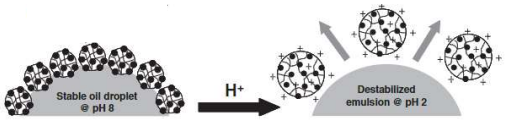
➢ Particle - oil/water interface contact angle



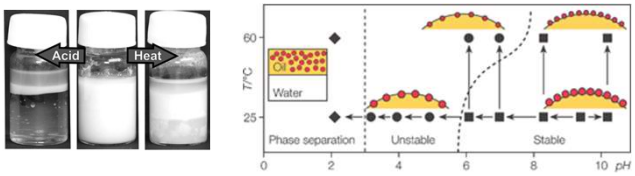
Read et al., *Langmuir* **2004**, 20, 18

➢ Dewetting induced demulsification
  ➢ pH-responsive surface groups (silica or latex particles)

- Microgels stabilized responsive emulsions



Fujii et al., *JACS* **2005**, 127, 7304



Ngai et al., *Chem. Comm.* **2005**, 331

➢ Swelling/deswelling or induced demulsification
  ➢ Change of particle deformability or/and interface elasticity

Play on the structural integrity of the adsorbed particle
-> New way of controlling Pickering emulsions stability

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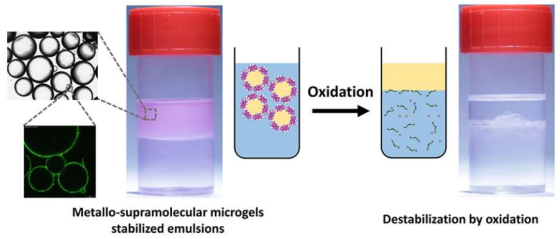
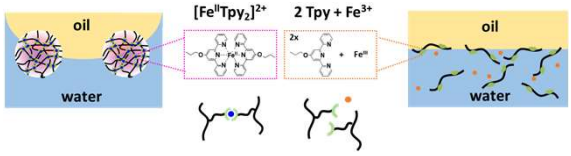
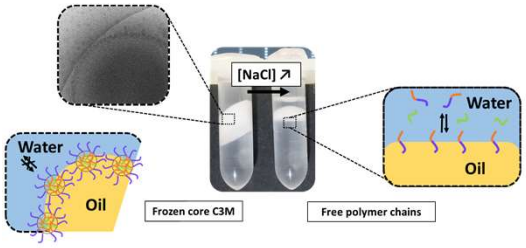
Oxidation-Responsive Emulsions Stabilized by Metallo-Supramolecular Microgels

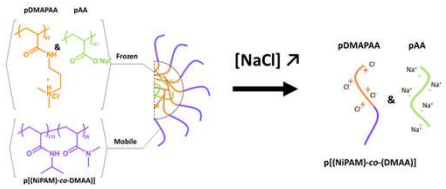




Es Sayed et al., *ACS Macro Letters* **2020,** *9*, 1040

Salt-Responsive Emulsions Stabilized by Complex Coacervate Core Micelles





Es Sayed et al.. *ACS Macro Letters* **2022,** *11*, 20

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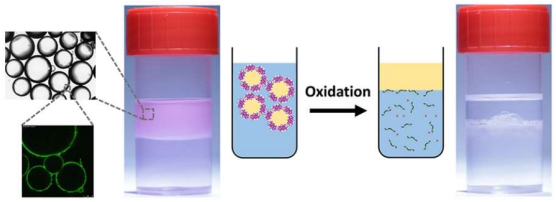
Oxidation-Responsive Emulsions Stabilized by Metallo-Supramolecular Microgels

Goals:

- Pickering emulsions stabilized by cleavable microgels
- Oxidation-responsive

Requirements:

- Colloidally stable particles
- Surface active particles
- Metallo-supramolucar crosslinks
- Oxidation-responsive crosslinks



Chemistry:

- Poly(*N*-isopropylmethacrylamide), pNiPMAM
- Terpyridine ligand
- Iron (II) transition metal

Es Sayed et al., *ACS Macro Lett.* **2020**, 9, 1040

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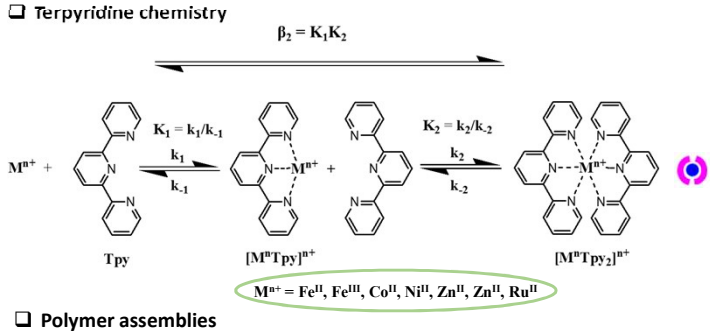
Terpyridine chemistry and macromolecular assemblies

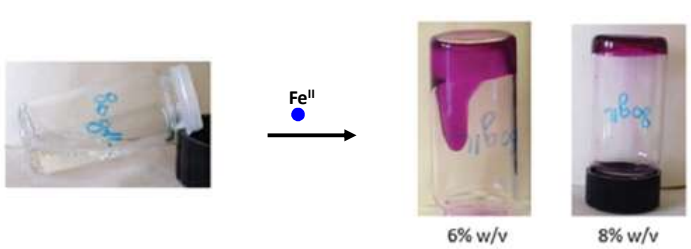
❑ **Terpyridine chemistry**

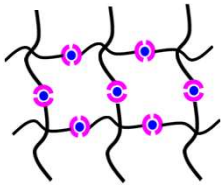


Selectivity
Wide range of bond strength (K_{ass}, β)
Dynamics (k_a, k_d)
Reversibility

Schubert et al., Terpyridine-based materials, Wiley, **2011**

❑ **Polymer assemblies**





➢ **Gelation induced by complexation**

Le Bohec et al., *Polymer Chemistry*, **2016**, 7, 6834
Gohy et al., *Macromolecules*, **2002**, 35, 4560

Design of supramolecular microgel

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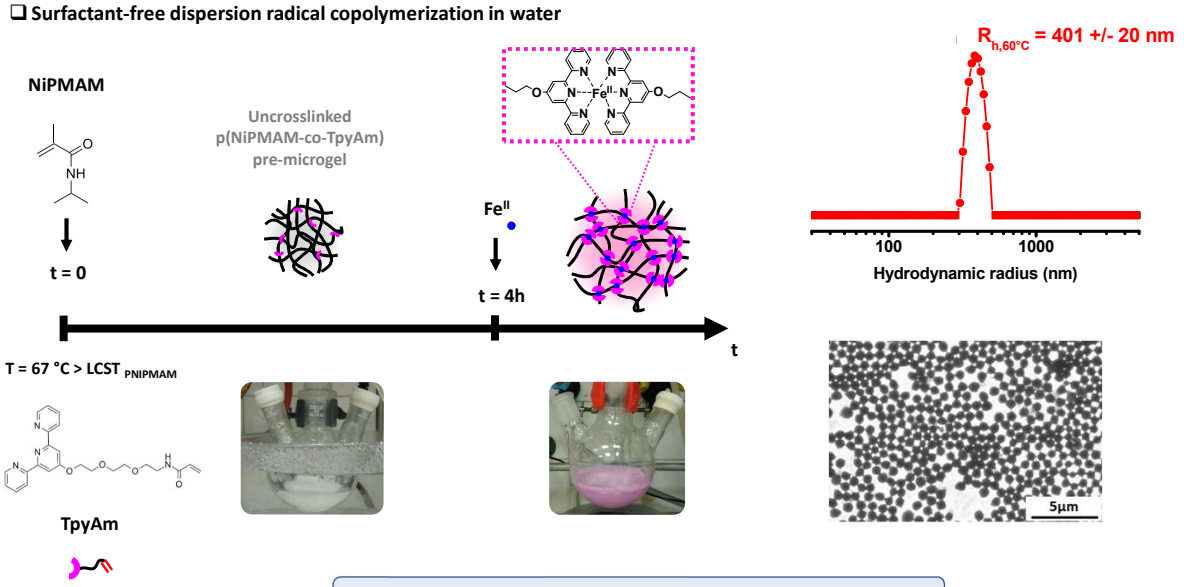
❑ Surfactant-free dispersion radical copolymerization in water



➢ Metallo-supramolecular crosslinked PNiPMAM microgel

Supramolecular microgel as emulsifier

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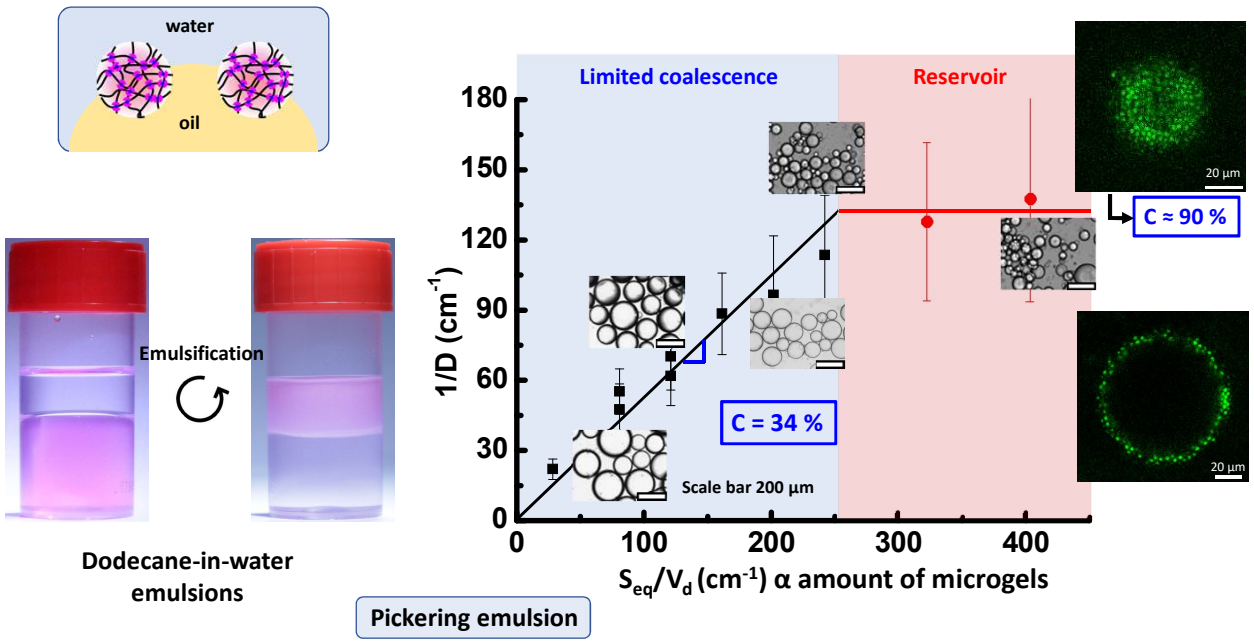

Pickering emulsion

Supramolecular microgel as emulsifier

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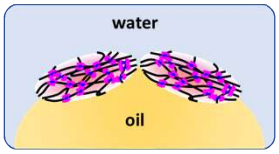
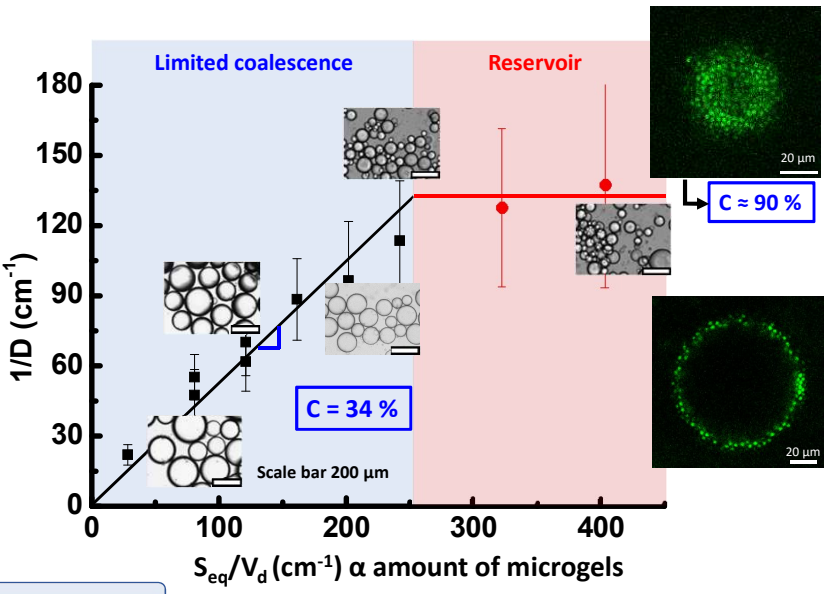


Flattening at interface

Dodecane-in-water emulsions



Pickering emulsion

Monteillet et al., Adv. Mat. Interf. **2014**, 1, 7, 1300121
Destribats et al., *Soft Matter* **2011**, 7, 7689

Oxidative cleavage of supramolecular microgel by KPS

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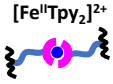
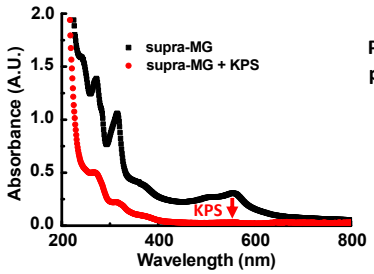
Molecular scale

$[Fe^{II}Tpy_2]^{2+}$



❑UV-Vis

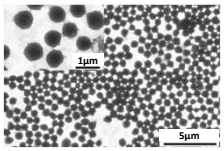


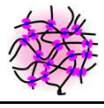
Potassium persulfate → KPS

2 Tpy + Fe^{3+}

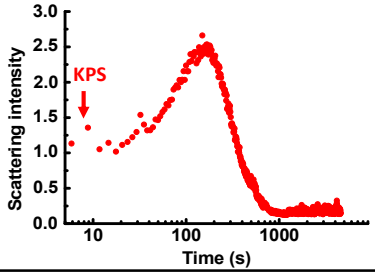
Complex cleavage

Particle scale

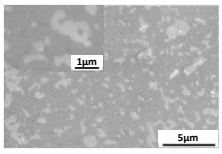




❑DLS



Potassium persulfate → KPS



Particle cleavage

Supramolecular microgel as responsive emulsifier

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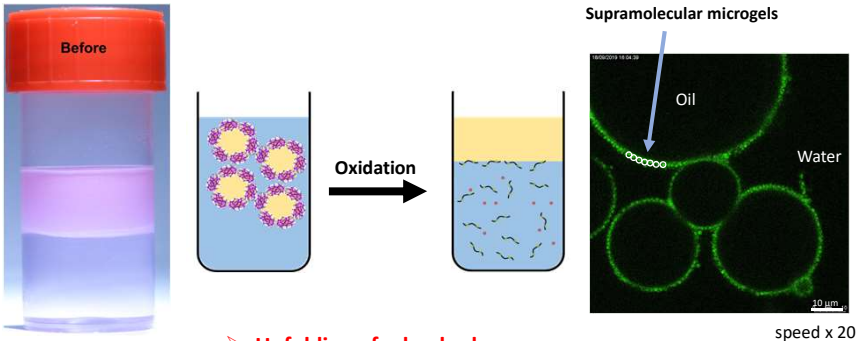
❑**Oxidation responsive Pickering emulsions**



speed x 20

- Decoloration
- Phase separation

➢ **Unfolding of adsorbed microgels into polymer chains**

- Fluorescence dilution
- Oil drops coalescence

Emulsion destabilization by oxidation

Perspectives

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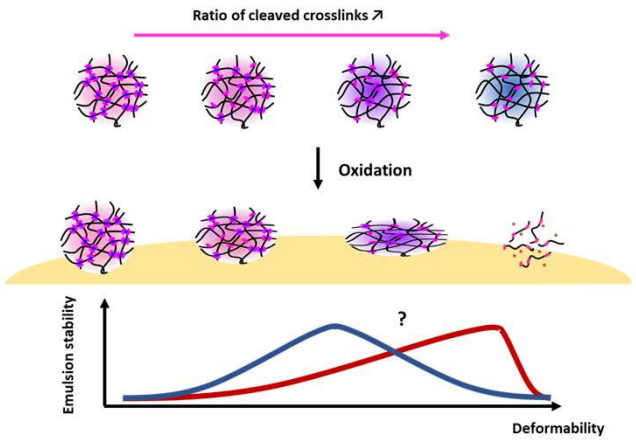
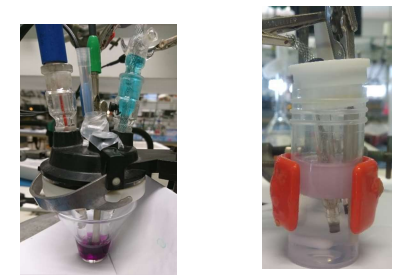
❑**Fundamentals of microgels stabilized emulsions**



-> Control the deformability by varying the crosslinking degree in-situ

-> Link with emulsion kinetic stability ?

❑**Electrochemical stimulation**



Cleavage of a $[Fe^{II}Tpy_2]^{2+}$ crosslinked hydrogel
Sandrine Laquerbe (ESPCI, Paris)

-> Electrochemically oxidize $[Fe^{II}Tpy_2]^{2+}$ at the drops surface?

Acknowledgements

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- Patrick Perrin
- Christophe Meyer

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https://kampermanlab.com/

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