Chemotactic and Electrotactic Self-Propelled Ionic Liquid Droplets

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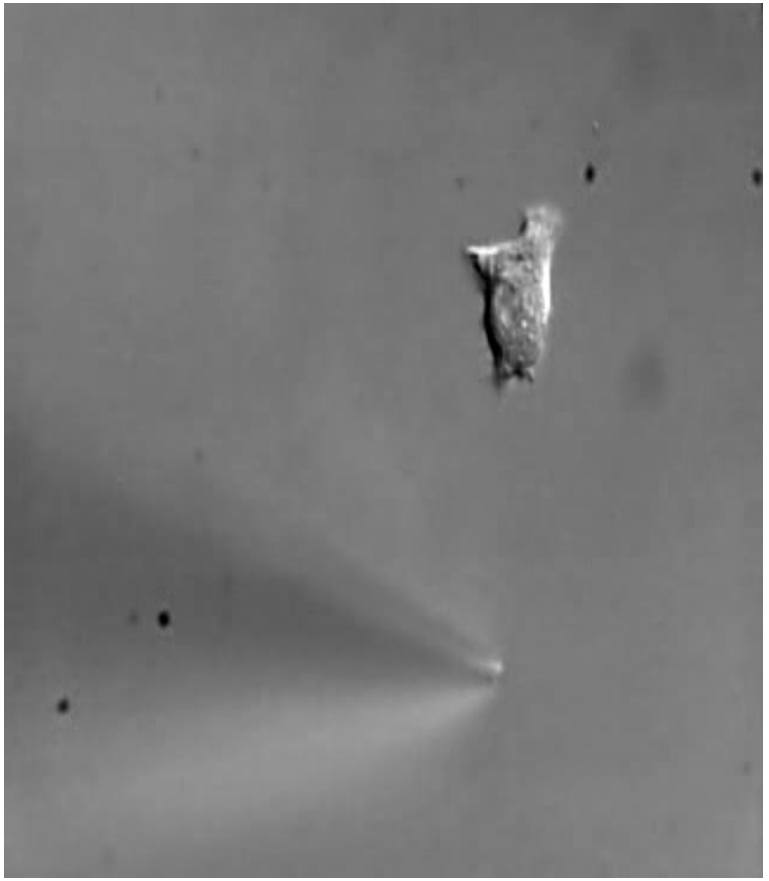
Chemotaxis

- Movement of an organism in response to a chemical stimulus
- Certain single and multicellular organisms have this ability
- Bacteria, Virus's and even some somatic cells i.e white blood cells
- Chemoattractant: food source
- Chemo repellent: toxin



Synthetic Systems

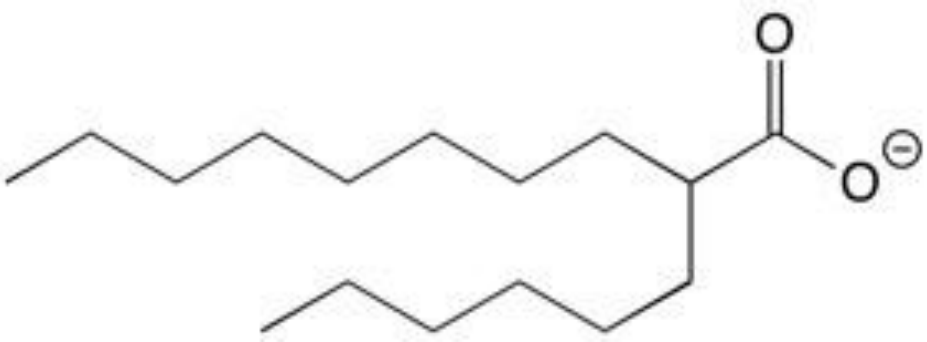
- Development of synthetic biomimetic “vehicles”
- These “vehicles” move in response to external stimuli
- Developing smart droplets
- Designed to move across the liquid/air interface
- Applications include micro-vehicles for chemical reactions, cargo transport to desired destinations, dynamic sensing, leak detection and drug delivery

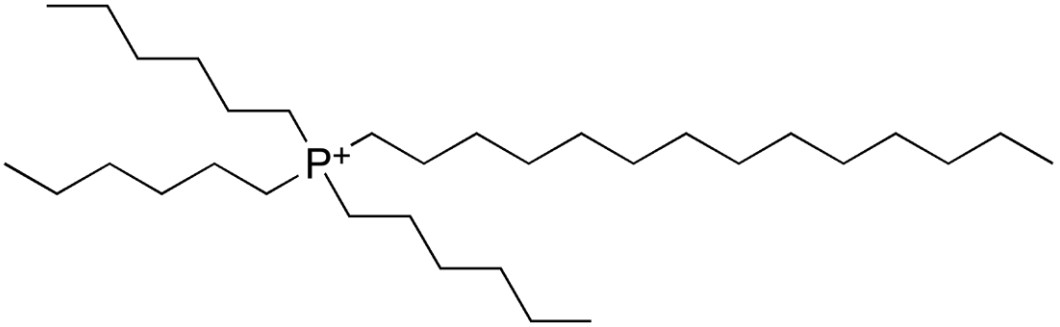
Introduction

- “Vehicle” movement has been achieved through the use of surfactant molecules
- Classical example is propelling a paper boat by applying a small amount of liquid soap to the end

Surfactants

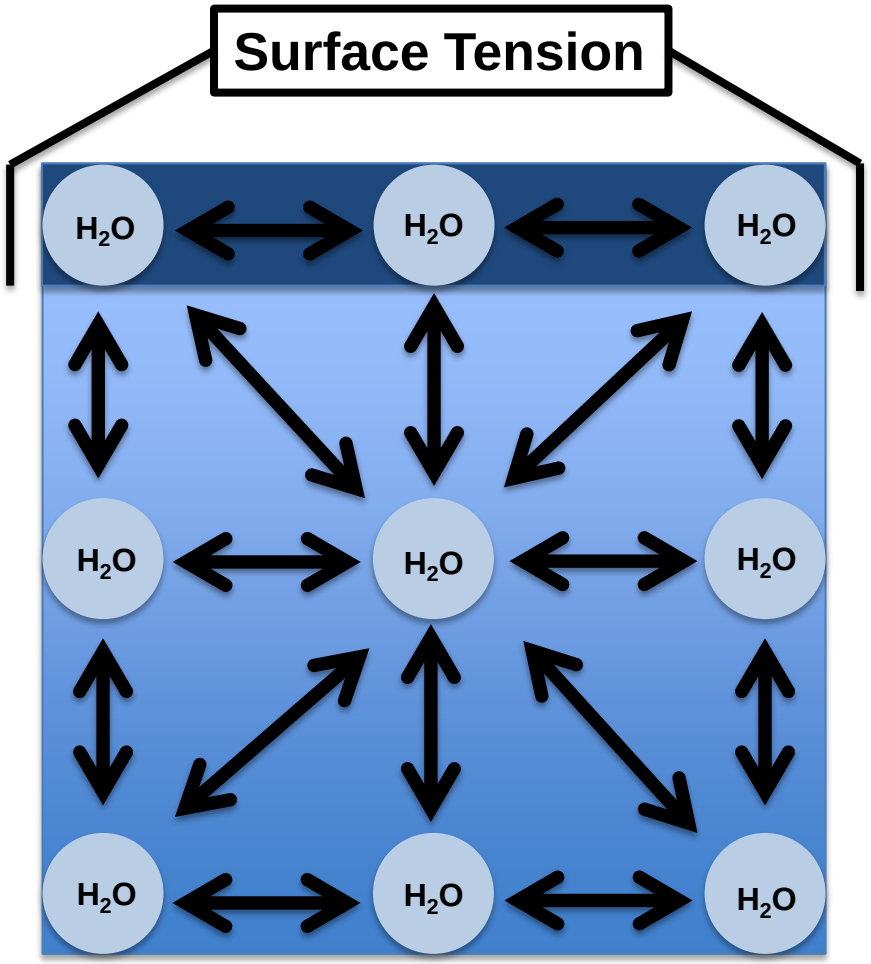
- Long chained molecules
- Charged hydrophilic “head”
- Hydrophobic “tails”
- Surface active
- Alter surface tension



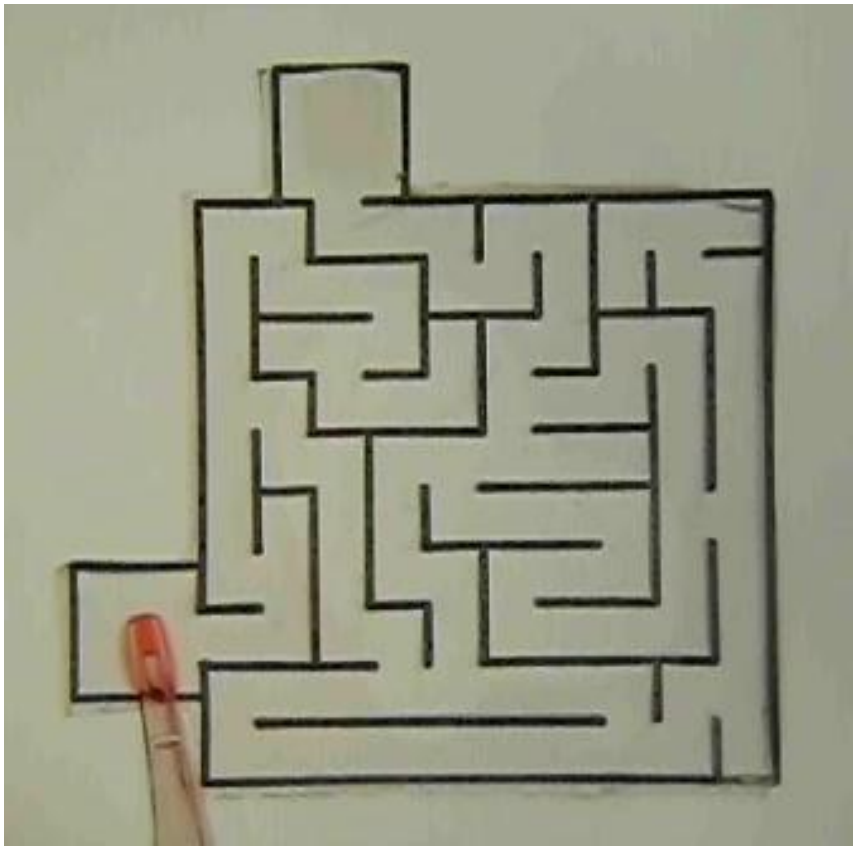


Surface Tension

- Contractile layer
- Surface molecules experience greater attraction to neighbours compared to bulk molecules
- Liquid flows from low to high surface tension
- Marangoni effect



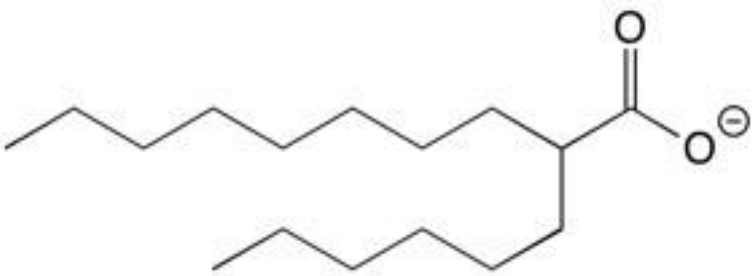
Chemotactic Droplet: Grzybowski's Droplet



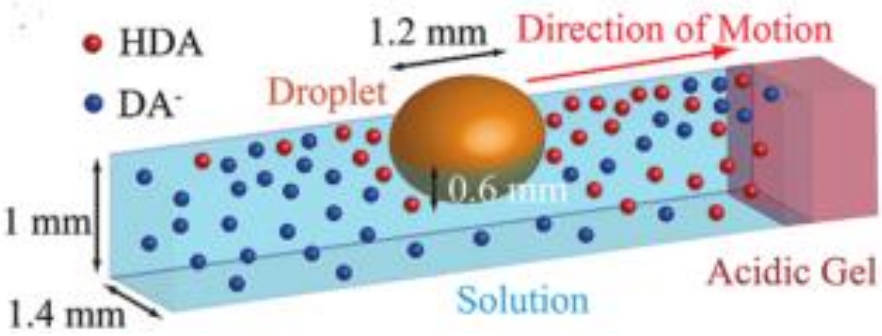
A. Grzybowski.. *J. AM. CHEM. SOC*. 2010, 132, 1198-1199

Grzybowski's Droplet

- Can solve complex maze
- pH sensitive surfactant
- Surfactant contained within organic droplet
- Follows pH gradient to exit



$pK_a \approx 8.3$



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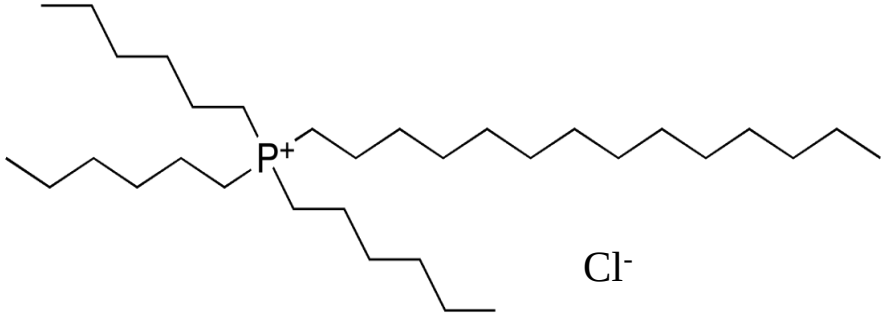
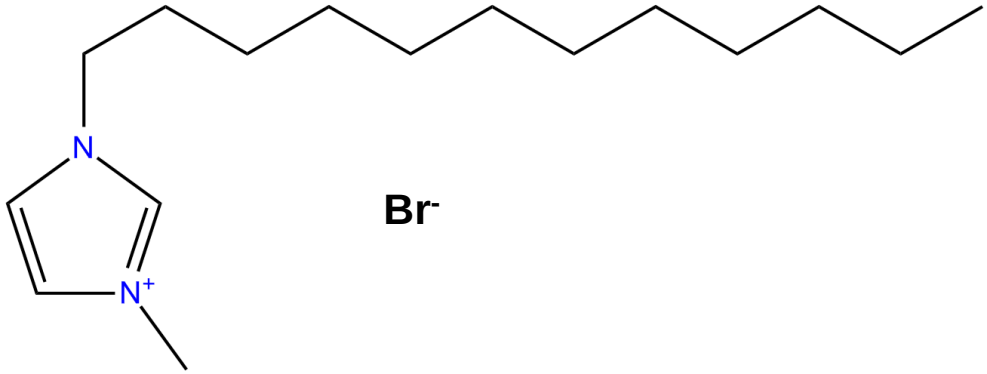
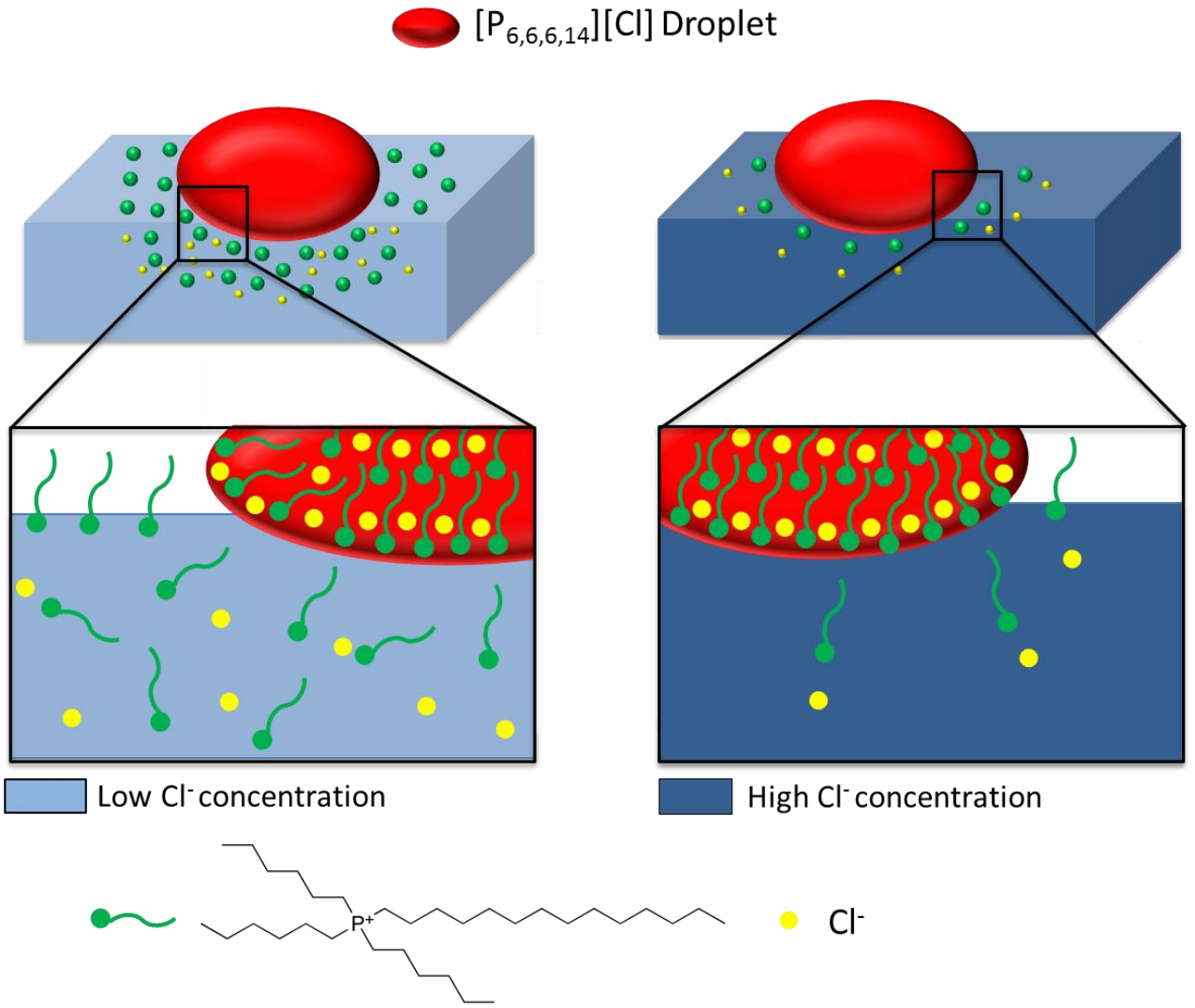
Ionic liquids

- Negligible vapour pressure
- High thermal stability
- High ionic conductivity
- Excellent solvents
- “Designer” solvents

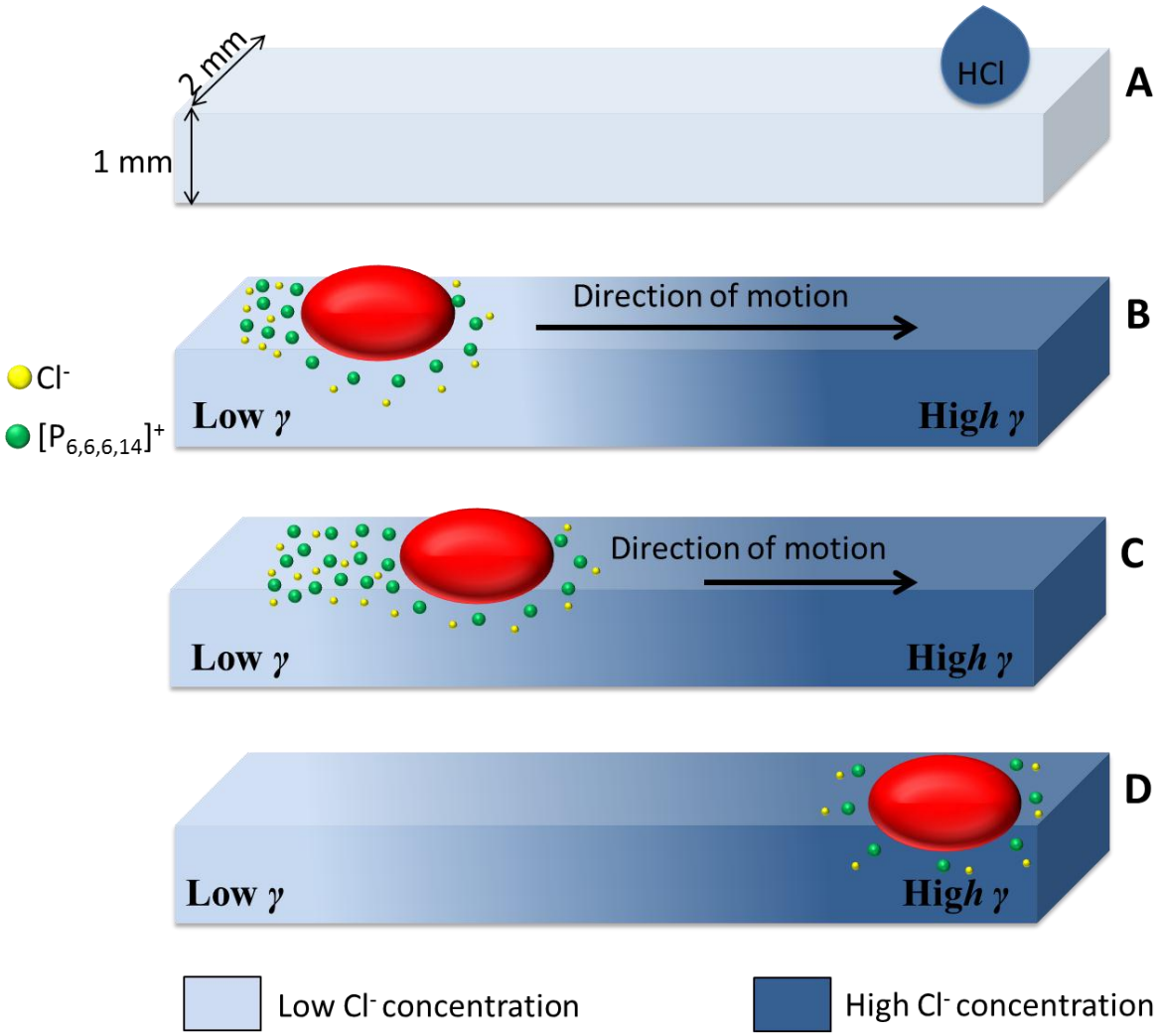




Droplet Composition

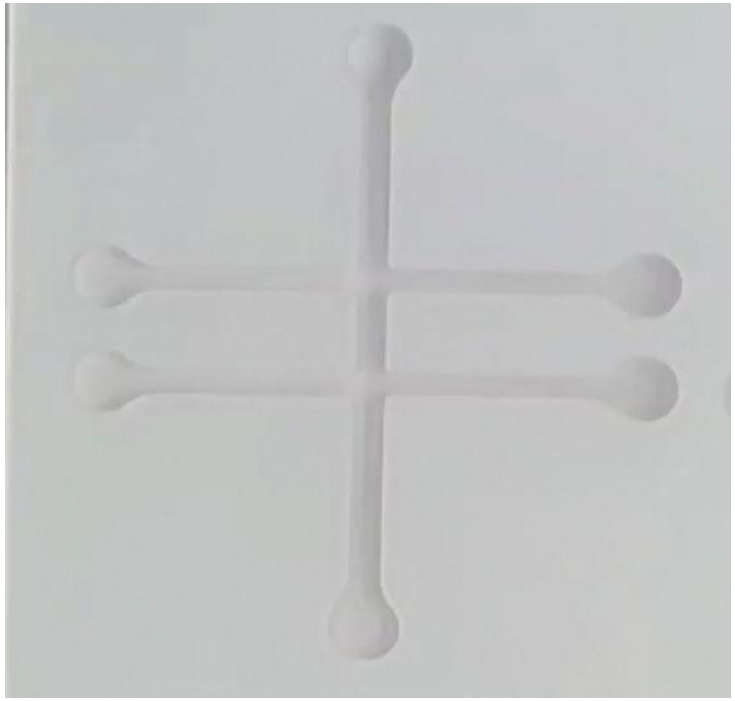


Droplet Movement



Gradient Generation

Acid – Base system:
Channel filled with a solution of 10^{-2} M NaOH, solution of 10^{-2} M HCl acts as the chemoattractant

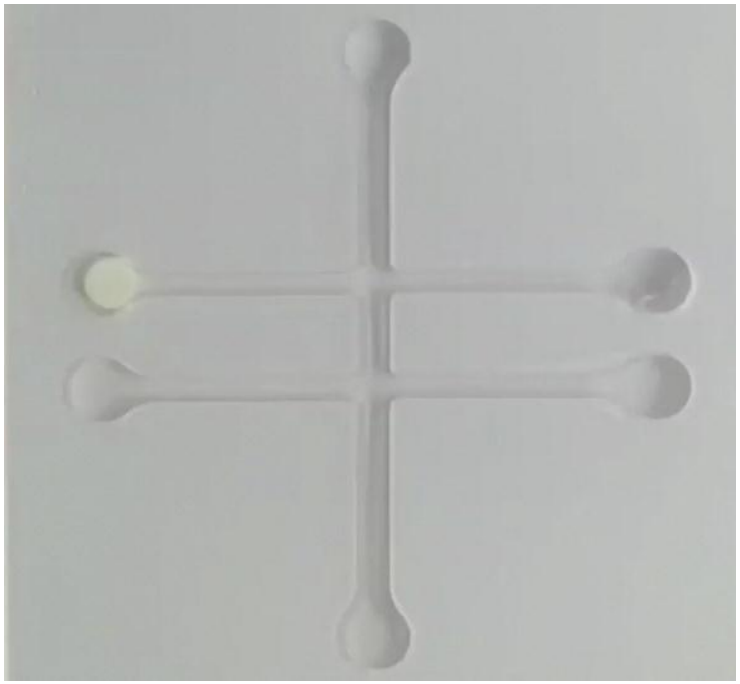


Speed x 2

Gradient Generation

Acid – Base system:

Channel filled with a solution of 10^{-2} M NaOH, poly acrylamide gel soaked with 10^{-2} M HCl acts as the chemoattractant

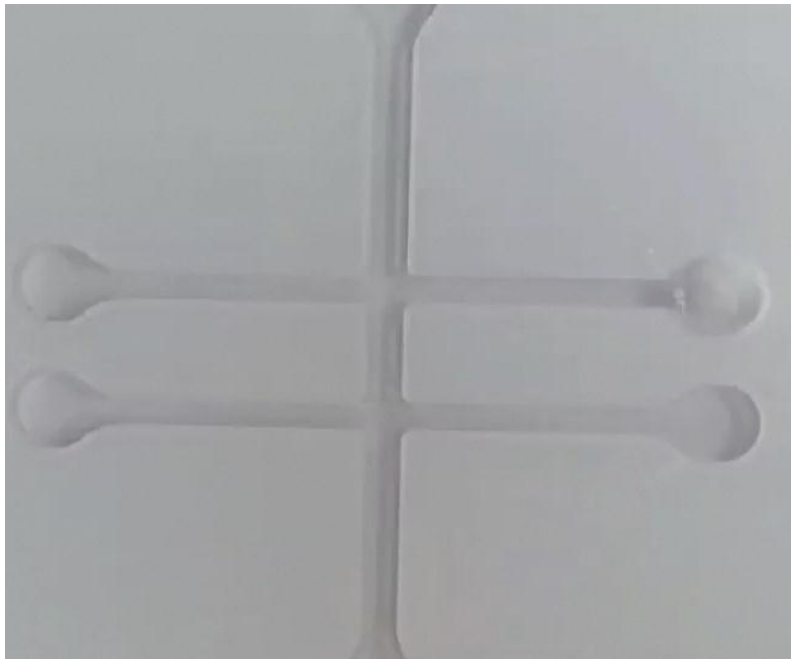


Speed x 4

Gradient Generation

Salt system :

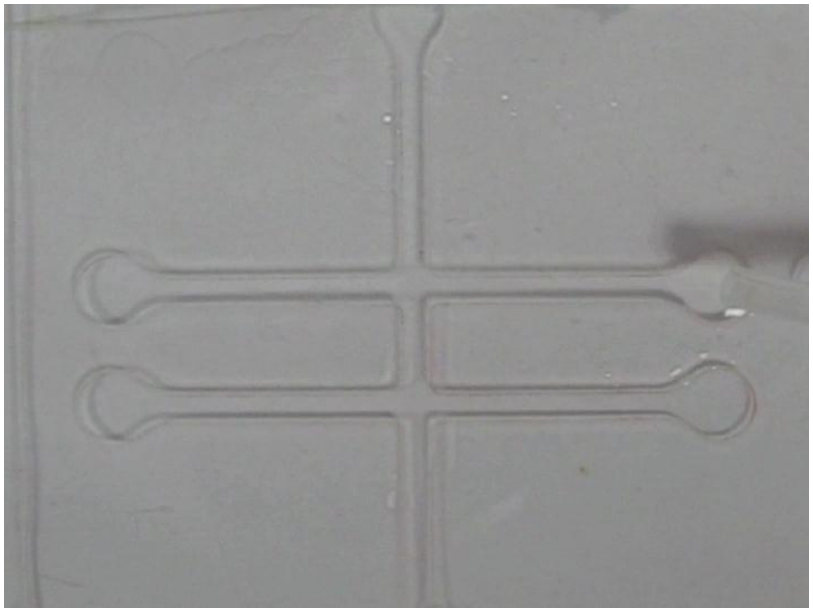
Channel filled with a solution of 10^{-5} M NaCl, crystals of salt act as the chemoattractant



Speed x 4

Multiple Droplets

Acid – Base system:
Channel filled with a solution of 10^{-2} M NaOH, solution of 10^{-2} M HCl acts as the chemoattractant



Chemotactic Droplets

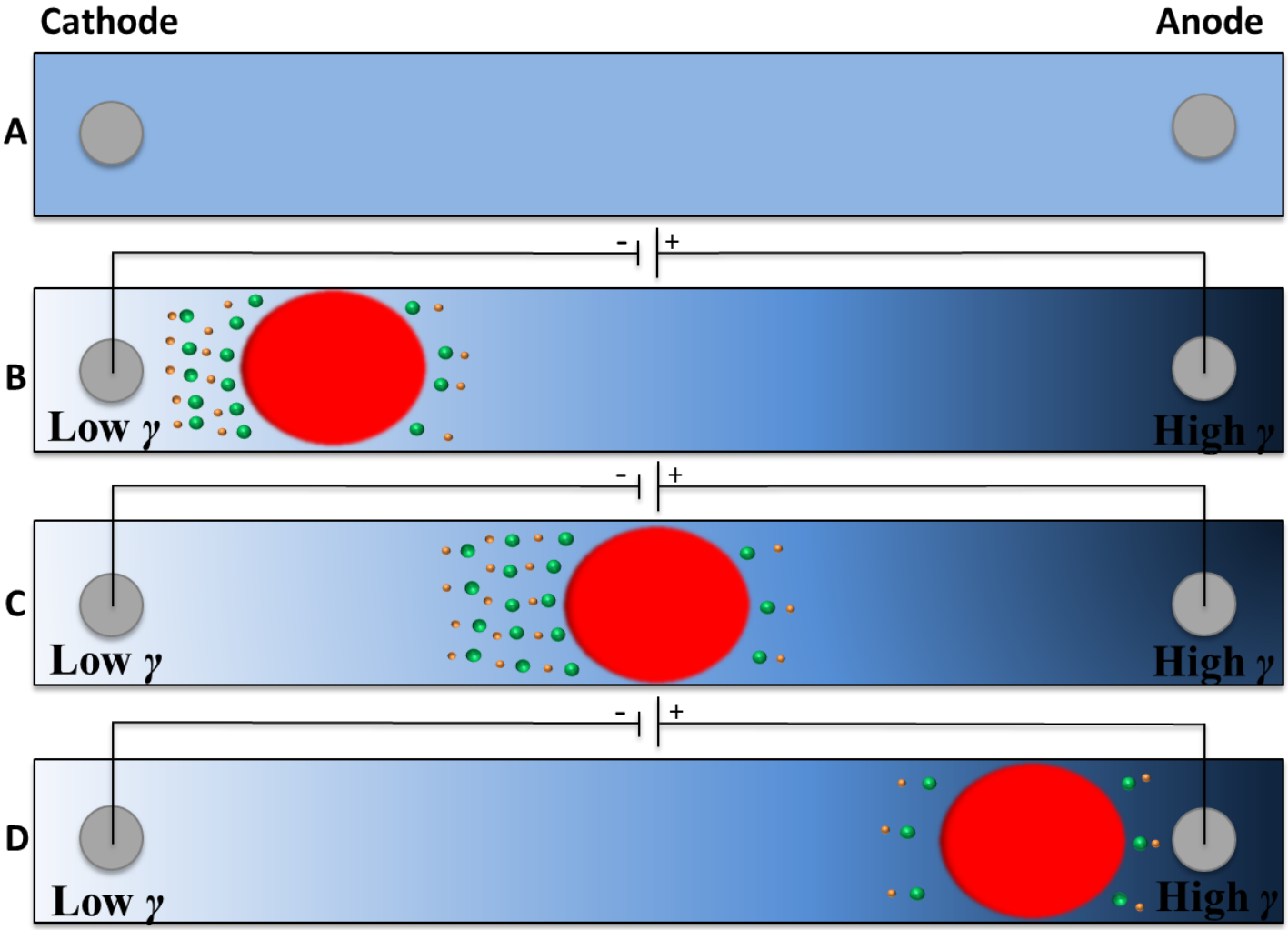
- **Droplets follow a Cl^- gradient to desired destinations**
- **Many methods for generation of gradients**
- **Droplet solely composed of IL**
- **Multiple droplets can be moved to destination**
- **Merging of droplets possible**
- **Chemical gradients will quickly come to equilibrium**
- **Droplet can only be moved to a single destination**

Francis, W.; Fay, C.; Florea, L. and Diamond, D. *Chem. Commun,* 2015, 51, 2342.

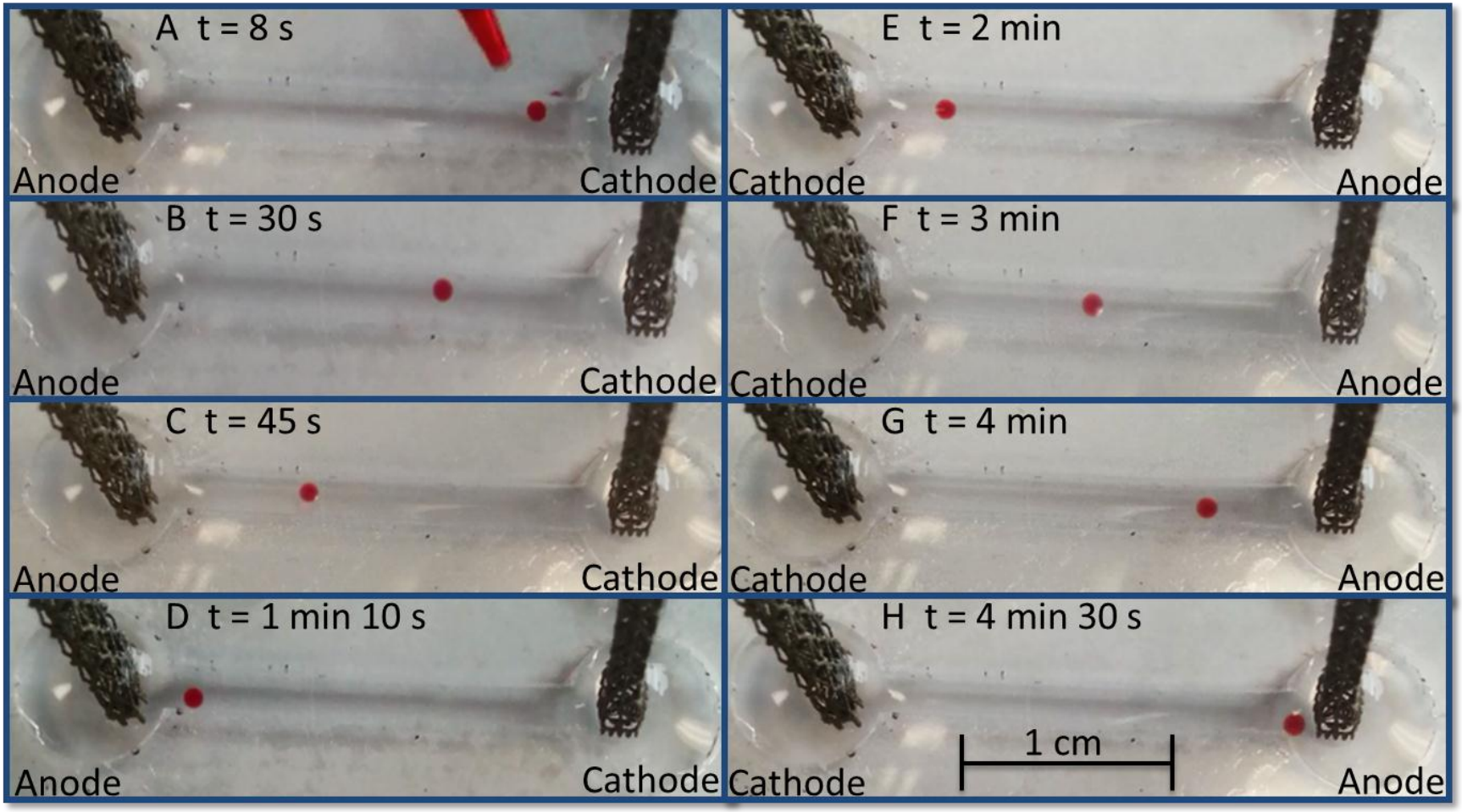
Electrotactic Droplets

- On demand generation of gradients at the electrodes
- Salt solutions used as electrolyte
- Control over length of gradients
- Reversible droplet movement
- Allows for droplet to be moved to several destinations

Droplet Movement



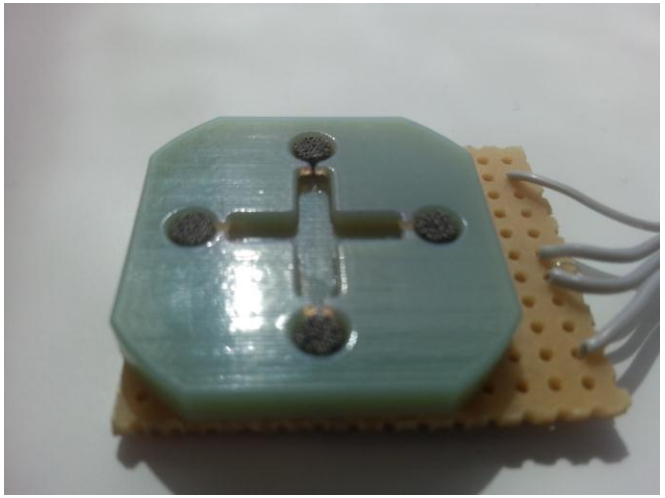
Reversible Movement



10^{-3} M NaCl used as electrolyte, 9 V applied across the solution.

Chip Design

- Chips 3D printed
- Electrodes - Realizer SLM-50 3D printer
- Channels - Objet350 Connex
- Electrodes embedded within the channels

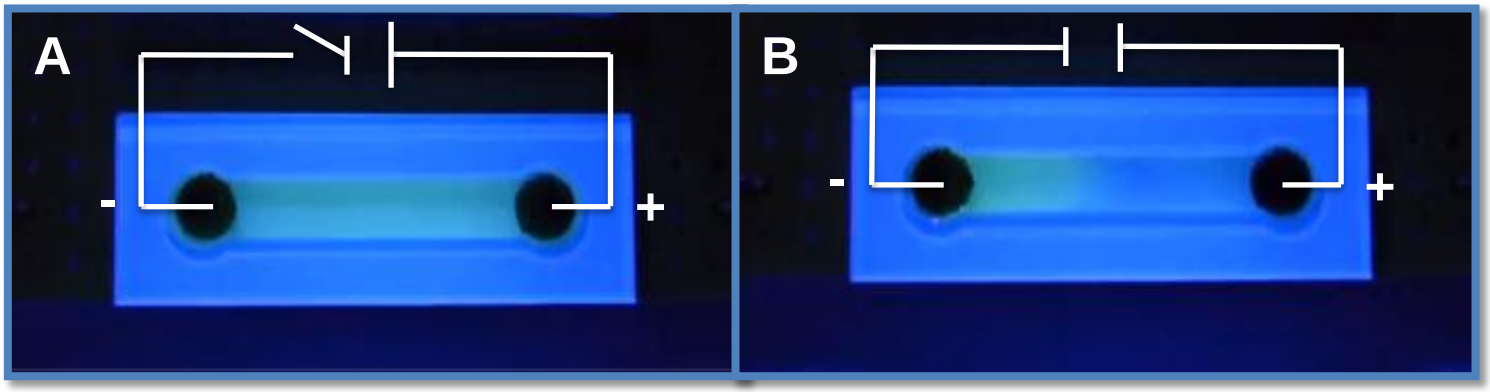


Example of Electrotactic Ionic liquids

NaCl 10^{-3} M , 9 V, Speed x 5

Electro-Generated Gradients

- Fluorescent dye : lucigenin
- Strongly quenched by Cl^-
- 369 nm LED source
- 10^{-3} M NaCl
- 10^{-4} M lucigenin
- Can be reversed

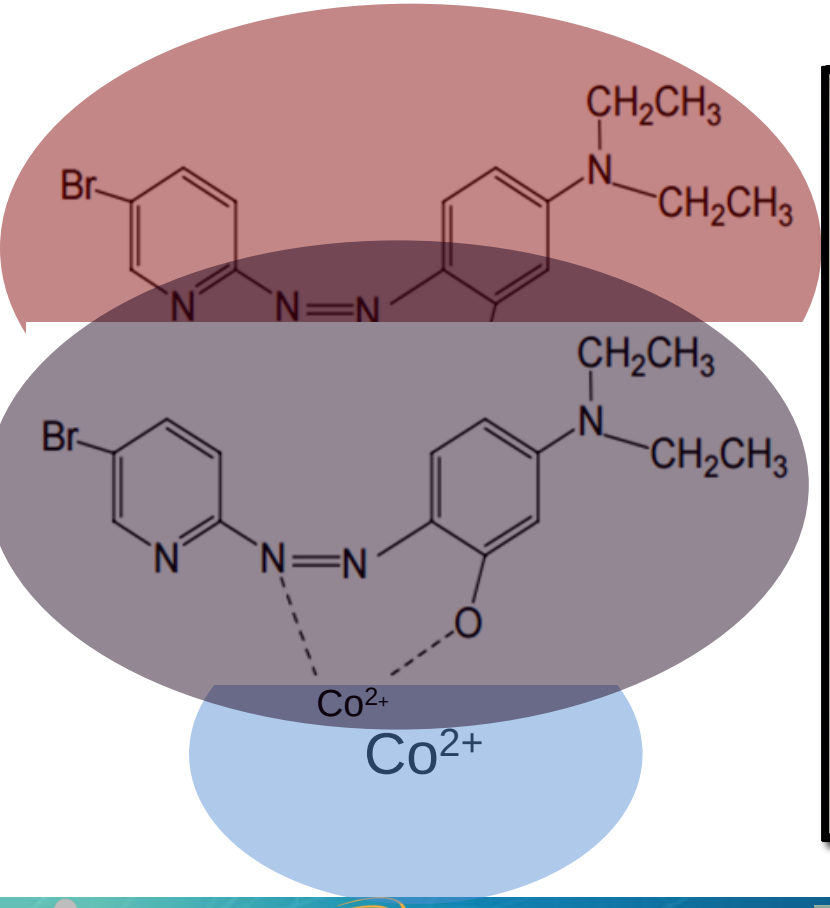


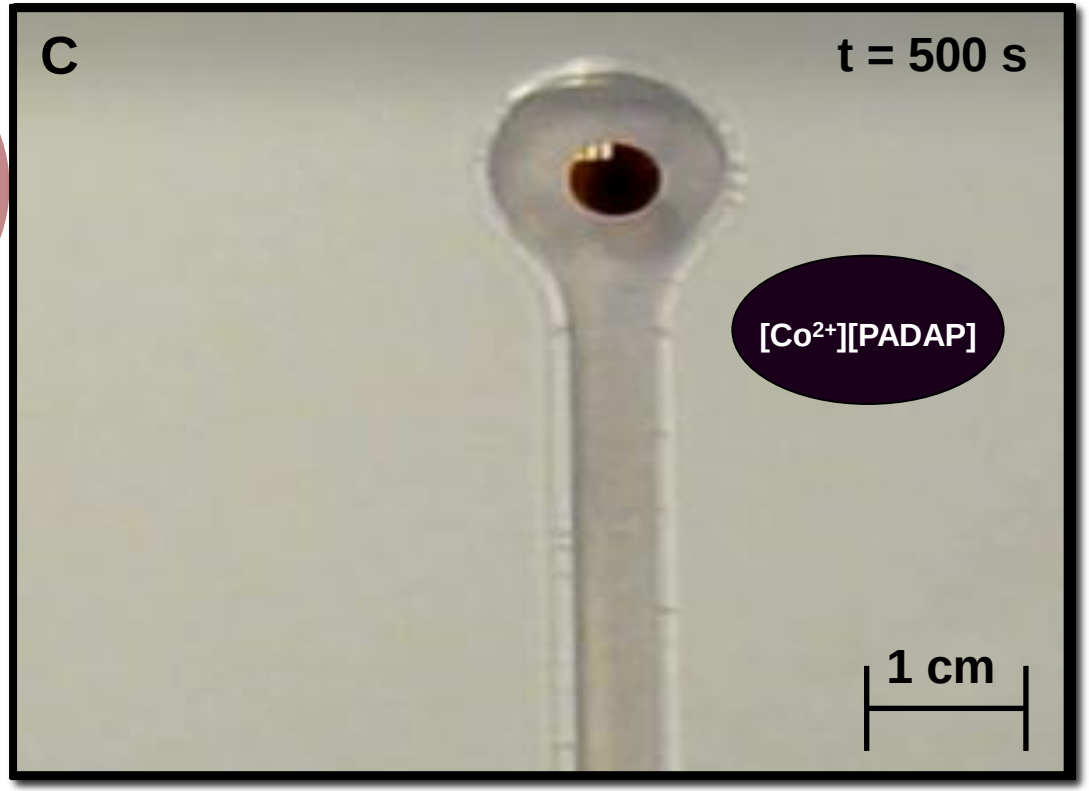
Adding Functionality

- Have droplets perform more sophisticated tasks
- Micro-vessels for chemical reactions
- Cargo transport to desired destinations
- Dynamic sensing units
- Leak detection

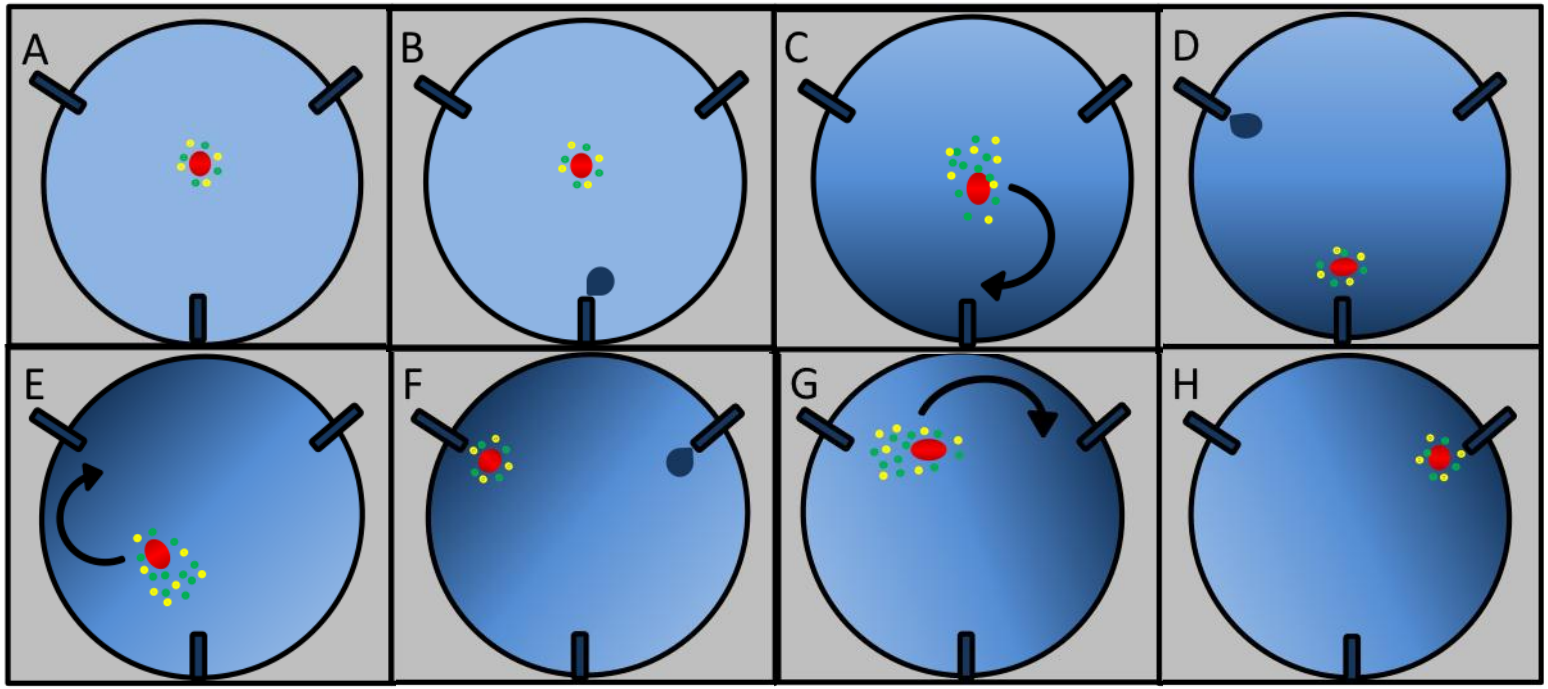
Chemical Reactions: Metal ion sensing

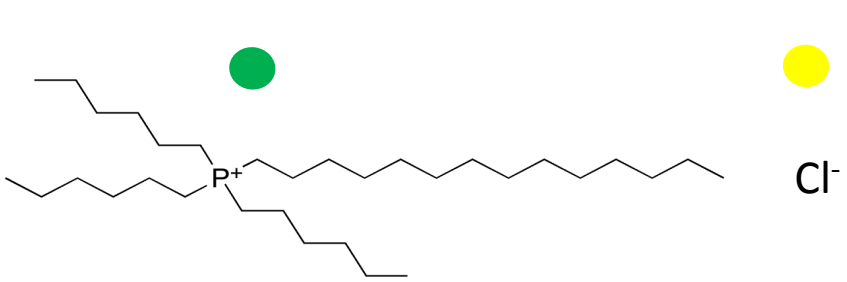
- Reactions take place inside droplet
- Predetermined locations
- Analytes: Co^{2+} and Cu^{2+}
- Metal sensing dye: PADAP





Leak Detection

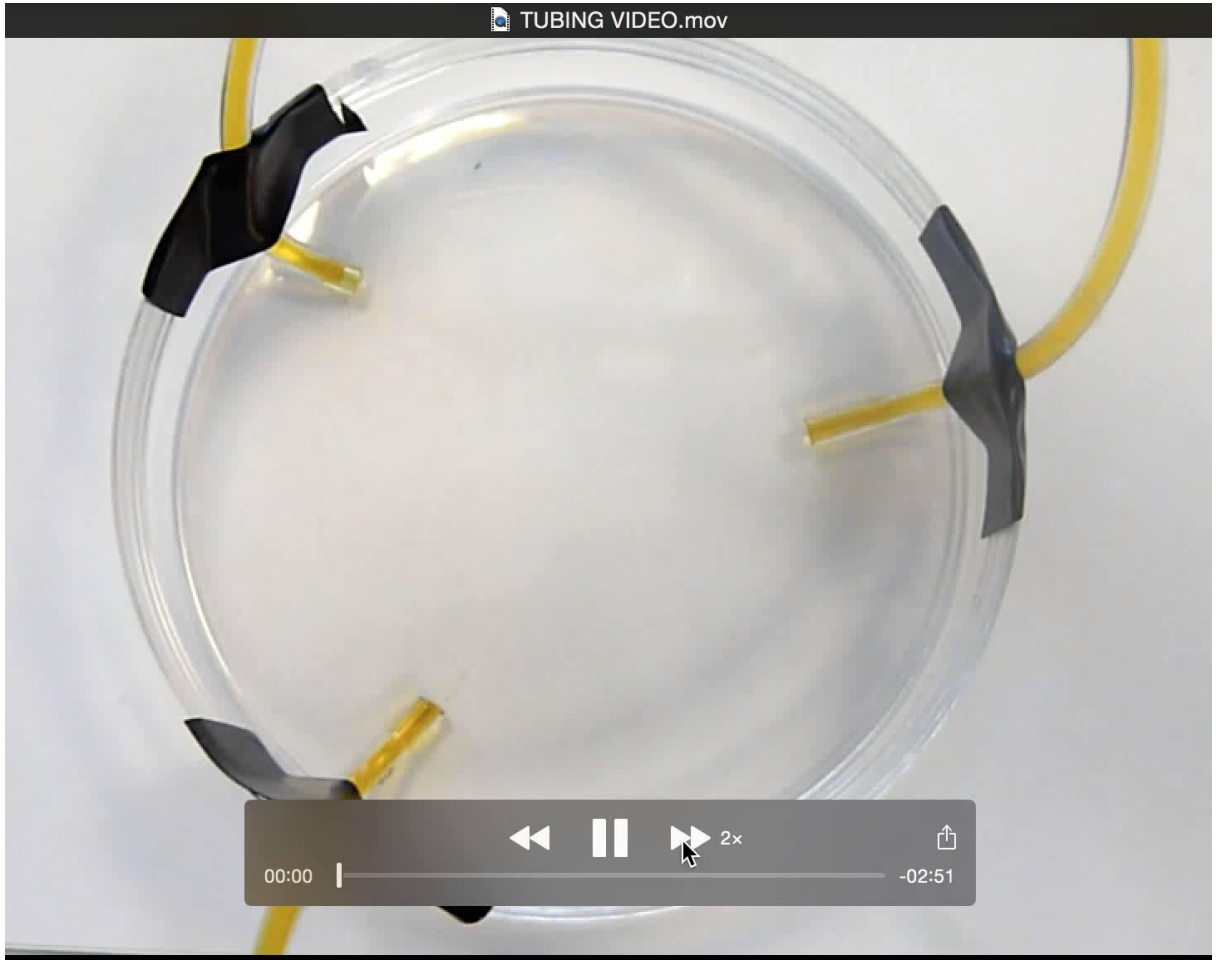




HCl 10^{-2} M

NaOH 10^{-2} M

Leak Detection



Speed x 5

Future Work

- Develop and optimise reactions within the droplets
- Novel tasks for droplets
- Developing new types of droplets (different Ionic liquids)
- Using other types of micro vehicles

Conclusion

- Chemo and electro tactic droplets
- Chemotactic: energy free autonomous movement
- Electrotactic: long lived chemical gradients, reversible movement to multiple destinations
- Vessels for chemical reactions
- Transport cargo to desired destinations
- Leak detection

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