# Supporting information

## Materials

*N*-isopropylacrylamide (NIPAm), *N,N'*-methylbisacrylamide (BIS), methacrylic acid (MA), potassium peroxodisulfate (KPS), styrene, sodium dodecyl sulfate (SDS) and Brij-98 were purchased from Sigma-Aldrich. Potassium nitrate ($KNO_3$) was purchased from Merck. Phosphonium based ionic liquids, trihexyltetradecyl phosphonium [$P_{6,6,6,14}$] chloride [Cl], phosphinate [Phos], dicyanamide [DCA] and bistriflamide [$NTf_2$], were purchased from Cytec; the other ionic liquids, butylmethylimidazolium bistriflamide [BMIM][$NTf_2$], methyltrioctylammonium bistriflamide [$N_{1,8,8,8}$][$NTf_2$] and Adogen 464 [$N_{1,8\text{-}10,8\text{-}10,8\text{-}10}$][Cl] were purchased from Sigma-Aldrich. The fluorescent dyes Pyrromethene 546 and Pyrromethene 605 were purchased from Exciton. PolyFluor$^{TM}$ 570 was purchased from PolySciences, Inc. All chemicals were used as received. Deionized water (DI) with a resistance of 18 MΩ.cm was used for the synthesis and characterization of the microgel particles and the preparation of the emulsions.

## Synthesis and characterization of the microgel particles

Core-shell microgels are synthesized in a two-step procedure. First, fluorescent cores, with a diameter of 0.2 μm and polydispersity < 5% are synthesized by emulsion polymerization. To this end, 3.75 g NIPAm, 48 g styrene, 100 mg SDS and 50 mg fluorescent dye are dissolved in 130 mL DI water. The mixture is stirred at 500 rpm, heated to 75°C and purged with $N_2$ for 15 minutes. The reaction is initiated by the addition of 100 mg KPS dissolved in 5 mL DI water and the reaction is left to proceed overnight. The reaction mixture is filtered and the cores are cleaned by repeated centrifugation and resuspension in DI water.

Second, a shell of NIPAm, MA and BIS is grown around the cores by precipitation polymerization. 1.0 g NIPAm, 100 μL MA and 40 mg BIS are dissolved in 95 mL of DI water. Then, 0.3 g cores are added and the mixture is sonicated for 2 min. The mixture is stirred at 500 rpm, heated to 75°C and purged with $N_2$ for 15 minutes. The reaction is initiated by the addition of 100 mg KPS dissolved in 5 ml DI water and the reaction is left to proceed for 2 hours. The reaction mixture is filtered and the composite microgels are cleaned by repeated centrifugation and resuspension in DI water. The average particle diameter, measured in dilute solution by DLS in a 15 mM $KNO_3$ solution, is determined as a function of pH and temperature.

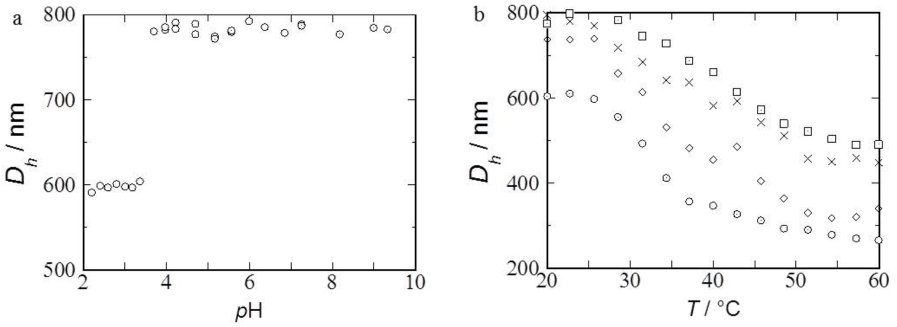


**Figure 1:** (a) Hydrodynamic diameter $D_h$ of microgels as a function of pH at room temperature, (b) hydrodynamic diameter $D_h$ as a function of temperature for different pH values: circles: pH = 3.2, diamonds: pH = 5.3, crosses: pH = 7.2, squares: pH = 11.8.

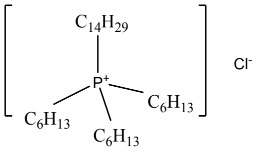
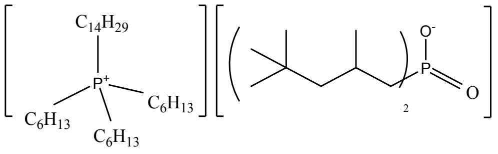
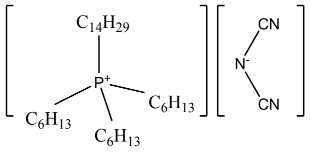
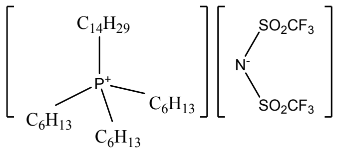
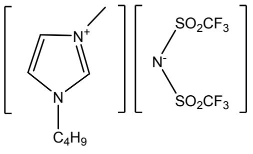
## Synthesis and characterization of the room temperature paramagnetic ionic liquid

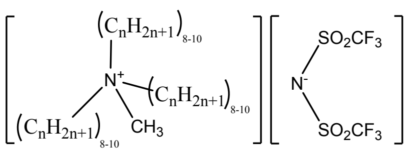
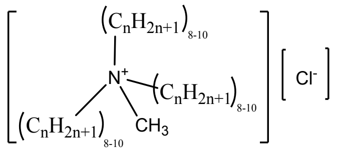
The room temperature paramagnetic ionic liquid $[P_{6,6,6,14}]$ $[FeCl_4]$ is prepared by mixing 15.2048 g of $[P_{6,6,6,14}][Cl]$ and 4,7498 g of iron(III) chloride in a 250 mL round-bottomed flask under a $N_2$ atmosphere at 50°C for 48 h, yielding a dark brown liquid. The product could not be analyzed by NMR because of its paramagnetic property. Analysis was therefore limited to elemental analysis and moisture analyzer for the water content. The elemental analysis, calculated for $C_{32}H_{68}PFeCl_4$, gives: C 56.39 %, H 9.99 %, experimentally found: C 56.84 %, H 10.22%. The water content is 1.02 %.

## Ionic liquid-water interfacial tension measurements

Interfacial tension between IL and water is measured through pendant drop tensiometry (Sinterface Pat-1). For steady state values of the interfacial tensions, we equilibrate the droplet for at least 1h. For all measurements, the droplet size is 6.0 mm$^3$.

**Table 1**: Commercial name, abbreviations, chemical structures and interfacial tension with water of the ionic liquids used.

| Commercial name | Abbreviation | Structure | Interfacial tension with water |
|---|---|---|---|
| Trihexyltetradecyl phosphonium chloride | $[P_{6,6,6,14}][Cl]$ |  | 7.3 |
| Trihexyltetradecyl phosphonium phosphinate | $[P_{6,6,6,14}][Phos]$ |  | 10.2 |
| Trihexyltetradecyl phosphonium dicyanamide | $[P_{6,6,6,14}][DCA]$ |  | 12.4 |
| Trihexyltetradecyl phosphonium bistriflamide | $[P_{6,6,6,14}][NTf_2]$ |  | 8.3 |
| Butylmethylimidazolium bistriflamide | $[BMIM][NTf_2]$ |  | 13.2[1] |

|  |  |  |  |
|---|---|---|---|
| Methyltrioctylammonium bistriflamide | $[N_{1,8,8,8}][NTf_2]$ |  | Not measured |
| Adogen 464 | $[N_{1,8\text{-}10,8\text{-}10,8\text{-}10}][Cl]$ |  | 2.5 |

### Preparation and characterization of the emulsion

The surfactant-stabilized emulsion was prepared by mixing for 2 min, using an Ultra Turrax, the Brij-98 solution ($c$ = 0.26 mM) with the IL (weight ratio 9:1). The microgel-stabilized emulsion was prepared by first diluting the microgel stock solution ($c$ = 27 g/L) to the desired concentration of particles and salt ($c$ = 2.7 g/L, $I$ = 15 mM and pH = 6) using DI water and a solution of 15 mM of $KNO_3$ and then mixing the solution with the IL (weight ratio 9:1). In this case, mixing is done by vortexing for 30 s the two macroscopic phases in a tube.

**Table 2**: Emulsion type for the different ILs.

| Anion | Cation | Emulsion type | Microgels in excess |
|---|---|---|---|
| $[Phos^-]$ | $[P^+_{6,6,6,14}]$ | IL-in-water | in water |
| $[DCA^-]$ | $[P^+_{6,6,6,14}]$ | IL-in-water | in water |
| $[NTf_2^-]$ | $[P^+_{6,6,6,14}]$ | IL-in-water | in water |
| $[NTf_2^-]$ | $[BMIM^+]$ | IL-in-water | in water |
| $[NTf_2^-]$ | $[N^+_{1,8,8,8}]$ | IL-in-water | in water |
| $[Cl^-]$ | $[N^+_{1,8\text{-}10,8\text{-}10,8\text{-}10}]$ | IL-in-water | in water |
| $[Cl^-]$ | $[P^+_{6,6,6,14}]$ | water-in-IL | in IL |

### Confocal microscopy

The emulsions are studied using a Zeiss Axiovert 200M confocal microscope fitted with a 100x oil immersion objective.

### Stability measurements

The stability of the emulsion against coalescence and Ostwald ripening is analyzed by measuring the droplet-size distribution over time using a Malvern Mastersizer 2000. The size distribution is characterized in terms of mean diameter defined as:

$$D_i = \frac{\sum_i N_i D_i^3}{\sum_i N_i D_i^2}$$

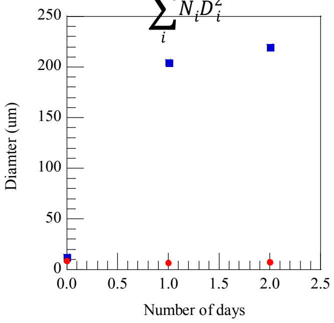


**Figure 2**: Mean droplet size distributions over time for a non-ionic surfactant-stabilized emulsion (blue) and a microgel-stabilized emulsion (red) prepared with [$P_{6,6,6,14}$][$NTf_2$].

## Effect of pH changes

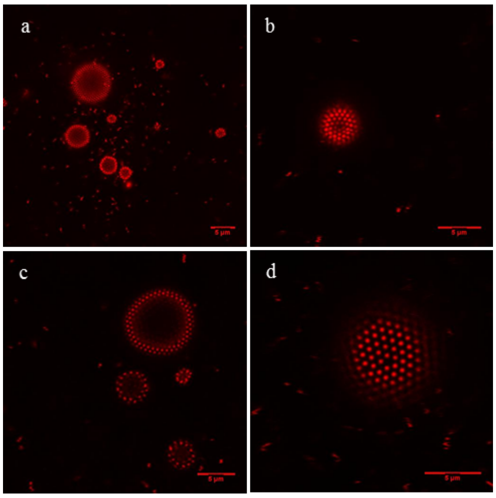


**Figure 3**: Confocal microscopy images of [BMIM][$NTf_2$] droplets in water stabilized with hexagonally packed microgel particles before and after quenching from acidic to basic (pH 4 (a) --> pH 9 (b)) and vice versa (pH 9 (c) --> pH 4 (d)). No changes in emulsion stability of interfacial structure are observed, confirming that the emulsions are not pH responsive.

## Reference

[1] R. L. Gardas, R. Ge, N. Ab Manan, D. W. Rooney, C. Hardacre, *Fluid Phase Equilib.* **2010**, *294*, 139-147.