Amphiphobic Surface-Active Ionic Liquids as Dynamic Micellar Phase-Transfer Catalysts for Biphasic Epoxidations

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Electronic Supplementary Information

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1. Experimental

1.1. Analytical methods, calculations, and characterization techniques

1.1.1. Materials

Chloroform ($CHCl_3$, puriss. and $CDCl_3$), D_2O, dichloromethane (CH_2Cl_2, puriss.), 1-methylimidazole, 1-bromobutane, 1-bromooctane, 1-bromododecane, 1-bromohexadecane, naphthalene, sodium acetate, sodium tungstate dihydrate ($Na_2WO_4 \cdot 2H_2O$), sodium tetrafluoroborate ($NaBF_4$), ammonium hexafluorophosphate (NH_4PF_6), Amberlite® IRA-402 (chloride form) and sodium hydroxide were purchased from *Sigma Aldrich* and *Deutero* ($CDCl_3$). Cis-cyclooctene (COE, >95 %) and phenylphosphonic acid (PPA) were purchased from *AlfaAesar*. Cyclooctene oxide (COO) was purchased from *TCI Chemicals*. Lithium bis(trifluoromethanesulfonyl)imide ($LiNTf_2$) was purchased from *BLD Pharmatech*. Hydrogen peroxide (H_2O_2, 50 wt.% in water) and 8-dram vials for epoxidation catalysis (TraceClean®) were purchased from *VWR*. Carbon grids for TEM measurements were purchased from *Micro to Nano*. 1-Methylimidazole and all alkyl/benzyl halides were distilled under vacuum and stored under an argon atmosphere until further use. All other purchased chemicals were used without further purification. Synthesis of imidazolium halides were carried out under *Schlenk* conditions, the following synthesis steps and catalysis runs were carried out under air, if not stated otherwise.

1.1.2. Attenuated total reflectance infrared spectroscopy (ATR-IR)

ATR-IR measurements were carried out on a *PerkinElmer* Frontier FT-IR spectrometer featuring an ATR plate with a diamond crystal with a 2 cm^{-1} resolution and 16 accumulated scans.

1.1.3. Dynamic light scattering (DLS)

DLS was performed on a Malvern Zetasizer Nano in quartz cuvettes using 173° angle backscattering mode. The respective amount of IL was dissolved in 1.4 ml aqueous H_2O_2 and measured at 20 °C. In order to investigate the substrate interaction, Cyclooctene (10 mmol) was added to the mixture. The biphasic system was shaken and after phase separation the aqueous phase is used for the measurement. Each sample was filtered by a syringe filter (LLG-Syringe filters SPHEROS, PTFE, 0.22 µm, 13 mm diameter by Lab Logistics Group GmbH). Micelle size distributions were interpreted from the correlograms using a general-purpose method.

1.1.4. Elemental analysis (EA)

Elemental analysis was performed at the Microanalytical Laboratory of the Technical University of Munich, Germany on a HEKAtech Euro EA CHNSO-Analyzer and a Varian AA280FS fast sequential AAS spectrometer.

1.1.5. Gas chromatography (GC)

The conversion X of COE was determined by analyzing the samples taken during the reaction using a Bruker 450 gas chromatograph (GC) with an Ultra 2 column (50 m, 0.32 mm, 0.5 µm) and a flame ionization detector. Because no other product except of COO could be detected, the conversion X_{COE} was calculated with the following formula:

$$X_{COO} = \frac{x_{COO}}{x_{COE,0}} \quad (1)$$

The amounts of COE and COO were obtained via the GC analysis using cyclooctane as internal standard.

1.1.6. Inductively coupled plasma mass spectrometry (ICP-MS)

To determine if the epoxidation catalyst Na_2WO_4 fully remains in the aqueous phase or is also contained in the organic phase after epoxidation catalysis of cyclooctene *via* salt metathesis with [OMIm][NTf_2], ICP-MS was conducted on a *Perkin Elmer* NexIon 350D ICP-MS instrument. The sample was prepared by stirring of the 1.0 ml of the organic layer with 1.0 ml Millipore Milli-Q® water over night. Subsequently, the aqueous phase was separated and immersed in 7.5 ml concentrated nitric acid and 2.5 mL H_2O_2 30 % (v/v) and treated in the microwave at 150 °C for 10 min. The microwave-digested samples were diluted 1/100 with Millipore Milli-Q® water. Each solvent was extra pure and checked for possible analyte contaminations before measurement. ^{183}W was used as target masses for the analyte and ^{115}In as an internal standard. Analyte quantification was carried out in standard mode with correction equation to avoid polyatomic interferences. External calibration was performed and the detection limit for W was 0.16 µg/L. Each sample was measured with five measurement replicates, a dwell time per 50 ms and an integration time of 750 ms. The metal concentration was blank corrected via measurement of blank samples.

1.1.7. Nuclear magnetic resonance spectroscopy (NMR)

Liquid state NMR spectra were recorded by a *Bruker* AVIII 400 US or a 600 MHz Bruker Avance II+ (^{1}H: 400 MHz, 16 scans; ^{11}B-NMR: 128 MHz, 256 scans; ^{13}C: 101 MHz, 1024 scans; ^{19}F: 376 MHz, 16 scans; ^{31}P: 161 MHz, 32 scans) at ambient temperature (298 K). In case of variable temperature experiments, the measurements were performed on a *Bruker* AV 400. The ^{1}H NMR spectroscopic chemical shifts δ are reported in ppm relative to tetramethylsilane. ^{1}H NMR spectra are calibrated against the residual proton and natural abundance carbon resonances of the respective deuterated solvent as an internal standard ($CDCl_3$: δ (^{1}H) = 7.26 ppm). The following abbreviations are used to describe signal multiplicities: s = singlet, d = doublet, t = triplet, p = quintet, m = multiplet.

1.1.8. Critical micelle concentration (CMC) measurements

CMC determination was performed by tensiometrical means and conductometry. For tensiometric analysis, a Krüss K11 tensiometer (Krüss GmbH, Germany) with a custom heated aluminum mantle for measurements above room temperature was used. Regarding the procedure, the Wilhelmy method of determining surface tensions was chosen, but instead of the standard platinum plates, 18 mm x 18 mm glass plates were used according to[1]. The reason for the use of glass plates is the decomposition of hydrogen peroxide at the platinum, hindering the determination of the surface tension. Every glass plate was cleaned with isopropyl alcohol and flamed-out in a Bunsen flame before the measurement. The surface tension of pure water was measured prior to each CMC analysis. For finding a CMC value, the surface tensions of SAIL solutions varying in concentration were determined. The concentration was altered by adding a concentrated solution of the SAIL to the pure solvent (50 % aqueous hydrogen peroxide). Between each addition steps, the surface tension or conductivity was measured with the aforementioned method. Alternatively, the concentrated or saturated solution can be diluted with the solvent. Combining both methods, a wide range of SAIL concentration can be achieved. By plotting the surface tension/ electrical conductivity against the logarithmic concentration of the IL, the CMC can be seen as a change in slope in the curve. Conductivity measurements were performed using a Metrohm 712 conductometer (Metrohm AG, Switzerland) with temperature compensation. Owing to the decomposition of hydrogen peroxide on platinum, a custom measuring cell using tin electrodes was used[1]. The cell was calibrated using commonly available standards (1413 µS/cm, Carl Roth Gmbh & Co. KG).

1.1.9. Transmission electron microscopy (TEM)

TEM measurements were carried out with a JEM 1400 plus microscope at 120 kV equipped with a Ruby CCD detector from JOEL. The samples were prepared by dissolving distinct amounts of the respective IL in distilled water and filtered by a syringe filter (LLG-Syringe filters SPHEROS, PTFE, 0.22 µm, 13 mm diameter by Lab Logistics Group GmbH). The Each sample (5 µL) was coated onto a continuous carbon film copper grid (300 mesh) by drop casting at room temperature. Prior to drop casting, the copper grids were glow discharged for 30 s and subsequently impregnated with the sample for 30 s before flushing the grid with 20 µL water.

1.2. Synthesis of precursors and (F)SAILs

1.2.1. Alkylimidazolium bromides

The procedure was adapted according to previous literature reports[2,3]. All 1(,2)-(di)alkyl-3-methylimidazolium bromides were synthesized by addition of 1-methylimidazole or 1,2-dimethylimidazole (1.0 equiv.) to the corresponding 1-bromoalkane (1.05 equiv.). The solution was degassed, heated stepwise to 50 °C and subsequently stirred under an argon atmosphere for 24 h at 50 °C. Volatile impurities were evaporated at 80 °C by using a turbomolecular pump (10^{-5} mbar) for 8 h. The resulting colorless ILs were obtained in quantitative yields and high purities (*via* NMR) and stored under argon atmosphere until use due to the high hygroscopy.

1.2.1.1. 1-Butyl-3-methylimidazolium bromide [BuMIm]Br

Colorless, slightly viscous liquid; 96% yield
^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ [ppm]: 10.26 (s, *J* = 1.7 Hz, 1H), 7.61 (t, *J* = 1.8 Hz, 1H), 7.48 (t, *J* = 1.8 Hz, 1H), 4.26 (t, *J* = 7.4 Hz, 2H), 4.05 (s, 3H), 1.83 (pseudo-p, 2H), 1.30 (h, *J* = 7.4 Hz, 2H), 0.87 (t, *J* = 7.4 Hz, 3H).
^{13}C-NMR (101 MHz, $CDCl_3$, 298 K) δ [ppm]: 137.46, 123.89, 122.33, 50.22, 36.67, 32.29, 19.66, 14.01.

1.2.1.2. 1-Octyl-3-methylimidazolium bromide [OMIm]Br

Colorless, viscous liquid; 97% yield
^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ [ppm]: 10.28 (s, 1H), 7.61 (s, 1H), 7.43 (s, 1H), 4.27 (t, *J* = 7.4 Hz, 2H), 4.06 (s, 3H), 1.84 (pseudo-p, *J* = 7.3 Hz, 2H), 1.31 – 1.10 (m, 10H), 0.79 (t, *J* = 6.6 Hz, 3H).
^{13}C-NMR (101 MHz, $CDCl_3$, 298 K) δ [ppm]: 137.51, 123.66, 121.87, 50.08, 36.65, 31.58, 30.28, 28.95, 28.84, 26.21, 22.49, 14.02.

1.2.1.3. 1-Dodecyl-3-methylimidazolium bromide [DoMIm]Br

White solid; 99% yield
^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ [ppm]: 10.30 (s, 1H), 7.61 (d, *J* = 1.8 Hz, 1H), 7.42 (d, *J* = 1.9 Hz, 1H), 4.25 (t, *J* = 7.4 Hz, 2H), 4.07 (s, 3H), 1.85 (pseudo-p, *J* = 7.3 Hz, 2H), 1.29 – 1.15 (m, 18H), 0.80 (t, *J* = 6.8 Hz, 3H).
^{13}C-NMR (101 MHz, $CDCl_3$, 298 K) δ [ppm]: 137.31, 123.78, 121.99, 50.12, 36.71, 31.86, 30.33, 29.56, 29.47, 29.35, 29.29, 28.98, 26.23, 22.64, 14.10.

1.2.1.4. 1-Hexadecyl-3-methylimidazolium bromide [HexDeMIm]Br

Off-white solid; 98% yield

^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ [ppm]: 10.29 (t, 2H), 7.62 (t, 1H), 7.42 (t, 1H), 4.24 (t, 2H), 4.06 (s, 3H), 1.84 (pseudo-p, 2H), 1.28 – 1.13 (m, 28H), 0.79 (t, 1H).

^{13}C-NMR (101 MHz, $CDCl_3$, 298 K) δ [ppm]: 137.25, 123.79, 121.99, 50.08, 36.69, 31.86, 30.31, 29.64, 29.60, 29.56, 29.47, 29.34, 29.30, 28.97, 26.22, 22.63, 14.08.

1.2.2. Alkylimidazolium bis((trifluoromethyl)sulfonyl)imides

The procedure was adapted in correspondence to previous literature reports[3]. According to the anion exchange procedure[2], the respective imidazolium bromides (1.0 eq.) were dissolved in deionized water and rinsed over 250 g Amberlite IRA 402 (OH), which was freshly activated by 1 M NaOH solution (Amberlite IRA 402(Cl) → Amberlite IRA 402(OH)). The basic fractions were collected and lithium bis((trifluoromethyl)sulfonyl)imide ([Li][NTf_2], 1.1 equiv.) was added to solution. The milky solution was stirred for 24 hours at room temperature. Then, the stirring was stopped and the product precipitated as second phase (liquid for butyl, octyl, dodecyl and solid for hexadecyl). In case of a liquid IL phase, the reaction mixture was concentrated to 50 ml. The lower ionic liquid phase was separated by centrifugation and washed with water (3x25 ml) and dried in vacuum (1x10^{-5} mbar) overnight to almost quantitatively yield the pure products (according to NMR) as colorless liquids or white solids.

1.2.2.1. 1-Butyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide [BuMIm][NTf_2]

Colorless liquid; 91% yield

^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ [ppm]: 8.77 (d, *J* = 1.7 Hz, 1H), 7.28 (dt, *J* = 5.8, 1.9 Hz, 2H), 4.17 (t, *J* = 7.5 Hz, 2H), 3.94 (s, 3H), 1.85 (pseudo-p, *J* = 6.8 Hz, 2H), 1.44 – 1.30 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$, 298 K) δ [ppm]: 136.35, 123.72, 122.29, 53.59, 50.12, 36.51, 32.06, 19.48, 13.35.

^{19}F-NMR (376 MHz, $CDCl_3$, 298 K) δ [ppm]: −79.03.

Elemental analysis calcd. (%) for $C_{10}H_{15}F_6N_3O_4S_2$: C 28.64, H 3.61, F 27.18, N 10.02, O 15.26, S 15.29; found: C 28.45, H 3.33, N 9.89, S 15.01.

1.2.2.2. 1-Octyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide [OMIm][NTf$_2$]

Colorless, slightly viscous liquid; 96 % yield

^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ [ppm]: 8.72 (s, 1H), 7.32 (t, *J* = 1.9 Hz, 1H), 7.29 (t, *J* = 1.8 Hz, 1H), 4.15 (t, 2H), 3.93 (s, 3H), 1.85 (p, 1H), 1.35 – 1.18 (m, 10H), 0.86 (t, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$, 298 K) δ [ppm]: 136.16, 123.86, 122.37, 50.35, 36.44, 31.73, 30.17, 29.03, 28.91, 26.21, 22.65, 14.11.

^{19}F-NMR (376 MHz, $CDCl_3$, 298 K) δ [ppm]: - 79.07.

Elemental analysis calcd. (%) for $C_{14}H_{23}F_6N_3O_4S_2$: C 35.37, H 4.88, F 23.97, N 8.84, O 13.46, S 13.49; found: C 35.41, H 4.79, N 8.78, S 13.44.

1.2.2.3. 1-Dodecyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide [DoMIm][NTf$_2$]

Colorless, very viscous liquid; 96% yield

^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ [ppm]: 8.74 (d, *J* = 1.8 Hz, 1H), 7.32 (s, 1H), 7.28 (s, 1H), 4.15 (t, *J* = 7.5 Hz, 2H), 3.93 (s, 3H), 1.85 (pseudo-p, *J* = 7.1 Hz, 2H), 1.36 – 1.19 (m, 18H), 0.87 (t, *J* = 6.7 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$, 298 K) δ [ppm]: 136.21, 123.81, 122.30, 50.36, 36.46, 32.02, 30.20, 29.70, 29.69, 29.58, 29.44, 29.41, 28.98, 26.24, 22.80, 14.23.

^{19}F-NMR (376 MHz, $CDCl_3$, 298 K) δ [ppm]: -79.04.

Elemental analysis calcd. (%) for $C_{18}H_{31}F_6N_3O_4S_2$: C 40.67, H 5.88, F 21.44, N 7.91, O 12.04, S 12.06; found: C 40.79, H 6.02, N 7.91, S 11.73.

1.2.2.4. 1-Butyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide [HexDeMIm][NTf$_2$]

White solid, 98% yield

^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ [ppm]: 7.31 (d, *J* = 1.9 Hz, 1H), 7.29 (d, *J* = 1.8 Hz, 1H), 4.19 – 4.11 (m, 2H), 3.93 (s, 3H), 1.85 (pseudo-p, *J* = 7.2 Hz, 2H), 1.37-1.19 (m, 28H), 0.87 (t, *J* = 6.7 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$, 298 K) δ [ppm]: 136.08, 123.70, 122.18, 50.23, 36.34, 31.93, 30.08, 29.71, 29.69, 29.66, 29.59, 29.48, 29.37, 29.31, 28.88, 26.13, 22.69, 14.12.

^{19}F-NMR (376 MHz, $CDCl_3$, 298 K) δ [ppm]: -79.04.

Elemental analysis calcd. (%) for $C_{22}H_{39}F_6N_3O_4S_2$: C 44.96, H 6.69, F 19.40, N 7.15, O 10.89, S 10.91; found: C 45.06, H 6.64, N 7.15, S 11.00.

1.2.3. Alkylimidazolium tetrafluoroborates

According to the anion exchange procedure[2], the respective imidazolium bromides (1.0 eq.) were dissolved in deionized water and rinsed over 250 g Amberlite IRA 402 (OH), which was freshly activated by 1 M NaOH solution (Amberlite IRA 402(Cl) → Amberlite IRA 402(OH)). The basic fractions were collected and sodium tetrafluoroborate ($NaBF_4$, 1.1 equiv.) was added to solution. The milky solution was stirred for 24 hours at room temperature. Then, the stirring was stopped and the product precipitated as second phase (liquid for butyl, octyl, dodecyl and solid for hexadecyl). In case of a liquid IL phase, the reaction mixture was concentrated to 50 ml. The lower ionic liquid phase was separated by centrifugation and washed with water (3x25 ml) and dried in vacuum ($1x10^{-5}$ mbar) overnight to almost quantitatively yield the pure products (according to NMR) as colorless liquids or white solids.

1.2.3.1. 1-Butyl-3-methylimidazolium tetrafluoroborate [BuMIm][BF_4]

^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ [ppm]: 8.85 (d, *J* = 1.7 Hz, 1H), 7.35 (d, *J* = 1.8 Hz, 1H), 7.31 (d, *J* = 1.8 Hz, 1H), 4.21 (t, *J* = 7.4 Hz, 2H), 3.98 (s, 3H), 1.89 (pseudo-p, 2H), 1.44 – 1.33 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H).
^{11}B-NMR (128 MHz, $CDCl_3$, 298 K) δ [ppm]: - 0.97.
^{13}C-NMR (101 MHz, $CDCl_3$, 298 K) δ [ppm]: 136.73, 123.68, 122.10, 50.02, 36.47, 32.03, 19.53, 13.46.
^{19}F-NMR (376 MHz, $CDCl_3$, 298 K) δ [ppm]: -151.57
Elemental analysis calcd. (%) for $C_8H_{15}BF_4$: C 42.51, H 6.69, B 4.78, F 33.62, N 12.39; found: C 42.16, H 6.52, N 12.31.

1.2.3.2. 1-Octyl-3-methylimidazolium tetrafluoroborate [OMIm][BF_4]

^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ [ppm]: 8.74 (s, 1H), 7.39 (t, *J* = 1.8 Hz, 1H), 7.32 (t, *J* = 1.8 Hz, 1H), 4.15 (t, 2H), 3.93 (s, 3H), 1.84 (p, *J* = 7.3 Hz, 2H), 1.34 – 1.20 (m, 10H), 0.85 (t, 3H).
^{11}B-NMR (128 MHz, $CDCl_3$, 298 K) δ [ppm]: - 0.98.
^{13}C-NMR (101 MHz, $CDCl_3$, 298 K) δ [ppm]: 136.30, 123.87, 122.24, 50.17, 36.31, 31.75, 30.15, 29.09, 28.97, 26.26, 22.66, 14.15.
^{19}F-NMR (376 MHz, $CDCl_3$, 298 K) δ [ppm]: -151.25.
Elemental analysis calcd. (%) for $C_{12}H_{23}BF_4N_2$: C 51.09, H 8.22, B 3.83, F 26.94, N 9.93; found: C 51.01, H 8.43, N 9.92.

1.2.3.3. 1-Dodecyl-3-methylimidazolium tetrafluoroborate [DoMIm][BF_4]

^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ [ppm]: 8.75 (s, 1H), 7.38 (d, *J* = 1.8 Hz, 1H), 7.30 (d, *J* = 1.9 Hz, 1H), 4.15 (t, *J* = 7.5 Hz, 2H), 3.93 (d, *J* = 2.4 Hz, 3H), 1.85 (t, *J* = 7.3 Hz, 2H), 1.29 – 1.22 (m, 18H), 0.86 (t, *J* = 6.6 Hz, 3H).
^{11}B-NMR (128 MHz, $CDCl_3$, 298 K) δ [ppm]: - 0.98.
^{13}C-NMR (101 MHz, $CDCl_3$, 298 K) δ [ppm]: 136.36, 123.87, 122.20, 50.19, 36.34, 32.00, 30.18, 29.71, 29.63, 29.49, 29.44, 29.07, 26.32, 22.78, 14.22.
^{19}F-NMR (376 MHz, $CDCl_3$, 298 K) δ [ppm]: - 151.32.
Elemental analysis calcd. (%) for $C_{16}H_{31}BF_4N_2$: C 56.82, H 9.24, B 3.20, F 22.47, N 8.28; found: C 57.42, H 9.78, N 8.19.

1.2.3.4. 1-Butyl-3-methylimidazolium tetrafluoroborate [HexDeMIm][BF_4]

^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ [ppm]: 8.91 (s, 1H), 7.30 (d, *J* = 1.9 Hz, 1H), 7.23 (d, *J* = 1.9 Hz, 1H), 4.17 (t, *J* = 7.5 Hz, 2H), 3.97 (s, 3H), 1.38 – 1.15 (m, 28H), 0.87 (t, *J* = 6.7 Hz, 4H).
^{11}B-NMR (128 MHz, $CDCl_3$, 298 K) δ [ppm]: - 0.97.
^{13}C-NMR (101 MHz, $CDCl_3$, 298 K) δ [ppm]: 137.03, 123.59, 121.92, 50.40, 36.58, 32.07, 30.20, 29.84, 29.80, 29.75, 29.66, 29.51, 29.09, 26.38, 22.84, 14.26.
^{19}F-NMR (376 MHz, $CDCl_3$, 298 K) δ [ppm]: - 151.78.
Elemental analysis calcd. (%) for $C_{20}H_{39}BF_4N_2$: C 60.92, H 9.97, B 2.74, F 19.27, N 7.10; found: C 61.28, H 10.19, N 7.06.

1.2.4. Alkylimidazolium hexafluorophosphates

According to the anion exchange procedure[2], the 1-dodecyl-3-methylimidiazole bromide (1.0 eq.) was dissolved in deionized water and rinsed over 250 g Amberlite IRA 402 (OH), which was freshly activated by 1 M NaOH solution (Amberlite IRA 402(Cl) → Amberlite IRA 402(OH)). The basic fractions were collected and ammonium hexafluorophospate (NH_4PF_6, 1.1 equiv.) was added to solution. The milky solution was stirred for 24 hours at room temperature. Then, the stirring was stopped and the product precipitated as a second liquid phase. The reaction mixture was concentrated to 50 ml. The lower ionic liquid phase was separated by centrifugation and washed with water (3x25 ml) and dried in vacuum ($1x10^{-5}$ mbar) overnight to almost quantitatively yield the pure product (according to NMR) as colorless liquid.

1.2.4.1. 1-Dodecyl-3-methylimidazolium hexafluorophosphate [DoMIm][PF_6]

^{1}H-NMR (400 MHz, $CDCl_3$, 298 K) δ [ppm]: 8.65 (s, 1H), 7.23 (t, 1H), 7.20 (t, 1H), 4.16 (t, 2H), 3.95 (s, 3H), 1.88 (t, 2H), 1.35 – 1.22 (m, 18H), 0.88 (t, *J* = 6.6 Hz, 3H).
^{13}C-NMR (101 MHz, $CDCl_3$, 298 K) δ [ppm]: 136.29, 123.76, 122.12, 50.24, 36.44, 32.06, 30.22, 29.76, 29.67, 29.52, 29.47, 29.11, 26.36, 22.81, 14.25.
^{19}F-NMR (376 MHz, $CDCl_3$, 298 K) δ [ppm]: - 135.53, - 139.93, - 144.32, - 148.72, - 153.12.
^{31}P-NMR (161 MHz, $CDCl_3$, 298 K) δ [ppm]: - 71.64, - 73.53.
Elemental analysis calcd. (%) for $C_{16}H_{31}F_6N_2P$: C 48.48, H 7.88, F 28.76, N 7.07, P 7.81; found: C 48.40, H 7.84, N 6.93.

2. Aggregation studies

2.1. Distribution of the ILs in the reaction phases and solubility measurements

^{1}H-qNMR-Spectroscopy experiments were conducted to examine the distribution of the ILs between the organic and aqueous phases. Sample preparation was done by dissolving 50 µL of the sampled phases in 950 µL $CDCl_3$ (organic) and 950 µL D_2O (aqueous). Potassium hydrogen phthalate (Sigma Aldrich) dissolved in D_2O was used as the external standard for all ^{1}H-qNMR NMR-measurements. The used spectrometer was a 600 MHz Bruker Avance II+ at the Northern Bavarian NMR Center at the University of Bayreuth, Germany which was also used for the following solubility determinations. Saturated solutions of SAILs in 50 wt.% aq. H_2O_2 at room temperature and 50 °C were prepared and either centrifuged at 3000 rpm for 5 minutes for the liquid ILs or filtered through a syringe filter (Chromafil Xtra PTFE-20/13, 0.2 µm, 13 mm diameter by Machery-Nagel GmbH & Co. KG) for the solid samples. 200 µL of clear sample IL-solutions were diluted with 200 µL of D_2O and the residual peroxide was decomposed with a platinum wire (1 cm, 0.3 mm, Roth). Following removal of the water, the residue was extracted with 800 µL of CDCl3 yielding the prepared sample. For sample preparation regarding solubility measurements in organic solvents, 50 µL of the saturated and syringe-filtered SAIL solution in the chosen solvent as well as 540 µL of $CDCl_3$ were mixed for the sample.

Table S1. Solubility of various SAILs in 50 wt.% hydrogen peroxide at room temperature (RT) and 50 °C.

SAIL	Solubility (mM)	
	RT	50 °C
[DoMIM][NTf_2]	0.33	1.7
[DoMIM][BF_4]	>200	
[OMIM][NTf_2]	2.6	6.0
[OMIM][BF_4]	>1700	
[DoMIM][PF_6]	0.81	3.1
[HexDeMIM][NTf_2]	0.63	0.55

Table S2. Solubility of various SAILs in cyclooctene and cyclooctene oxide.

SAIL	Solubility (mM)	
	RT	60 °C (cyclooctene oxide)
[DoMIM][NTf_2]	9.5	>240
[DoMIM][BF_4]	16.5	
[DoMIM][PF_6]	7.8	
[OMIM][NTf_2]	14.7	
[HexDeMIM][NTf_2]	12.7	

2.2. CMCs of the SAILs

2.2.1. Tensiometric CMC determinations

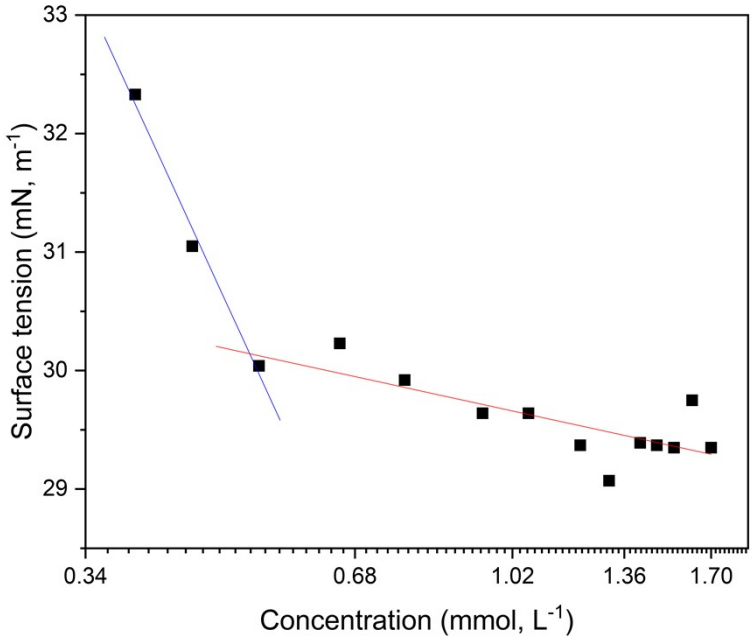

Figure S1. Surface tension in dependence of the [DoMIM][NTf_2] concentration in 50 % hydrogen peroxide at 50 °C.

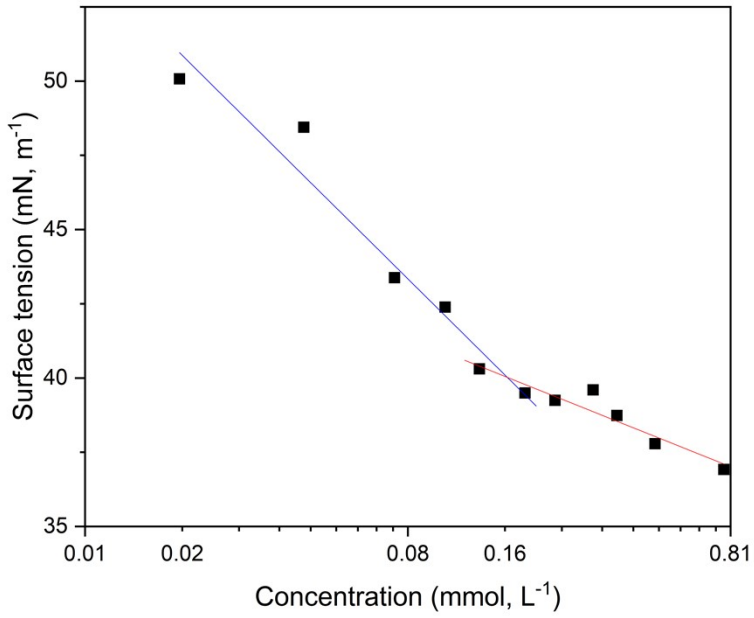

Figure S2. Surface tension in dependence of the [DoMIM][PF_6] concentration in 50 % hydrogen peroxide at room temperature.

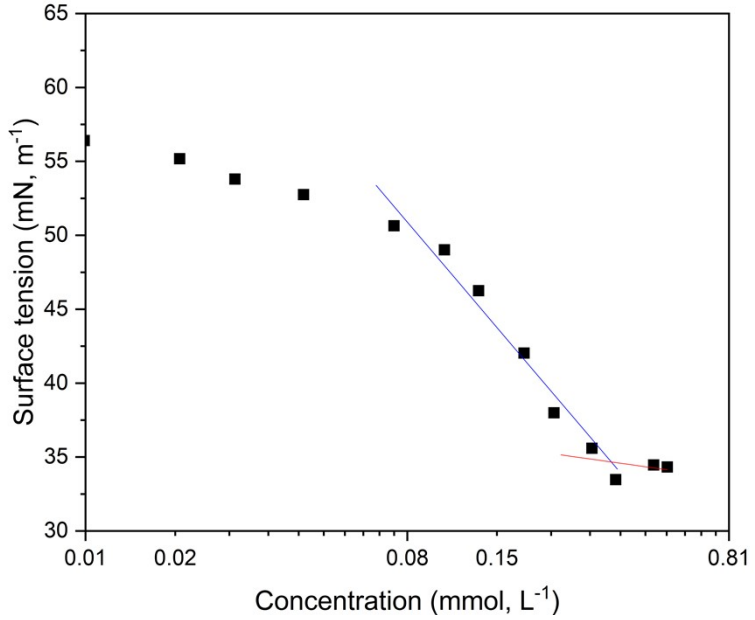

Figure S3. Surface tension in dependence of the [DoMIM][PF_6] concentration in 50 % hydrogen peroxide at 50 °C.

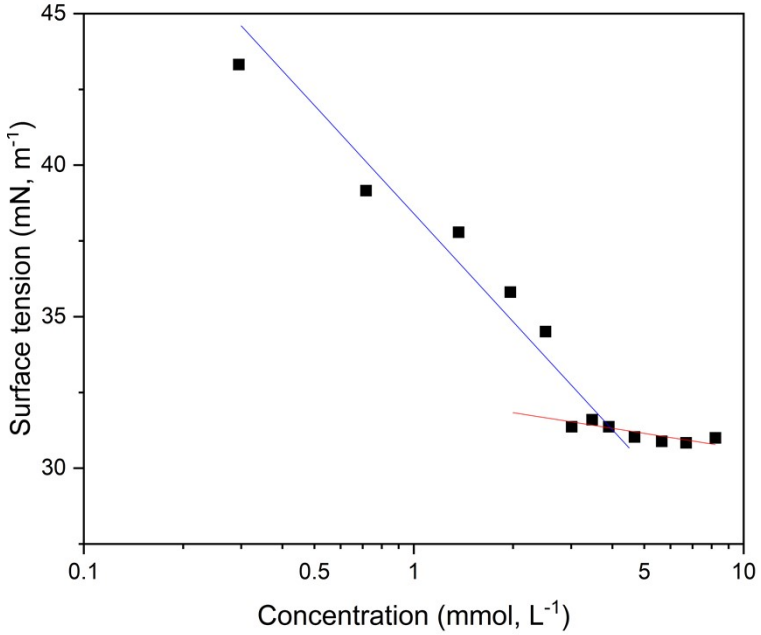

Figure S4. Surface tension in dependence of the [DoMIM][BF_4] concentration in 50 % hydrogen peroxide at room temperature.

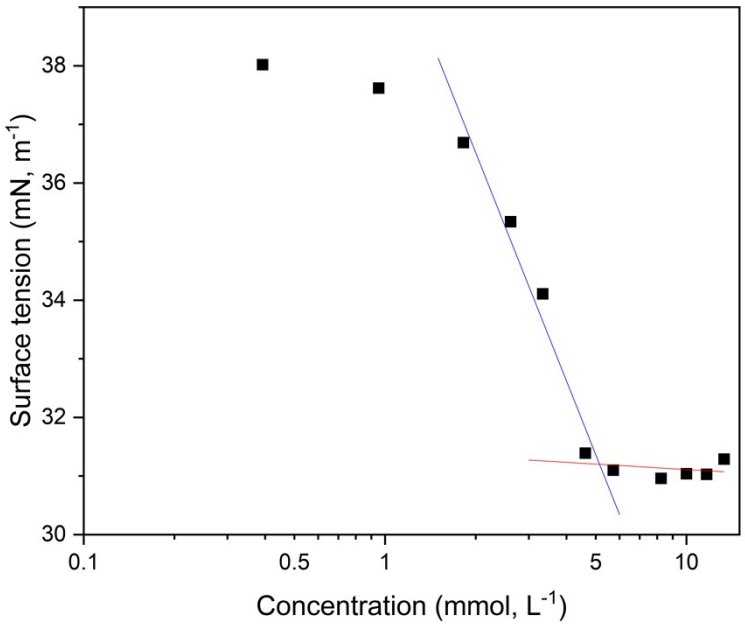

Figure S5. Surface tension in dependence of the [DoMIM][BF_4] concentration in 50 % hydrogen peroxide at 50 °C.

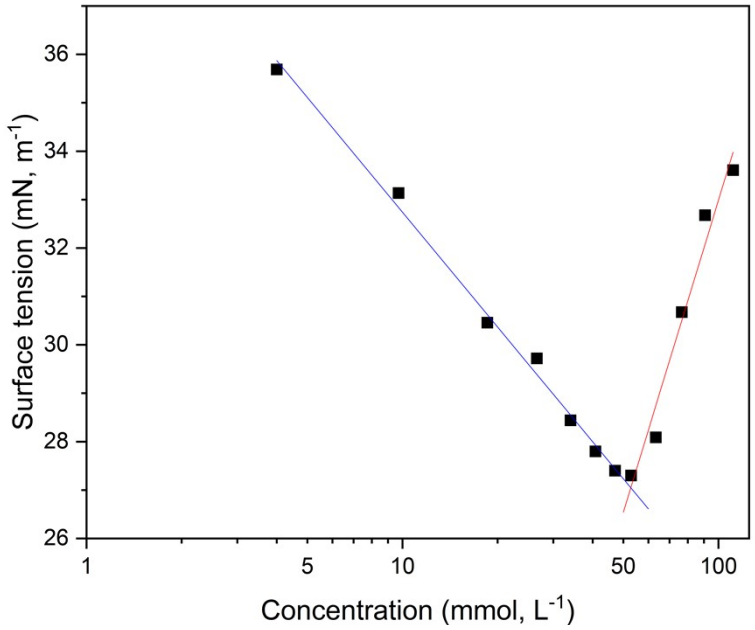

Figure S6. Surface tension in dependence of the [OMIM][BF_4] concentration in 50 % hydrogen peroxide at room temperature.

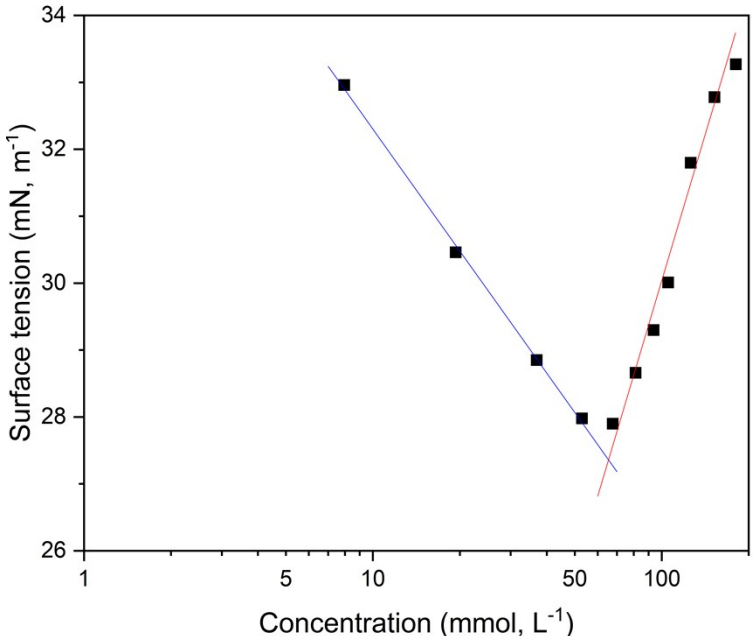

Figure S7. Surface tension in dependence of the [OMIM][BF_4] concentration in 50 % hydrogen peroxide at 50 °C.

Table S3. Tensiometric CMC of various [AlkylMIM][NTf_2] ionic liquids in 50 % hydrogen peroxide at reaction temperature (50 °C).

SAIL	CMC (mM, 50 °C)
[DoMIM][NTf_2]	0.52
[OMIM][NTf_2]	4.01
[HexDeMIM][NTf_2]	n.a.*
[BMIM][NTf_2]	n.a.*

*The CMC could not be determined in the concentration range from 0.03-20 mmol/L.

Table S4. Tensiometric CMC of different [RMIM][BF_4/PF_6] (R = Do, O) ionic liquids in 50 wt.% aqueous hydrogen peroxide.

SAIL	CMC (mM)	
	RT	50 °C
[DoMIM][PF_6]	0.16	0.35
[DoMIM][BF_4]	4.0	5.15
[OMIM][BF_4]	52	65

2.2.2. Conductometric CMC determinations

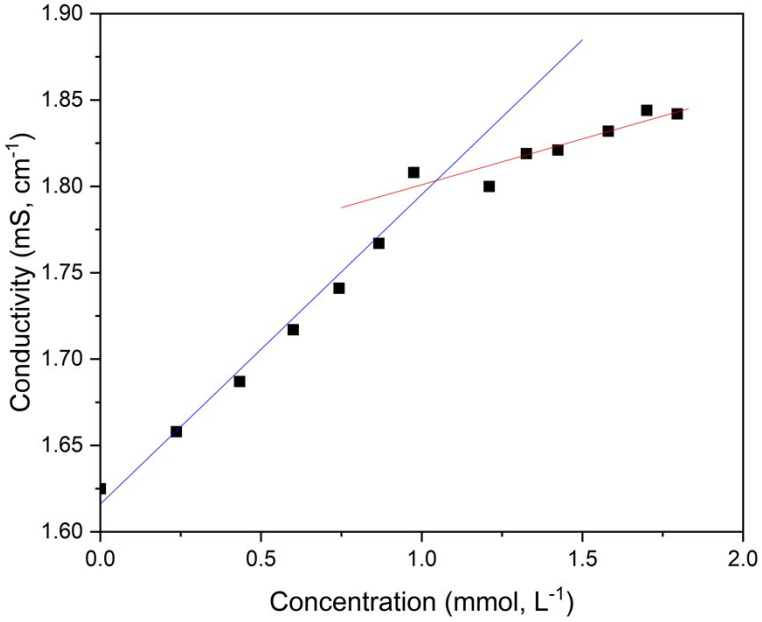

Figure S8. Conductivity in dependence of the [OMIM][NTf_2] concentration in 50 % hydrogen peroxide at room temperature.

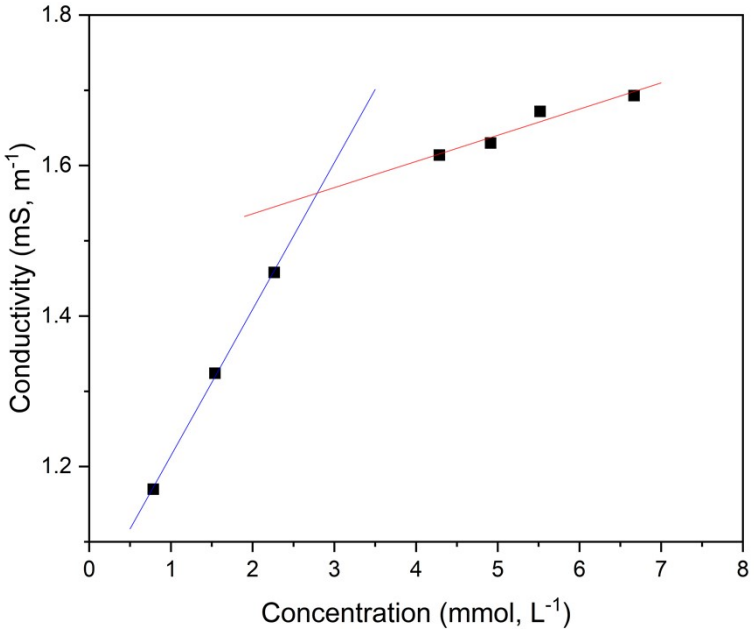

Figure S9. Conductivity in dependence of the [DoMIM][BF_4] concentration in 50 % hydrogen peroxide at room temperature.

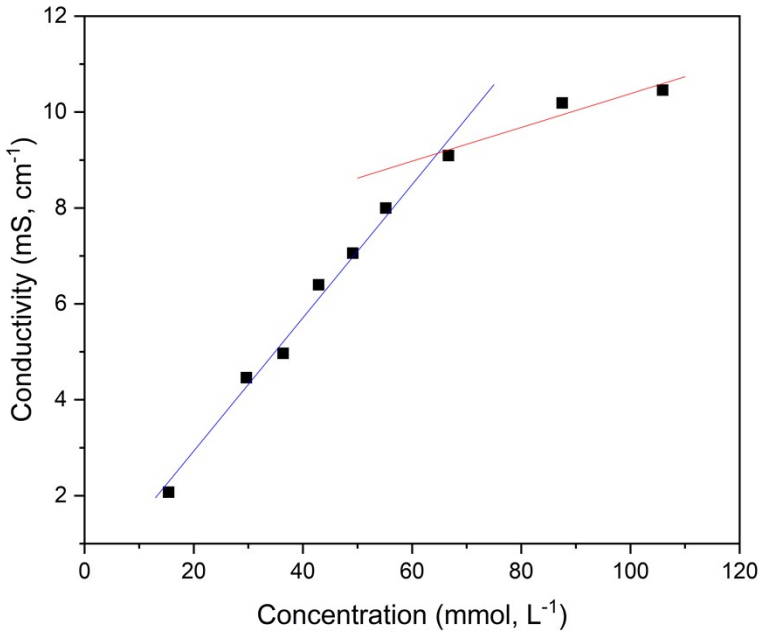

Figure S10. Conductivity in dependence of the [OMIM][BF_4] concentration in 50 % hydrogen peroxide at room temperature.

Table S5. Conductometric CMC of various SAILs in 50 % hydrogen peroxide at room temperature (RT) compared with respective tensiometric data and conductometrically-measured references.

SAIL	Conductometric (mM)	Tensiometric (mM)
[OMIM][NTf_2]	1.1	
[DoMIM][BF_4]	2.8 (2.3)[1]	4.0
[OMIM][BF_4]	65 (47)[1]	53

2.3. Micelle size distribution via DLS

2.3.1. Size distribution of [BF_4]-ILs micelles in aqueous media

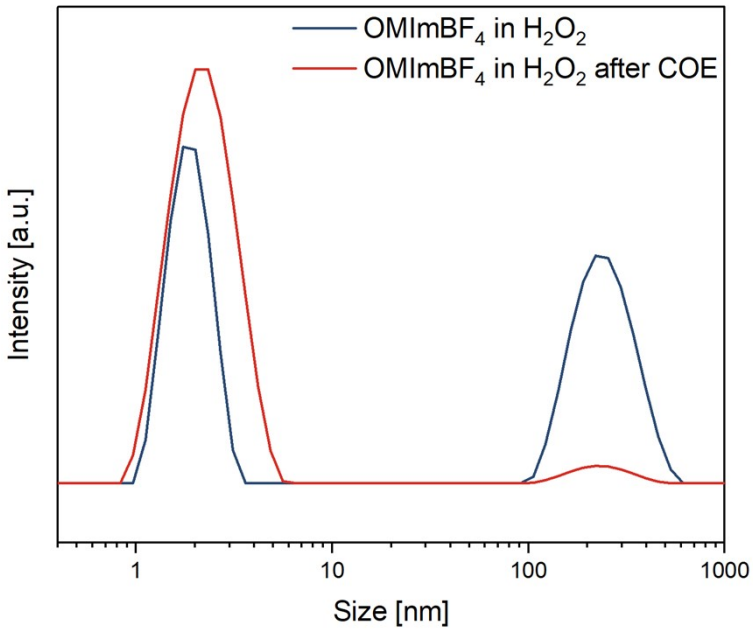

Figure S11. DLS measurements of [OMIm][BF_4] in H_2O_2 (357 mmol/L) at room temperature prior and after treatment with COE.

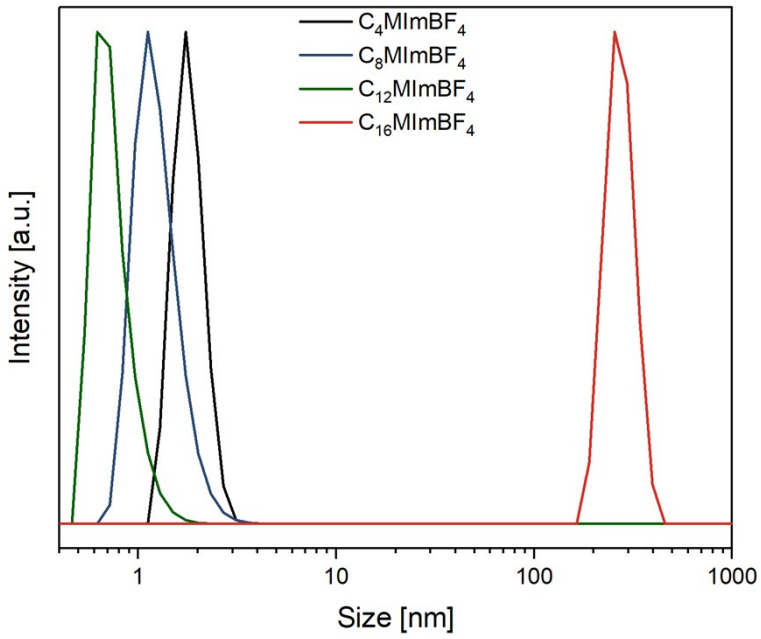

Figure S12. DLS measurements of [BF_4]-ILs with different chain lengths in H_2O_2 (357 mmol/L for C_4 and C_8 and saturated solutions (<357 mmol/L) for C_{12} and C_{16}) at room temperature.*

*Note that in case of [HexDeMIm][BF_4] the small primary micelles are not detected by DLS, most likely due to the significant difference in their scattering intensities compared to their spherical agglomerates.

2.4. Micelle size characterization via TEM

2.4.1. Micelles of [NTf_2]-ILs micelles in water

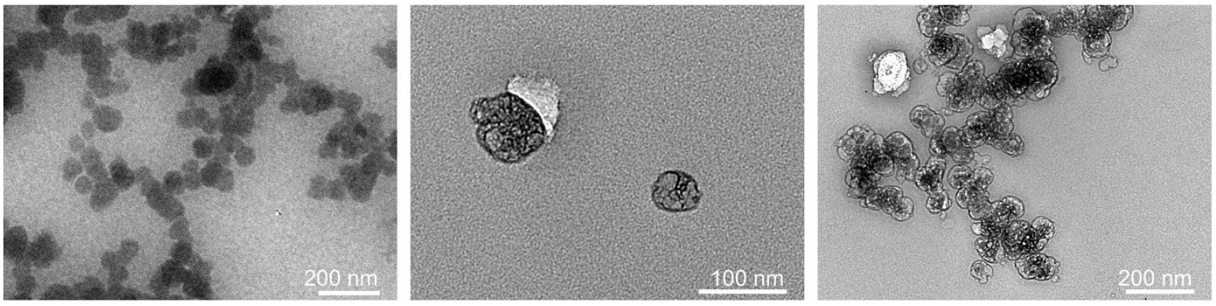

Figure S13. TEM pictures of [OMIm][NTf_2] micelles in an aqueous solution (saturated solution in water).

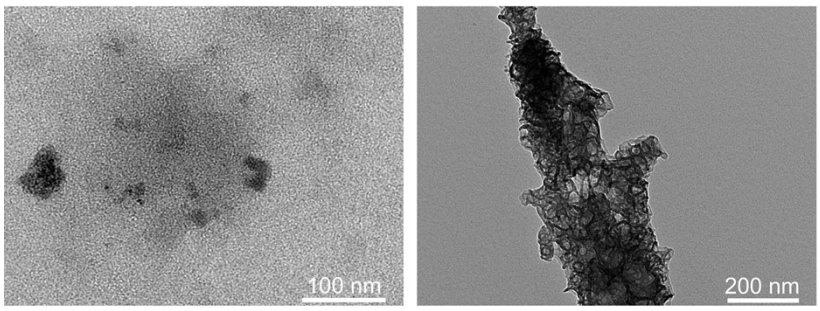

Figure S14. TEM pictures of [DoMIm][NTf_2] micelles in an aqueous solution (saturated solution in water).

2.4.2. Micelles of [BF_4]-ILs micelles in water

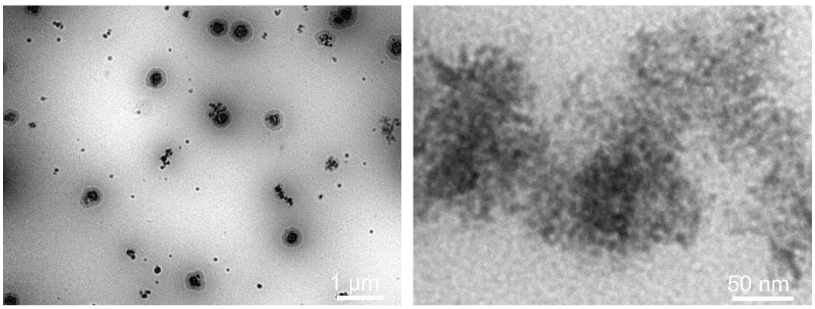

Figure S15. TEM pictures of [BuMIm][BF_4] micelles in an aqueous solution (356 mmol/L in water).

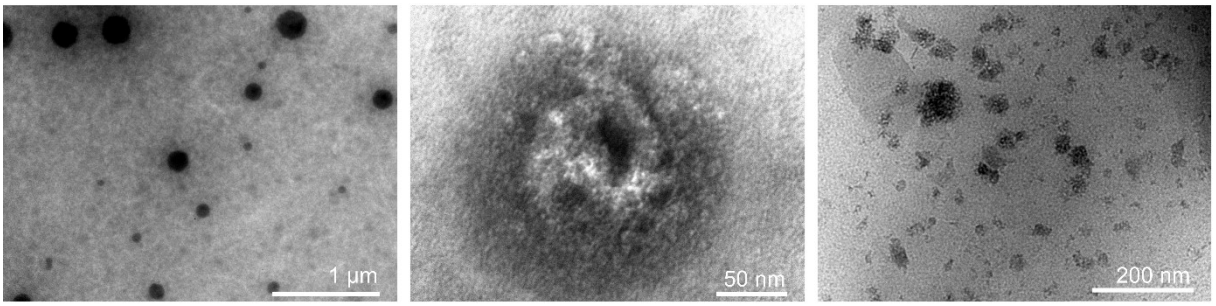

Figure S16. TEM pictures of [OMIm][BF_4] micelles in an aqueous solution (356 mmol/L in water).

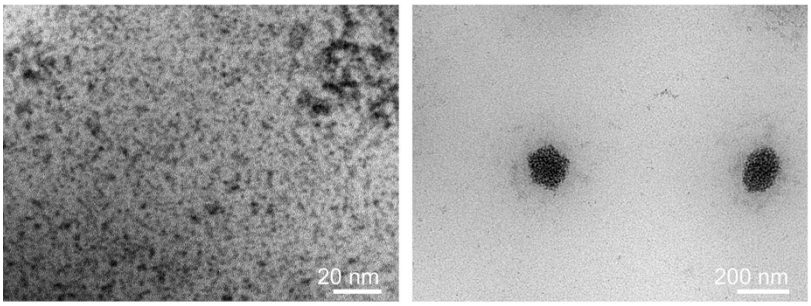

Figure S17. TEM pictures of [DoMIm][BF_4] micelles in an aqueous solution (saturated solution in water).

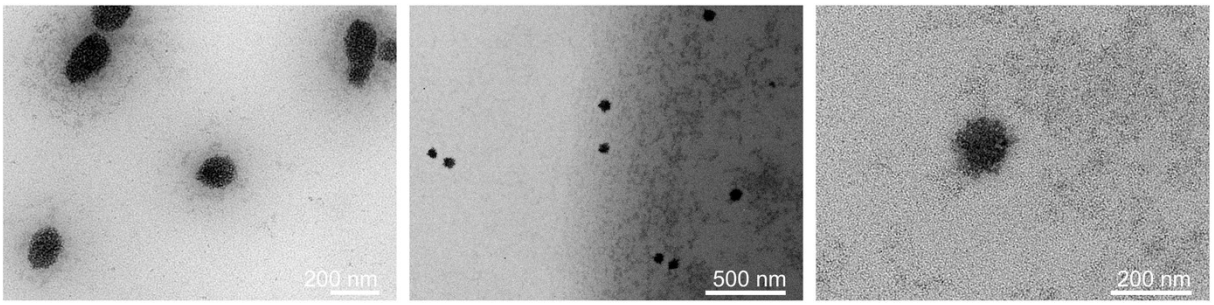

Figure S18. TEM pictures of [DoMIm][BF_4] micelles in an aqueous solution (2.7 mmol/L in water).

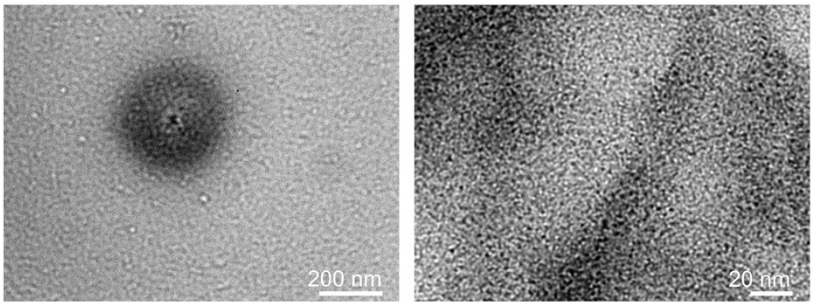

Figure S19. TEM pictures of a [HexDeMIm][BF_4] micelles in an aqueous solution (saturated solution in water).

2.4.3. Micelles of [PF_6]-ILs micelles in water

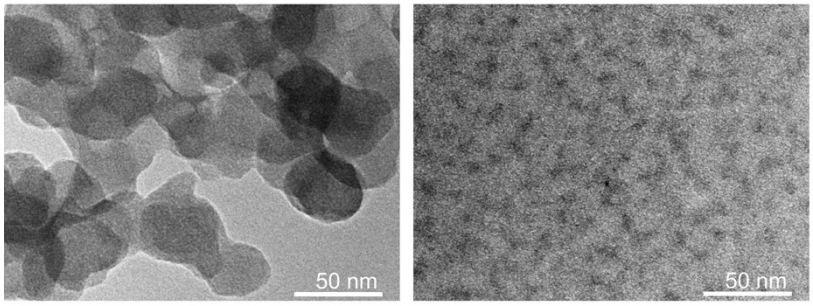

Figure S20. TEM pictures of a [DoMIm][PF_6] micelles in an aqueous solution (saturated solution in water).

2.5. ATR-IR measurements

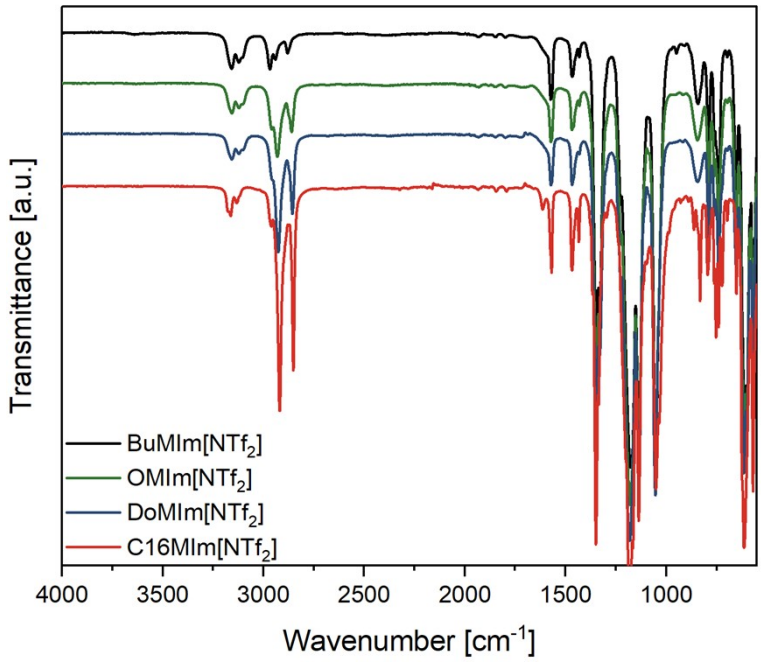

Figure S21. ATR-IR measurement of [NTf_2]-ILs with different chain lengths.

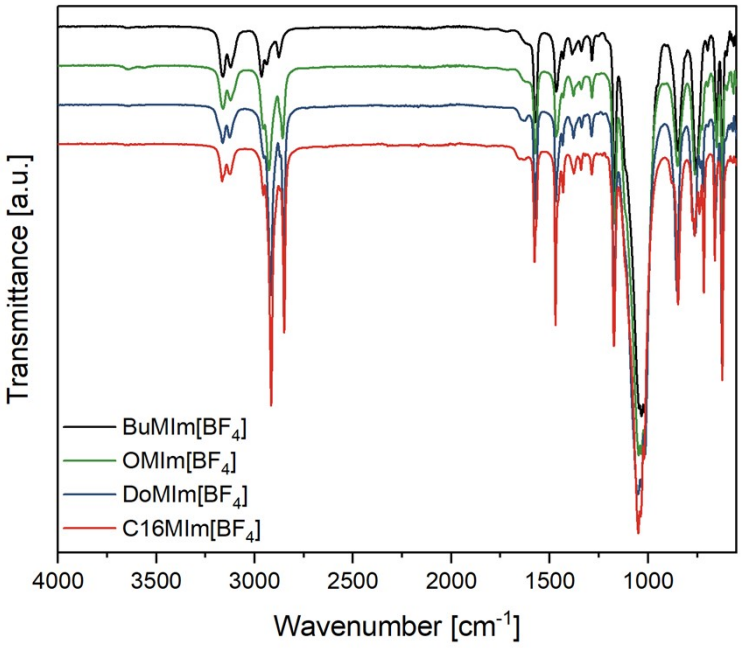

Figure S22. ATR-IR measurement of $[BF_4]$-ILs with different chain lengths.

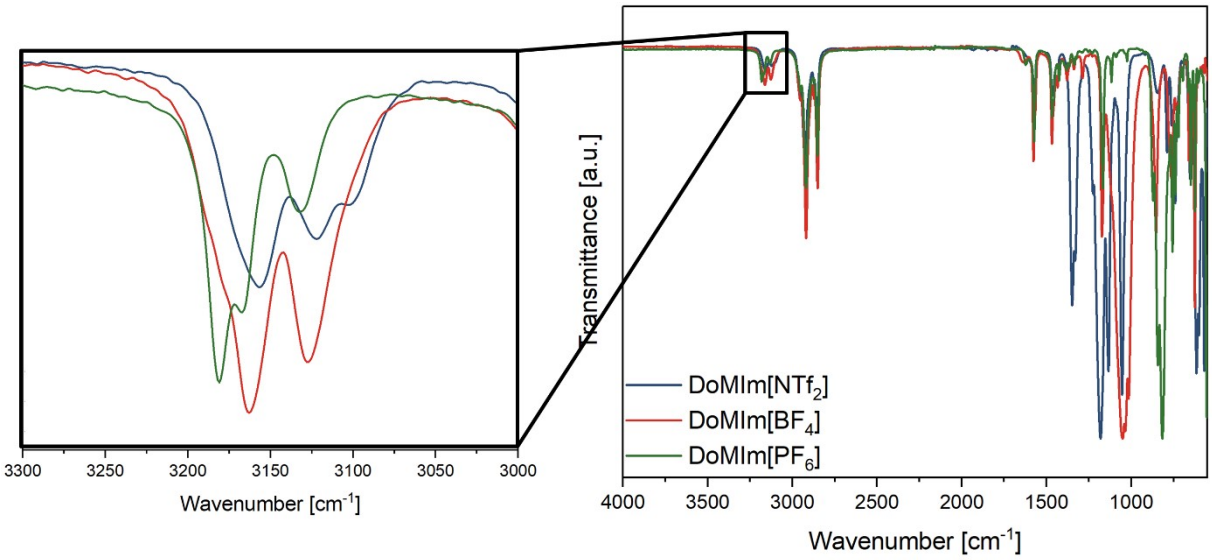

Figure S23. ATR-IR measurement of [DoMIm][X] with X = NTf_2, BF_4 and PF_6.

3. Epoxidation Catalysis

Catalytic experiments were conducted in a magnetically-stirred 10mL glass reactor at ambient pressure with an attached, water-cooled reflux condenser. Heating was done with a temperature-controlled oil bath at 50 °C. Prior to each experiment, the COE, the IL, the tungstate as well as the PPA were stirred and preheated to the desired temperature in the glass reactor. Unless mentioned otherwise, 20 mmol (2.2 g) of COE as the organic phase, 0.74 mmol of IL, 0.5 mmol (0.17 g) of Na_2WO_4 dihydrate and 1 mmol (0.16 g) of PPA were used. To start the experiment, 25 mmol (1.4 g, 1.7 mL) of H_2O_2, the aqueous phase, was added to the reactor. The stirring speed was kept constant at 1250 rpm and the reaction time was 1.5 hours. Samples for the GC-analysis were drawn at intervals of 5 min – 20 min from the stirred reaction mixture through a septum using a syringe and dissolved in 1 mL of heptane in a 1.5 mL vial. To study the phase behavior of the ILs, 0.3 mL samples of the organic and aqueous phases were drawn with a syringe after complete phase separation and kept for further analysis via ^{1}H-qNMR-Spectroscopy.

Note that in all cases where cyclooctene was epoxidized the selectivity values >99%.

3.1. Scaled-up Epoxidation Catalysis with [OMIM][NTf_2]

To illustrate the phase transfer of SAILs, the catalytic run using [OMIM][NTf_2] was scaled up and performed in a Fisher Porter bottle with a volume of 90 ml (see Figure S18). All employed chemicals were scaled up by the factor of ten. Reaction parameters, except an adjusted stirring to 1000 rpm, were maintained as previously described.

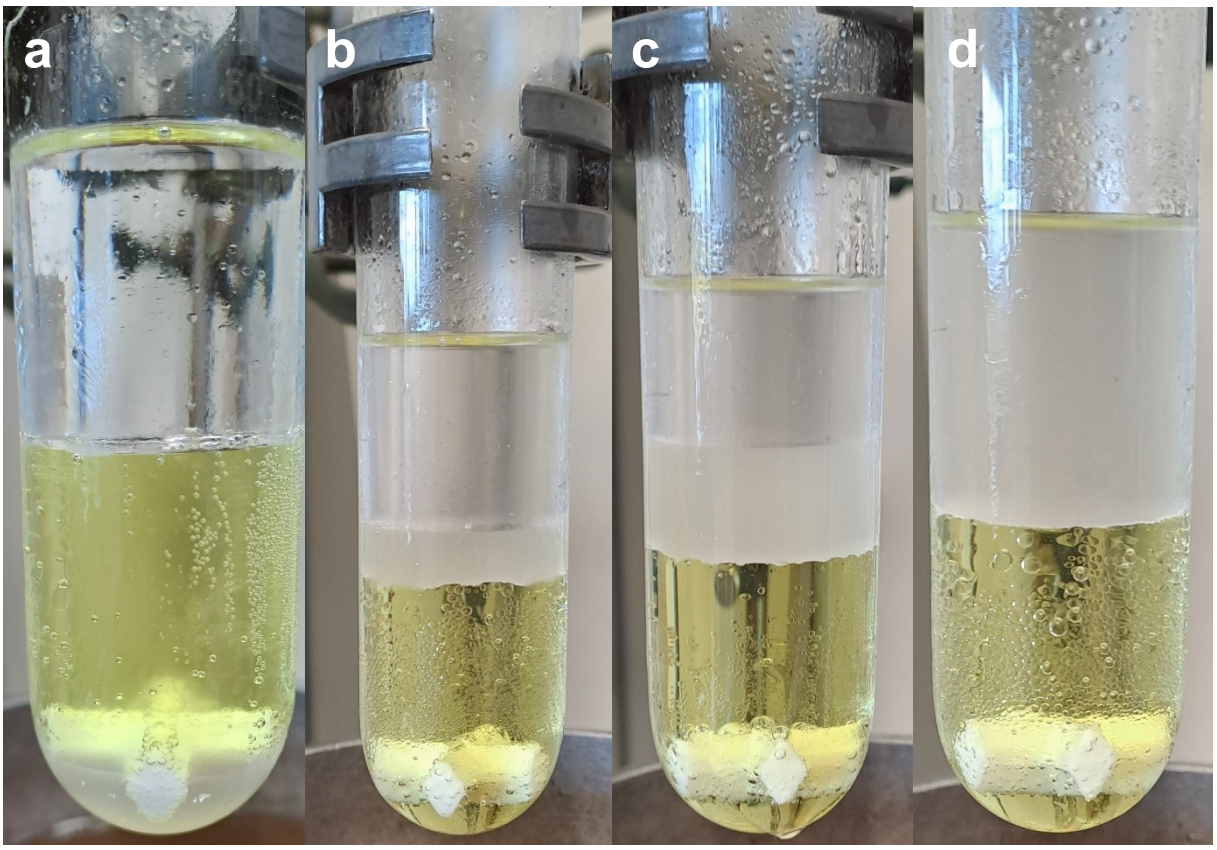

Figure S24. Pictures of the scaled up epoxidation of cyclooctene with [OMIm][NTf_2] and Na_2WO_4 after phase separation at certain time intervals. a) start of the reaction b) after 30 min c) after 60 min d) after 180 min.*

*Note that with increasing reaction time and cyclooctene oxide content [OMIm][NTf_2] is transferred to the organic phase. At low product concentrations the IL forms a third middle phase, which is rendered to a homogeneous organic phase (COE/COO/SAIL) during the course of the reaction.

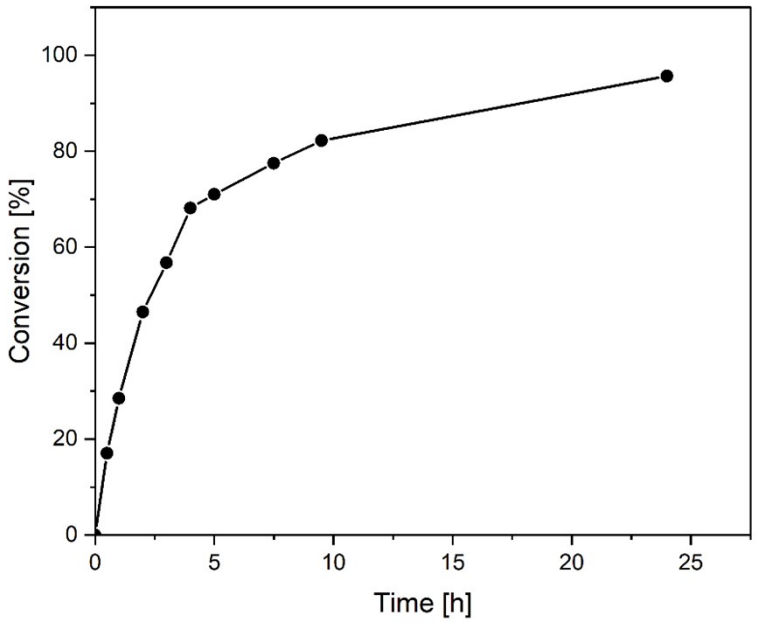

Figure S25. Conversion of cyclooctene in the scaled up epoxidation catalysis via salt metathesis with [OMIm][NTf_2] and Na_2WO_4. Reaction conditions: 50 °C, 1000 rpm, 5 mol% [OMIm][NTf_2], 2.5 mol% Na_2WO_4, 5 mol% PPA, 13 ml cyclooctene (10 mmol, 1 equiv.) and 14 ml 50 wt% aqueous H_2O_2 (25 mmol, 2.5 equiv.).

3.2. Epoxidation Catalysis with $[BF_4]$- and $[PF_6]$-SAILs

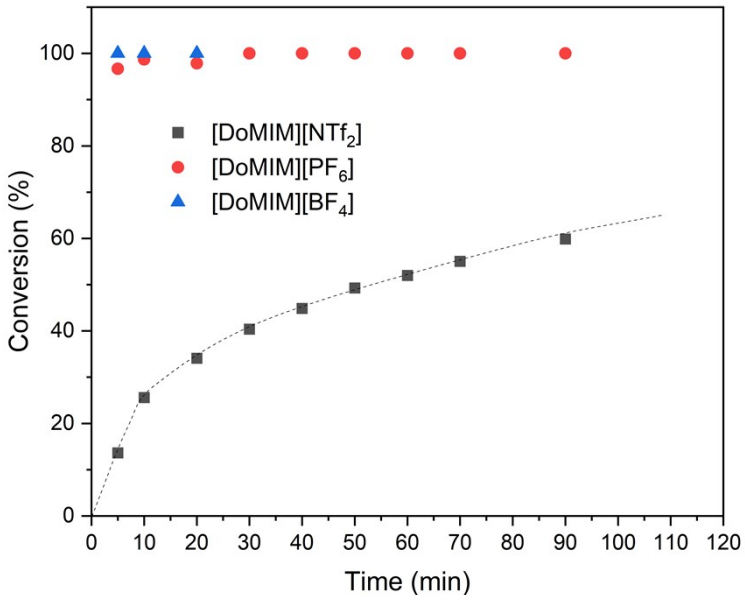

Figure S26. Conversion of COE to COO with various [DoMIM][X] SAILs (X = NTf_2^-, PF_6^-, BF_4^-) and sodium tungstate. Reaction conditions: 50 °C, 1250 rpm, 3.7 mol% SAIL (0.74 mmol, 3.7 equiv.), 165 mg sodium tungstate dihydrate (0.5 mmol, 2.5 equiv.), 158 mg PPA (1 mmol, 5.0 equiv.), 2.593 mL COE (20 mmol, 100 equiv.) and 1.423 mL 50 wt.% aq. H_2O_2 (25 mmol, 125 equiv.).

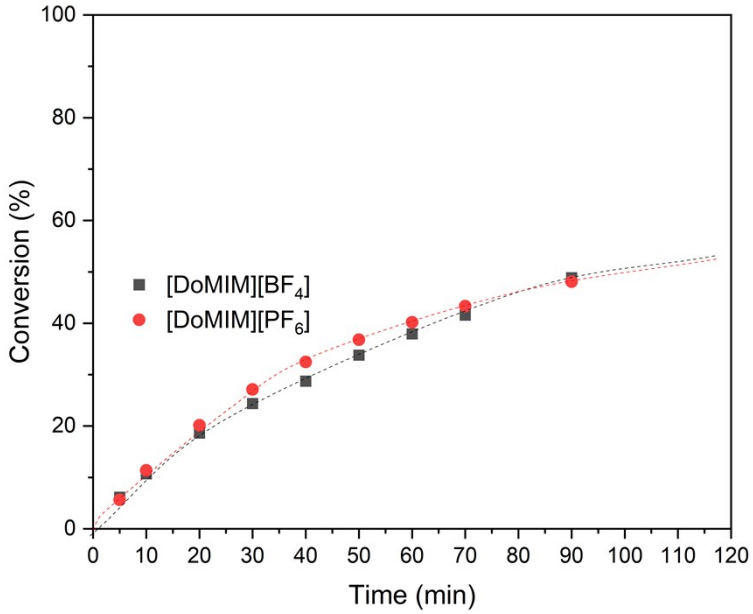

Figure S27. Conversion of COE to COO with composite [DoMIM][BF_4]/[DoMIM][PF_6] and sodium tungstate. Reaction conditions: 50 °C, 1250 rpm, 0.11 mol% SAIL (0.05 mmol, 0.25 equiv.), 8.2 mg sodium tungstate dihydrate (0.025 mmol, 0.125 equiv.), 7.9 mg PPA (0.05 mmol, 0.25 equiv.), 2.593 mL COE (20 mmol, 100 equiv.) and 1.423 mL 50 wt.% aq. H_2O_2 (25 mmol, 125 equiv.).

3.3. Epoxidation Catalysis with [NTf_2]-SAILs

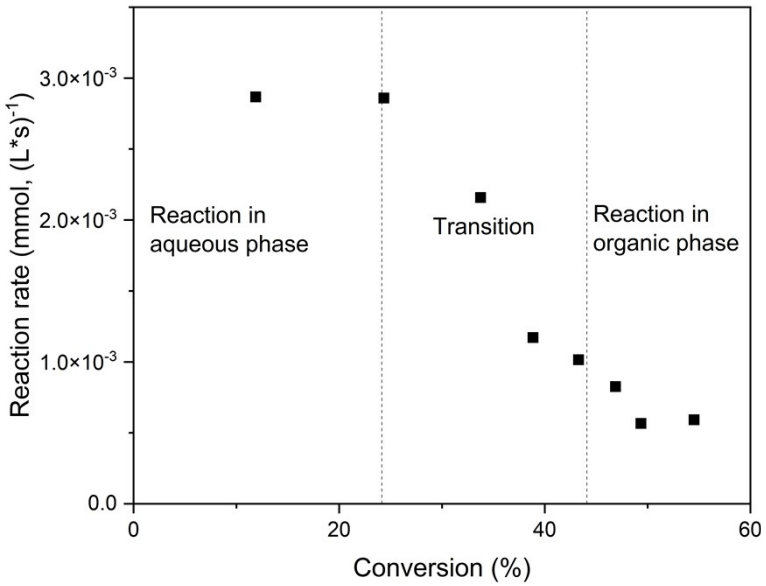

Figure S28. Reaction rate plotted against the Conversion of COE to COO with [OMIM][NTf_2] and sodium tungstate. Reaction conditions: 50 °C, 1250 rpm, 3.7 mol% SAIL (0.74 mmol, 3.7 equiv.), 165 mg sodium tungstate dihydrate (0.5 mmol, 2.5 equiv.), 158 mg PPA (1 mmol, 5.0 equiv.), 2.593 mL COE (20 mmol, 100 equiv.) and 1.423 mL 50 wt.% aq. H_2O_2 (25 mmol, 125 equiv.).

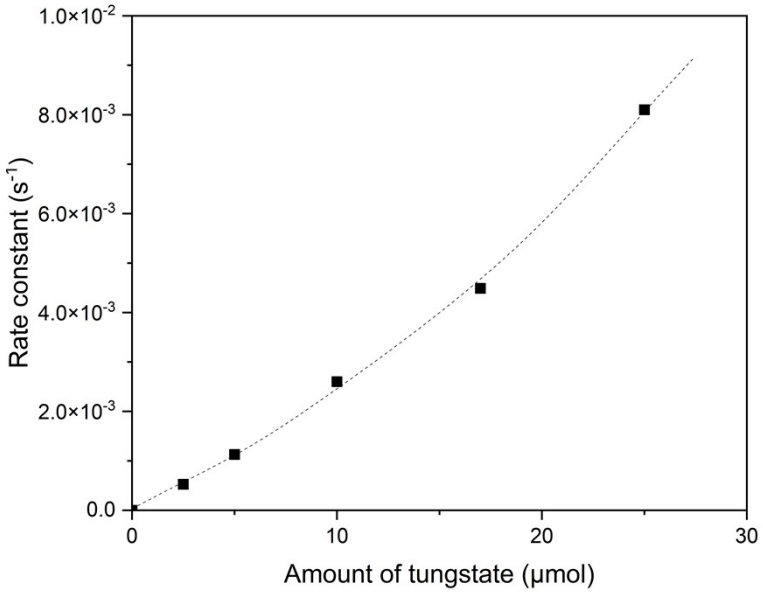

Figure S29. Rate constant of COE to COO epoxidation with composite [DoMIM][BF_4] and varying amounts of sodium tungstate. Reaction conditions: 50 °C, 1250 rpm, 17.0 mg SAIL (0.05 mmol, 0.25 equiv.), 0-8.2 mg sodium tungstate dihydrate (0-0.025 mmol, 0-0.125 equiv.), 7.9 mg PPA (0.05 mmol, 0.25 equiv.), 2.593 mL COE (20 mmol, 100 equiv.) and 1.423 mL 50 wt.% aq. H_2O_2 (25 mmol, 125 equiv.).

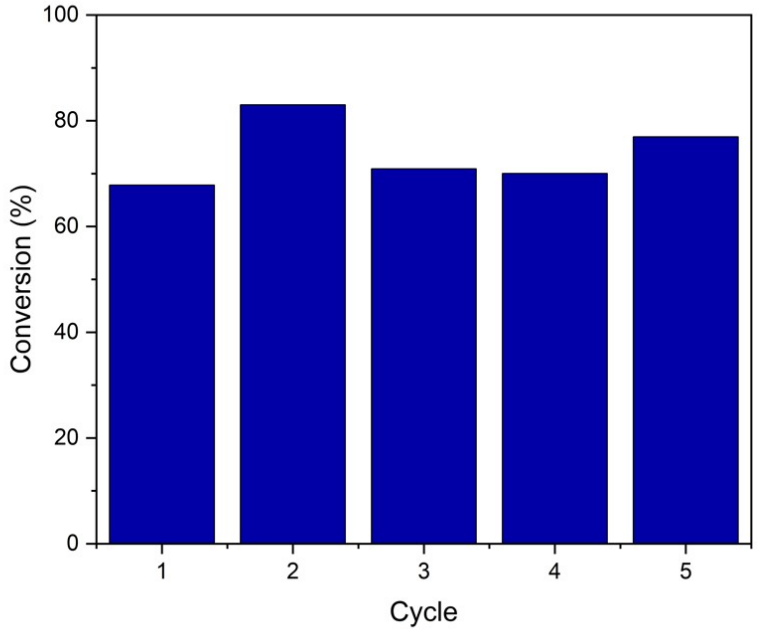

Figure S30. Five reaction/recycling cycles of [DoMIM][NTf_2]/Na_2WO_4/PPA-catalyzed COE epoxidations. No activity decline could be detected. Reaction conditions: 50 °C, 1250 rpm, 400 mg SAIL (0.74 mmol, 3.7 equiv.), 165 mg sodium tungstate dihydrate (0.5 mmol, 2.5 equiv.), 158 mg PPA (1 mmol, 5.0 equiv.), 2.5 mL COE (20 mmol, 100 equiv.) and 1.423 mL 50 wt.% aq. H_2O_2 (25 mmol, 125 equiv.), 2h reaction time.

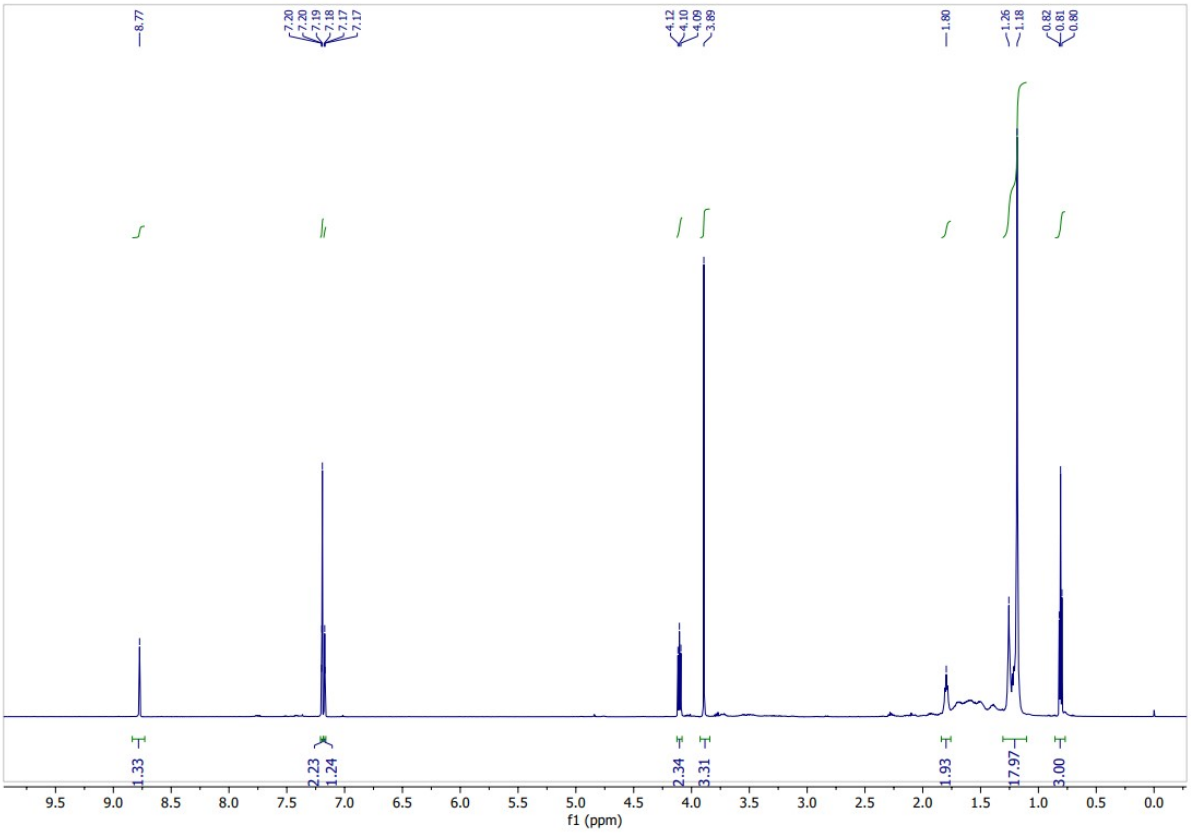

Figure S31. ^{1}H-NMR (600 MHz, 300 K, $CDCl_3$) of the [DoMIM][NTf_2]-SAIL after all five cycles.

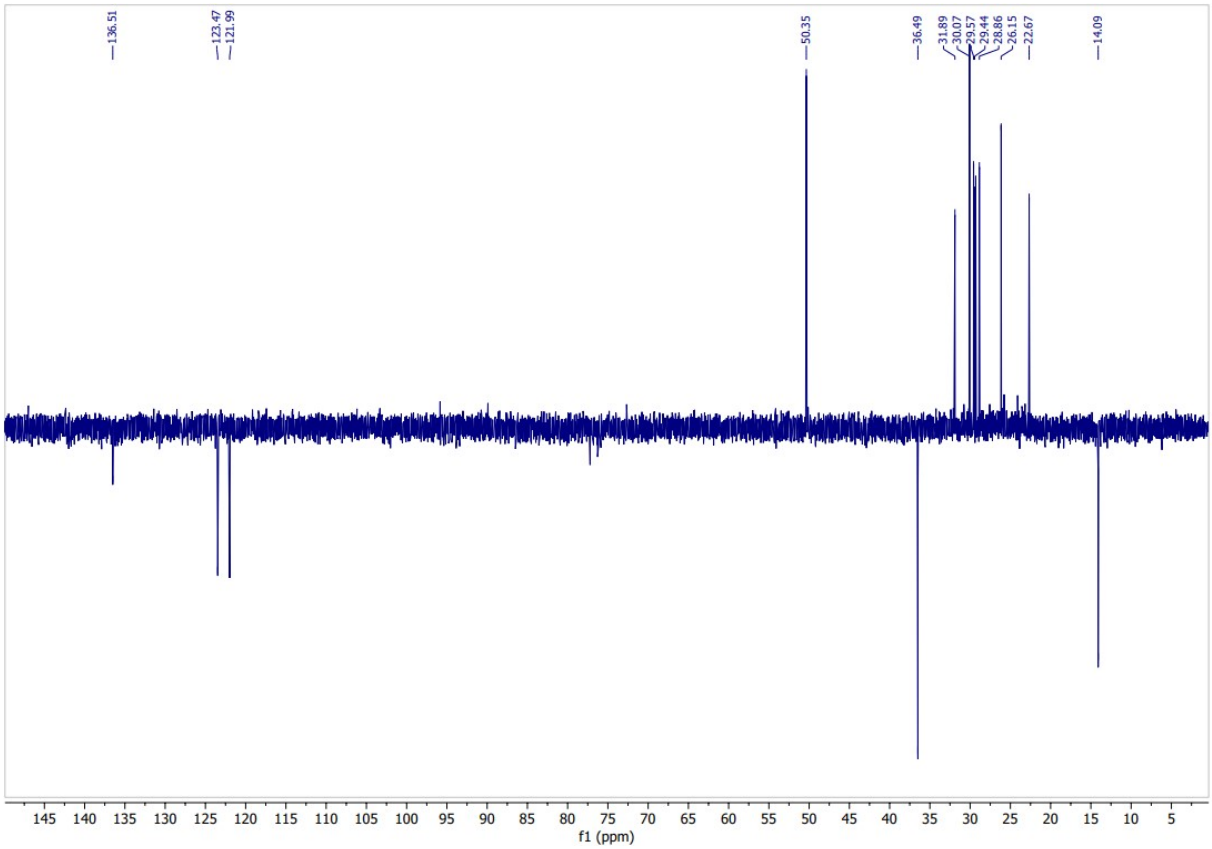

Figure S32. ^{13}C-NMR (DEPT135, 151 MHz, 300 K, $CDCl_3$) of the [DoMIM][NTf_2]-SAIL after all five cycles.

4. References

1. B. Zehner, F. Schmidt, W. Korth, M. Cokoja and A. Jess, *Langmuir* **2019**, *35*, 16297-16303.
2. F. Schmidt, B. Zehner, W. Korth, A. Jess and M. Cokoja, *Catal. Sci. Technol.* **2020**, *10*, 4448
3. P. Bonhôte, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram and M. Grätzel, *Inorg. Chem.* **1996**, *35*, 1168.