Supporting Information

Catalysis at room temperature ionic liquid|water interface: H_2O_2 generation

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1. Chemicals and Materials

Decamethylferrocene (DMFc, 97%, ABCR), methyltrimethoxysilane (97%, ABCR), room temperature ionic liquids 1-butyl-3-methylimidazoliumbis(trifluoro-methylsulfonyl)imide (C_4mim N$(Tf)_2$, Iolitec) and 1-decyl-3-methylimidazolium bis(trifluoro-methylsulfonyl)imide (C_{10}mim N$(Tf)_2$, IoLitec), $HClO_4$, (70%, Fluka), KI (pure p.a., POCh), (KPF_6 (99% ABCR), NaCl (>99.99%, Fluka), $NaClO_4$ (>99%, Fluka), NaSCN (purum, Fluka), KNO_3 (pure p.a., POCh), and KBr (pure p.a., POCh), Amplex UltraRed (Life Technologies), graphite powder (d < 20 μm, CAS 7782-42-5, Sigma-Aldrich) and argon gas (Multax) were used as received. Horseradish peroxidase was for Sigma-Aldrich. Aqueous solutions were prepared with demineralized and filtered water from ELIX system (Millipore).

2. Apparatus and Procedures

Shake flask experiments were done as follows: Samples 2 and 3 were fixed on a Vortex mixer for 30 min. During this treatment an emulsion was formed and the samples were centrifuged to separate the phases. For starch and iodide–based H_2O_2 detection, the aqueous phase was sampled and 200 μL of 0.1 M KI and 10% starch solution was added.

Cyclic voltammetry and square-wave voltammetry (SWV) were recorded with a Biologic Bipotentiostat SP-300. Carbon paste electrode (CPE), silver-silver chloride electrode (Ag|AgCl|3M KCl) and a Pt wire were used as working, reference and counter electrodes, respectively. All measurements were performed at room temperature (23 ± 2 °C).

Carbon paste electrode (CPE) of 3 mm diameter was prepared by filling a carbon paste rotating disc electrode tip (ALS Co. Ltd) with RTIL-based carbon paste. The latter was prepared from 200 μl of 5 mM DMFc in C_4mim N$(Tf)_2$) or C_{10}mim N$(Tf)_2$ and 250 mg

graphite powder (20 μm diameter from Sigma-Aldrich) by grinding in a mortar. It was polished on printing paper (80 g/m^2) before use.

SECM measurements were carried out with a CHI900B SECM workstation (CH Instruments). Pt microelectrodes were made by sealing a Pt wire (25 μm diameter, Goodfellow, England) using PC-10 micropipette puller (Narishige) into borosilicate glass capillaries, polished with P2000 grit silicon carbide sand paper and 50 μm alumina slurry. $Hg|Hg_2SO_4|K_2SO_{4(sat)}$ was used as reference electrode to avoid possible contribution of Cl^- oxidation to the measured oxidation current. The Pt microelectrode in the aqueous phase served as SECM probe and its position was controlled by stepper motors in the X, Y and Z directions.

Optical micrographs were obtained by DMIRE2 microscope in inverted configuration (Leica Microsystems GmbH). Samples were excited with a tungsten lamp with a dichroic filter set for excitation within the wavelength range 500 – 600 nm. The detection was made for wavelength between 575−650 nm by a DC152QC-FI sCMOS camera (scientific CMOS, Andor Technology) attached to the third optical port of the microscope. The objective was a HC PL FLUOTAR with 10× magnification (numerical aperture NA = 0.3, Leica). In the presence of H_2O_2, Amplex UltraRed is oxidized to a strongly fluorescent resorufin derivative. The recorded intensities were converted to a false colour image.

The optical readout experiments with fluorogenic substrate were performed with glass pipettes (orifice diameter ca. 100 μm) prepared with a PC-10 micropipette puller (Narishige) from borosilicate glass (1.5 mm inner diameter, 1.7 mm outer diameter with filament from Harvard Apparatus) using 5 mm pulling distance. In order to avoid penetration of aqueous electrolyte and to produce a stable liquid|liquid interface, the inner part of pipette was hydrophobized by silanization with vapors of methyltrimethoxysilane.

3. Flask experiments

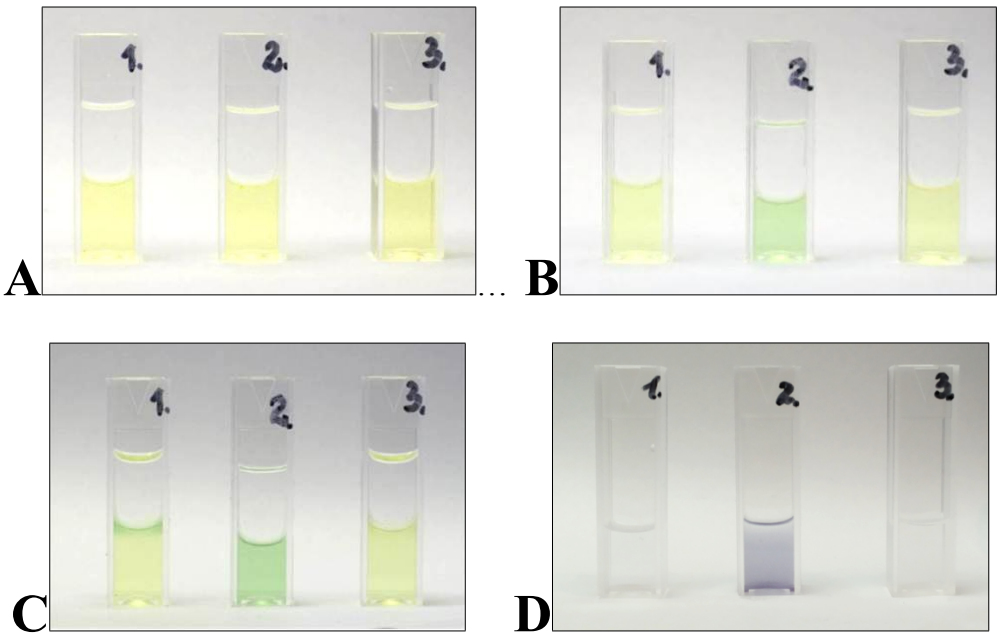

Fig. S1 Results of shake flask experiments. Cuvette 1 and 2 contained 0.1 M aqueous $HClO_4$ (upper phase) and 5 mM DMFc solution in C_{10}mim $N(Tf)_2$ (bottom phase). Cuvette 3 contained 0.1 M aqueous $NaClO_4$ (upper phase), 5 mM DMFc solution in C_{10}mim $N(Tf)_2$ (bottom phase). Photographs taken before (A) and after (B) 30 min and (C) 24 h of experiment. Cuvette 1 was not shaken. Photograph (D) shows decanted aqueous phase after addition of 200 µL 0.1 M KI and 10% starch aqueous solution.

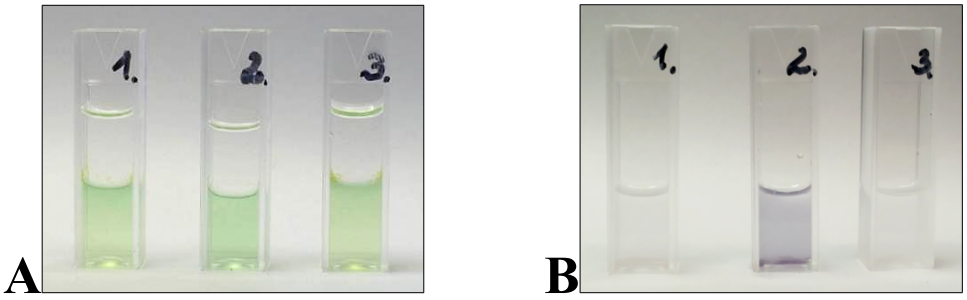

Fig. S2 Results of shake flask experiments. Cuvette 1 and 2 contained 0.1 M aqueous $HClO_4$ (upper phase), 5 mM DMFc solution in C_4mim $N(Tf)_2$ (bottom phase). Cuvette 3 contained 0.1 M aqueous $NaClO_4$ (upper phase), 5 mM DMFc solution in C_4mim $N(Tf)_2$ (bottom phase). Photographs were taken after (A) 24 h of experiment. Cuvette 1 was not shaken. Photograph (B) shows decanted aqueous phase after addition of 200 µL 0.1 M KI and 10% starch aqueous solution.

4. **SECM Approach curves to RTIL based carbon paste electrode**

SECM approach curves to a CPE made of graphite particles and DMFc solution in C_{10}mim $N(Tf)_2$ were recorded in order to provide further evidences of H_2O_2 generation and regeneration of the electron donor. The anodic tip current corresponding to H_2O_2 oxidation reaches its highest values when DMFc is present in RTIL and the potential of the CPE allows DMFc regeneration. The H_2O_2 flux is considerably lower than in similar experiments performed with a CPE made of the less viscous RTIL (compare figure 2A in the main text).

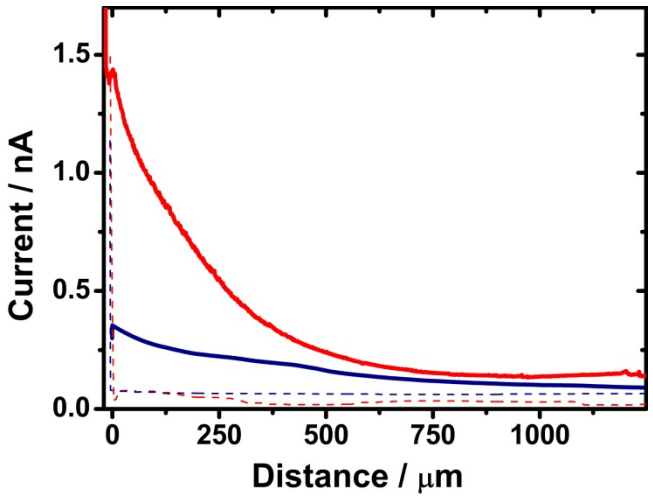

Fig. S3 The approach curves to a CPE prepared from 5 mM DMFc solution in C_{10}mim $N(Tf)_2$ immersed in 0.1 M aqueous $HClO_4$. Tip potential 0.6 V. CPE unbiased (blue solid), and CPE potential -0.85 V (red solid). Dotted curves correspond to analogous experiments in the absence of DMFc in C_{10}mim $N(Tf)_2$.

5. **Cyclic voltammetry with RTIL based carbon paste electrode**

The comparison of cyclic voltammograms obtained with a CPE prepared with DMFc solution in in C_4mim $N(Tf)_2$ and C_{10}mim $N(Tf)_2$ as a binder was performed to confirm the electrochemical redox reaction of DMFc and to check the possibility of leakage of $DMFc^+$ produced in electrochemical reaction. Indeed the stability of voltammograms indicates that $DMFc^+$ remains in the RTIL phase in CPE. The difference between the current values for voltammetric peak reflects the difference in the viscosity of RTILs.

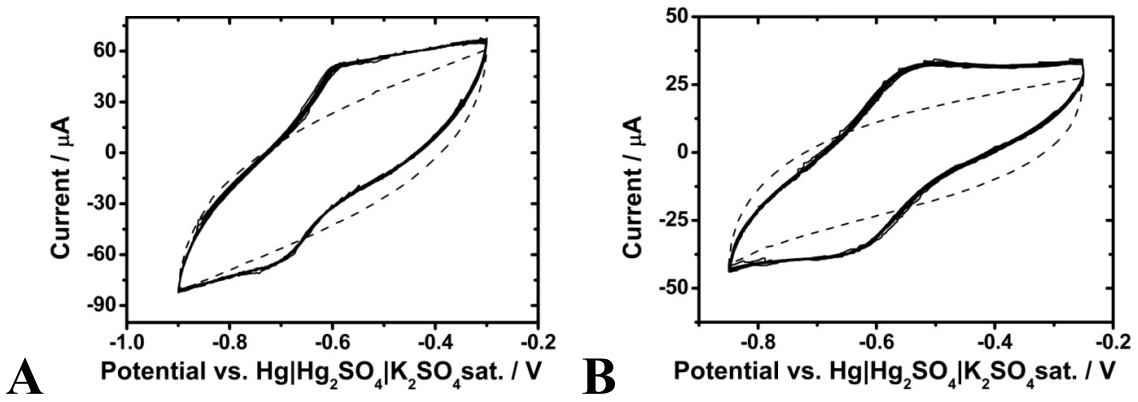

Fig. S4 Cyclic voltammetry (solid lines, first 50 scans) obtained with CPE prepared from 5 mM DMFc solution in (A) C_4mim $N(Tf)_2$ and (B) C_{10}mim $N(Tf)_2$ immersed in 0.1 M aqueous $HClO_4$. The dashed lines were obtained in the absence of DMFc, Scan rate 50 mV s^{-1}.

6. Square wave voltammetry with RTIL carbon paste electrode

Square Wave Voltammetry with a CPE prepared with DMFc solution in in C_4mim $N(Tf)_2$ and C_{10}mim $N(Tf)_2$ as a binder in a number of aqueous electrolytes was performed to estabilish the mechanism of the electrode process. It was found that peak potential is independent of the anion of the aqueous electrolyte within the measurement error. This indicates that the electrooxidation of DMFc is not followed by anion insertion from the aqueous phase. Considering the stability of the cyclic voltammograms during subsequent scanning it was concluded that electrochemical formation of $DMFc^+$ cation is followed by C_4mim^+ or $C_{10}mim^+$ cation transfer to the aqueous phase to maintain electroneutrality of the phase (see eq. 2 in the main manuscript).

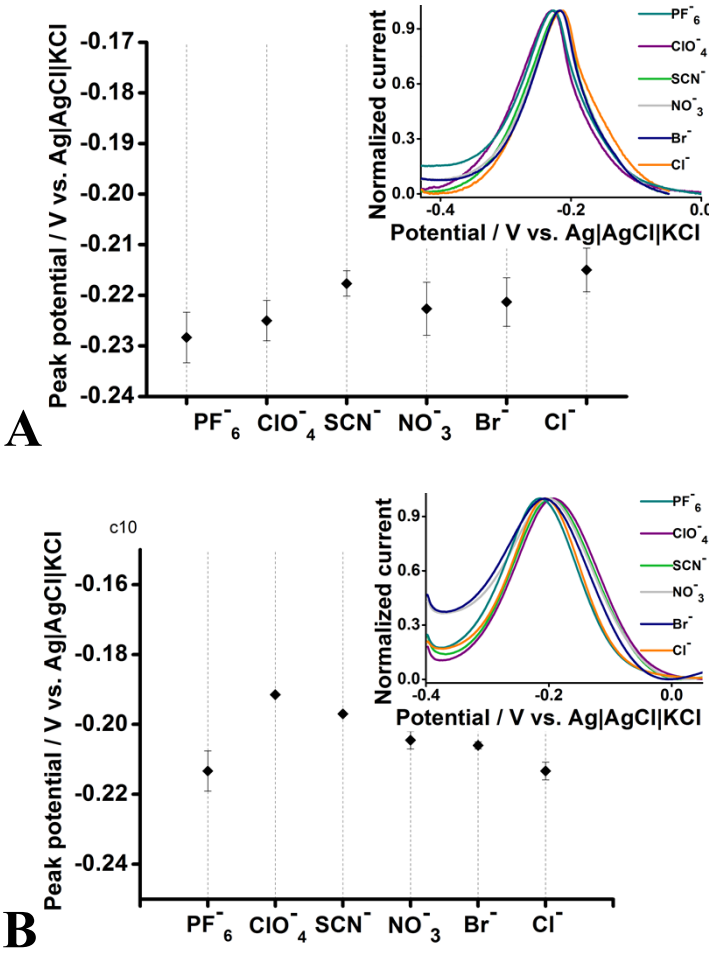

Fig. S5 The dependence of peak potential obtained with CPE prepared from 5 mM DMFc solution in (A) C_4mim $N(Tf)_2$ and (B) C_{10}mim $N(Tf)_2$ immersed in aqueous 0.1 M electrolyte solution as a function of anion type present in aqueous phase. Inset shows square wave voltammograms used as a source of data points. Parameters for SWV were: frequency 8 Hz, step potential 1 mV, amplitude 50 mV.

7. Optical image of the RTIL filled pipette

The position, shape, and stability of RTIL|aqueous solution interface was checked by optical examination of the pipette filled with C_4mim $N(Tf)_2$ and immersed in 0.1 M $HClO_4$. A pipette with its narrowest interior recessed from its orifice was chosen in order to be able to observe the liquid junction without obscuration by the contour of the pipette orifice. Liquid junction is formed at the place of its surface energy minimum. Optical micrographs in figure S6 show a stable and flat interface. No meniscus shape folding of the junction is seen. A stable liquid|liquid interface is only possible, when the inner wall of the pipette is hydrophobised.

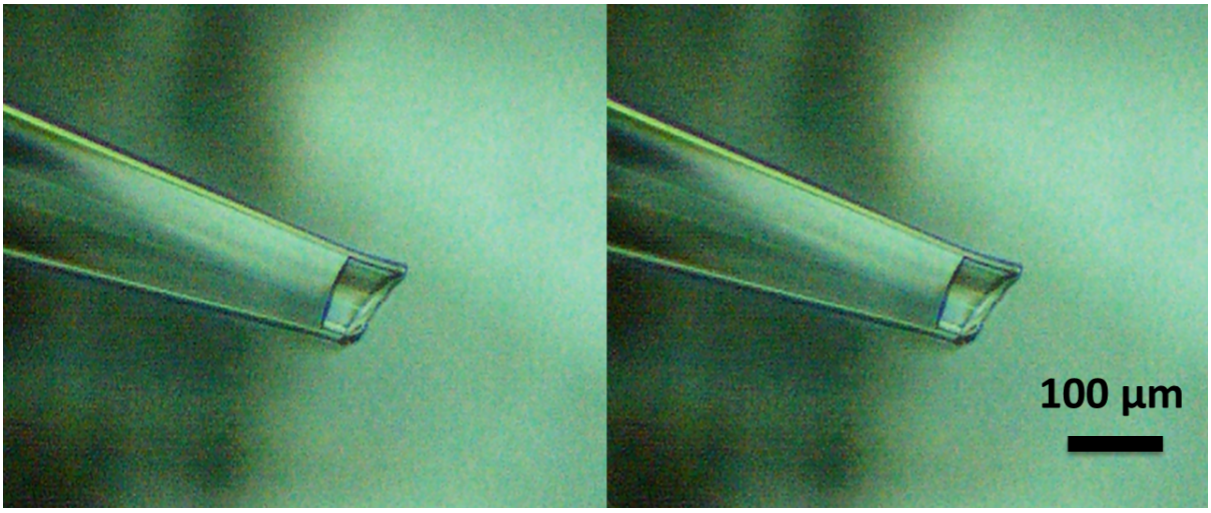

Fig. S6 Optical image of a glass pipette filled withC_4mim $N(Tf)_2$ immersed in 0.1 M aqueous $HClO_4$. The image on the left was recorded immediately after immersion and the image on the right 30 s later.

8. Fluorescence emission from C_{10}mim $N(Tf)_2$-filled capillary

A pipette with hydrophobised interior filled with 5 mM DMFc in C_{10}mim $N(Tf)_2$ was immersed in aqueous acidic solution containing a compound (Ampex RedUltra) whose oxidised form is fluorescent. It is oxidised specifically by H_2O_2 in the presence of horseradish peroxidase. The micrographs in figure S7 represent the fluorescence intensity in a false colour scale. It is clearly seen that the fluorophore is produced at the RTIL|aqueous solution interface and is extracted into hydrophobic RTIL. The fluorescence intensity and expansion rate of fluorescent zone towards pipette bulk is lower than in case of less viscous RTIL (compare figure 3C in the main article).

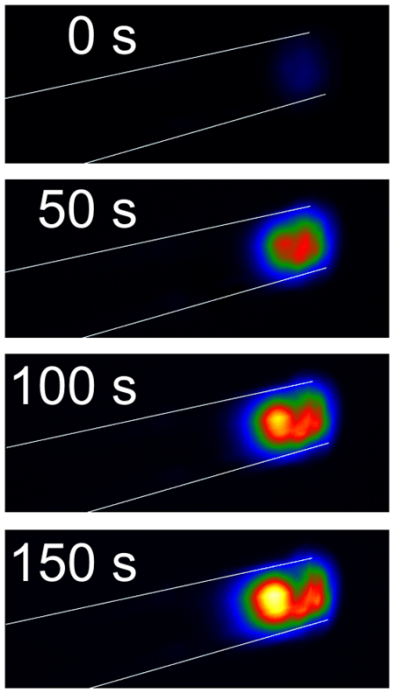

Fig. S7 Fluorescence micrographs of the area close to the pipette tip. The light intensity scale runs from black to yellow. The pipette containing 5 mM DMFc solution in C_{10}mim $N(Tf)_2$ was immersed in 0.1 mg ml^{-1} HRP and 30 μM Amplex UltraRed® in 0.1 M aqueous $HClO_4$. Time elapsed after pipette immersion in aqueous phase is marked on every image. Image dimensions are 725×300 μm^2. The pipette contour is marked by white lines.