Supporting Information

Separating Convective from Diffusive Mass Transport Mechanisms in Ionic Liquids by Redox Pro-fluorescence Microscopy

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Supplementary Figures

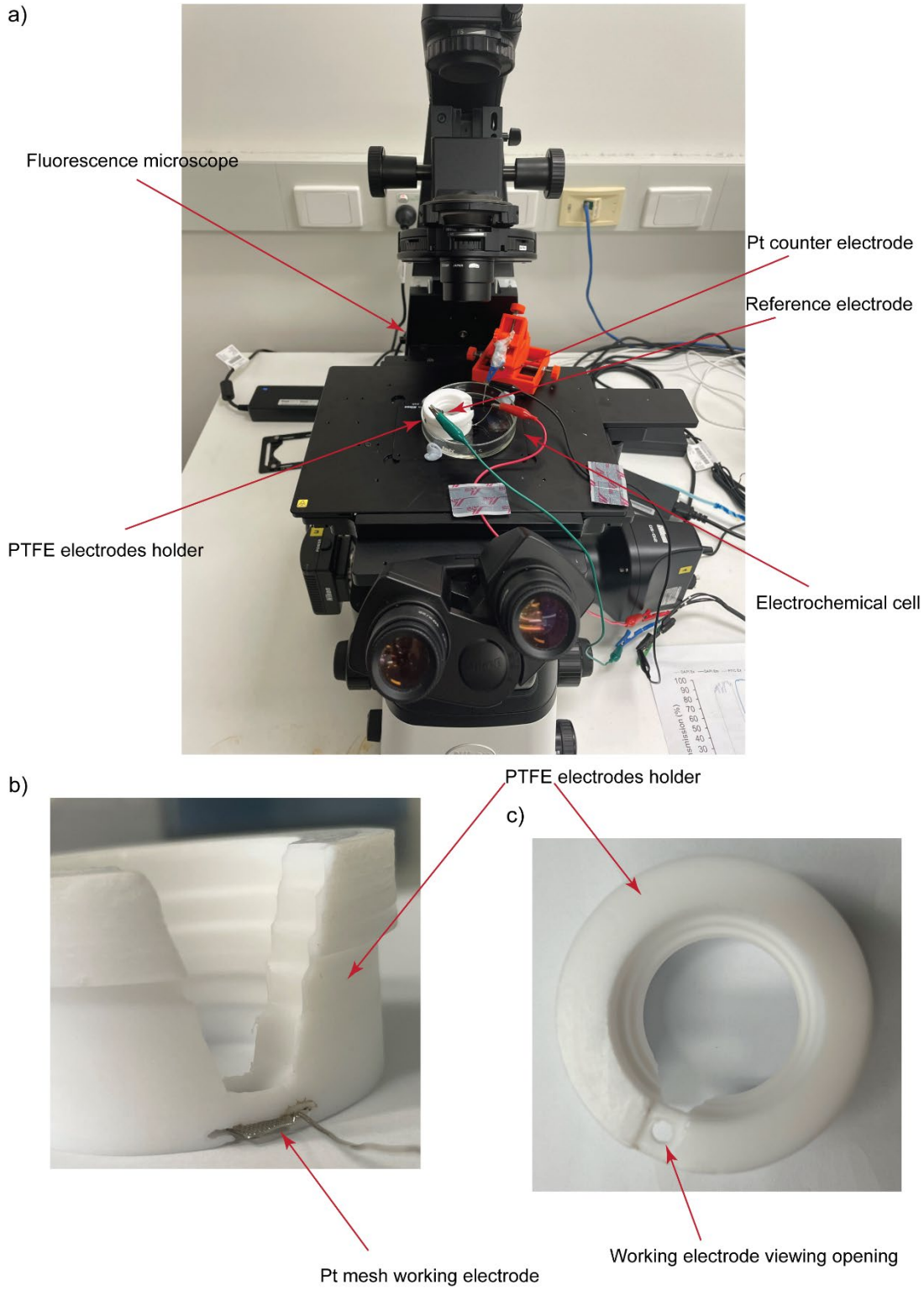

Figure S1. Experimental setup for the collection of ECL and fluorescence time-resolved micrographs. (a) A Petri dish, resting on the sample stage of an inverted fluorescence microscope, is loaded with the electrolytic solution and fitted with a custom PTFE electrodes holder. (b) Side view of the PTFE electrode holder showing the horizontal slot for the Pt mesh working electrode. The platinum mesh position is sitting parallel and ~2 mm away from the bottom glass surface of the Petri dish. (c) Bottom view of the PTFE holder.

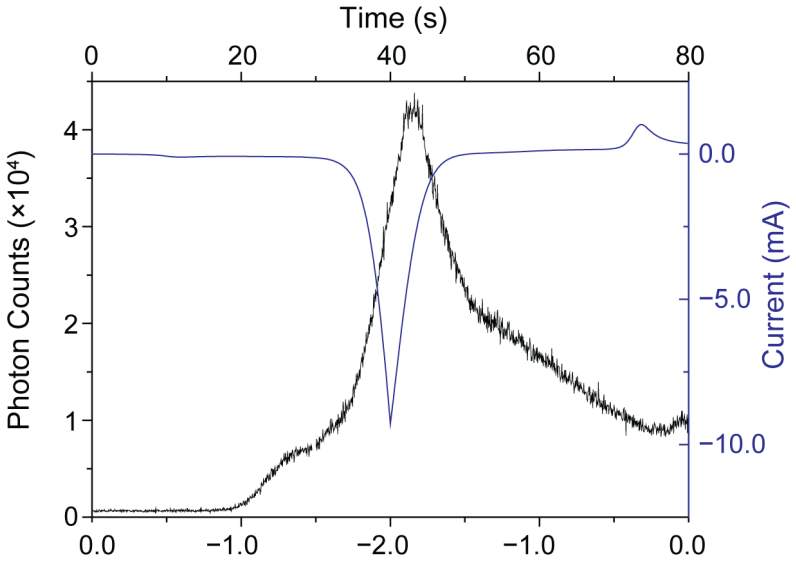

Figure S2. Overlaid plots of simultaneously acquired photon counts (black trace) and current (blue trace) during the cathodic electrolysis at a platinum mesh electrode of an 0.4×10^{-3} M **AMP–luc** oxygen-saturated solution in [EMIM][$EtSO_4$]. The potential was swept cyclically from 0.0 V to−2.0 V, and back, at a scan rate of 0.05 V/s. The emission peak corresponds to ~ 4.20×10^4 photon/s.

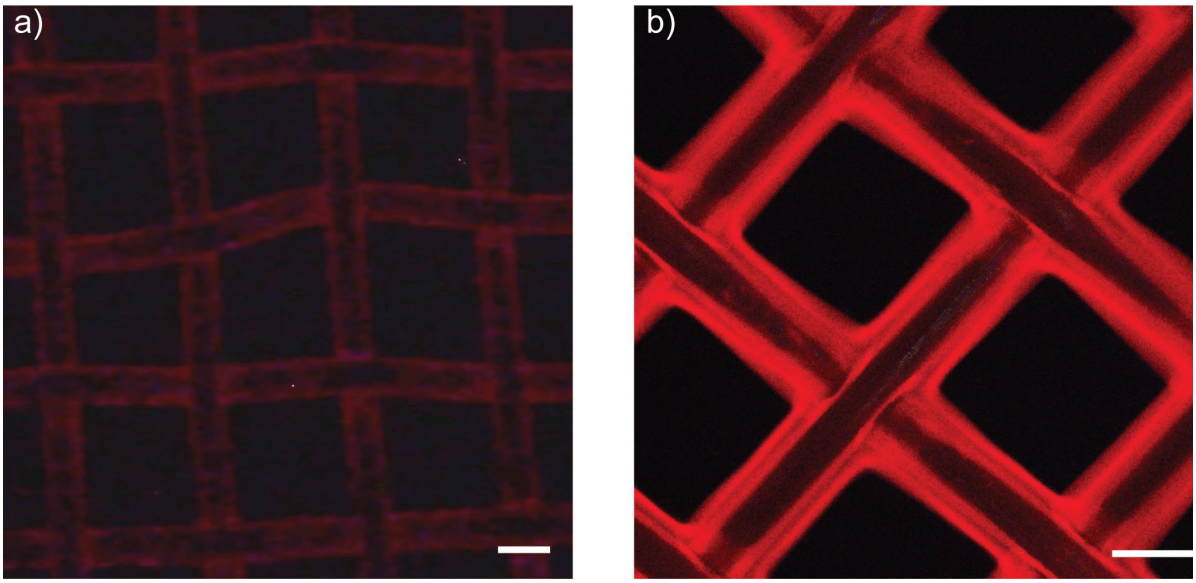

Figure S3. Full field of view for the ECL micrographs shown partially cropped in Figure 1b of the main text. (a) The ECL image was captured in a dark room, ~ 2.0 s after a −2.0 V cathodic pulse (30 s long) is applied to a Pt mesh immersed in a 0.4×10^{-3} M **AMP–luc** oxygen-saturated solution in [EMIM][$EtSO_4$]. (b) A similar experiment as in (a) but carried out in a molecular solvent-based electrolyte (0.4×10^{-3} M **AMP–luc** in oxygen-saturated 0.2 Bu_4NClO_4/DMSO, Video S1). The micrograph shown in (a) is edited to maximise contrast. Scale bars are 100 μm.

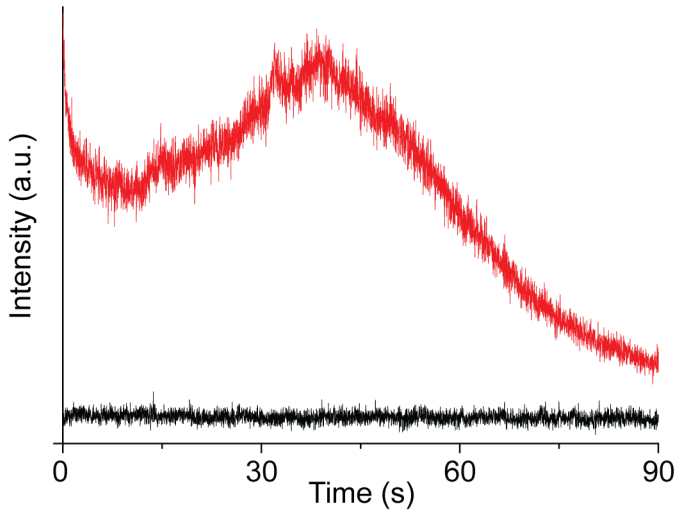

Figure S4. Time evolution of the electrochemically generated light emission (ECL) upon the electrolysis at a platinum mesh electrode of an **AMP–luc** solution (0.4×10^{-3} M in [EMIM][$EtSO_4$]). The room temperature ionic liquid solution was either oxygen-saturated (red trace) or argon-saturated (black trace). Electrolytic solutions were bubbled with either oxygen (red trace) or argon (black trace) for at least 20 min prior to the ECL experiments. To trigger the ECL the voltage of the working electrode was stepped from open circuit to −2.5 V vs Ag/AgCl for 30 s. The ECL is monitored at 626 nm (emission slit set to 20 nm). The experiment with the argon-saturated **AMP–luc** solution was performed under positive argon pressure and with a small amount of oxygen scavenger (ammonium sulfite 0.5 % w/v) added to the solution.

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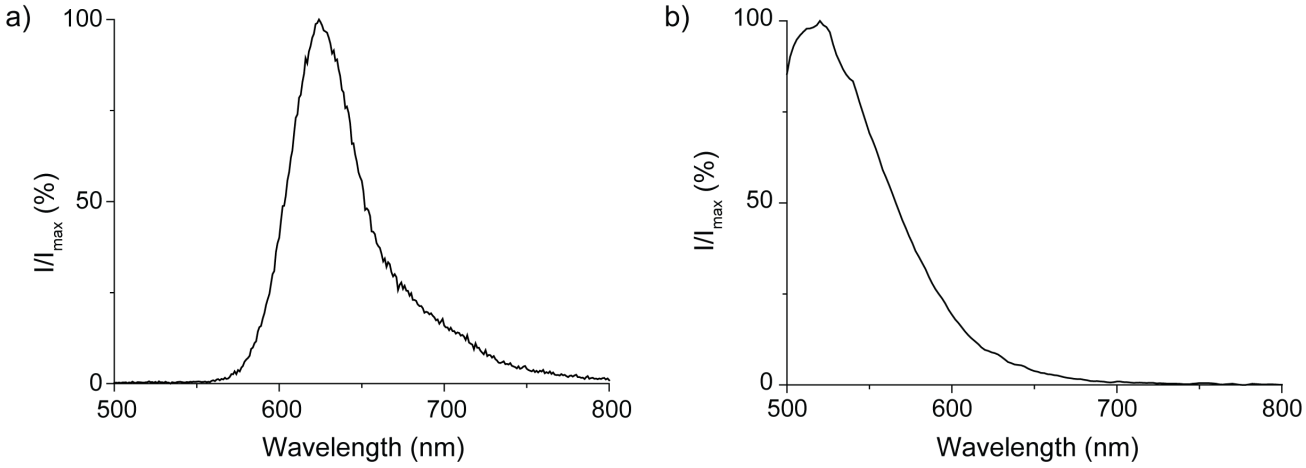

Figure S5. (a) Spectrum of the chemically induced **AMP–luc** luminescence. Argon gas was bubbled through an **AMP–luc** solution (0.4×10^{-3} M, 0.2 M Bu_4NClO_4/DMSO) for at least 20 min prior to the experiment. A quartz cuvette (10×10×40 mm) was loaded with KO_2 (0.02 g) and placed inside the spectrometer sample compartment (Varian, Palo Alto, California). Using silicone tubing (diameter 3.0 mm) AMP–luc solution (4 mL) was transferred in one portion from a syringe to the cuvette containing the KO_2 powder, avoiding ambient light to interfere with the ECL recording. Spectral acquisition started once the injection was completed, and recording a full spectrum took ~1.5 s. Throughout all the procedure a gentle flow of argon gas was maintained inside the sample compartment. (b) Fluorescence spectrum recorded ~30 s after the **AMP–luc** sample injection to the cuvette containing KO_2. The excitation wavelength was set to 474 nm and the emission slit to 20 nm.

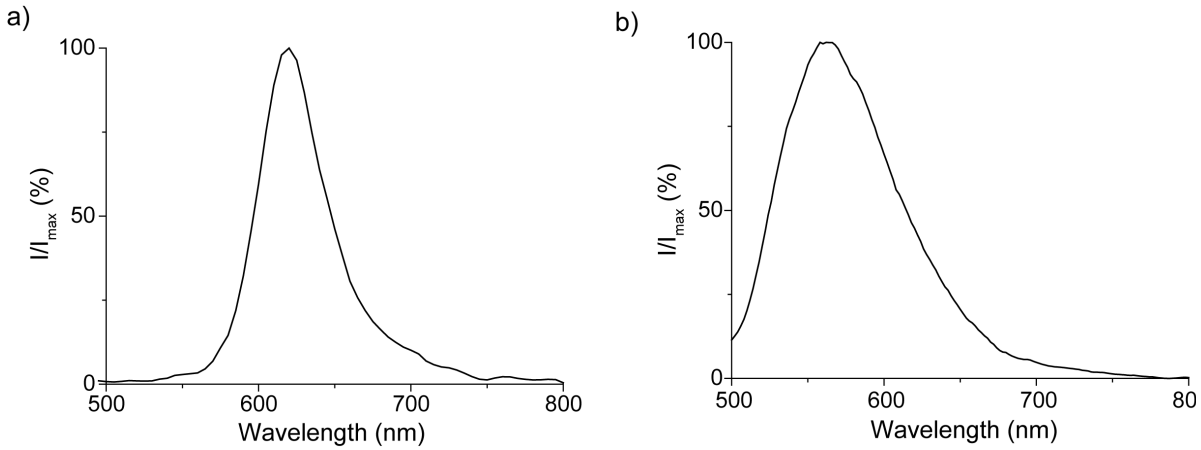

Figure S6. (a) Spectrum of the chemically induced **AMP–luc** luminescence. Argon gas was bubbled through an **AMP–luc** solution (0.4×10^{-3} M in [EMIM][$EtSO_4$]) for at least 20 min prior to the experiment. A quartz cuvette (10×10×40 mm) was loaded with KO_2 (0.02 g) and placed inside the spectrometer sample compartment (Varian, Palo Alto, California). Using silicone tubing (diameter 3.0 mm) **AMP–luc** solution (4 mL) was transferred in one portion from a syringe to the cuvette containing the KO_2 powder, avoiding ambient light to interfere with the ECL recording. Spectral acquisition started once the injection was completed, and recording a full spectrum took ~1.5 s. Throughout all the procedure a gentle flow of argon gas was maintained inside the sample compartment. (b) Fluorescence spectrum recorded ~30 s after the **AMP–luc** sample injection to the cuvette containing KO_2. The excitation wavelength was set to 474 nm and the emission slit to 20 nm.

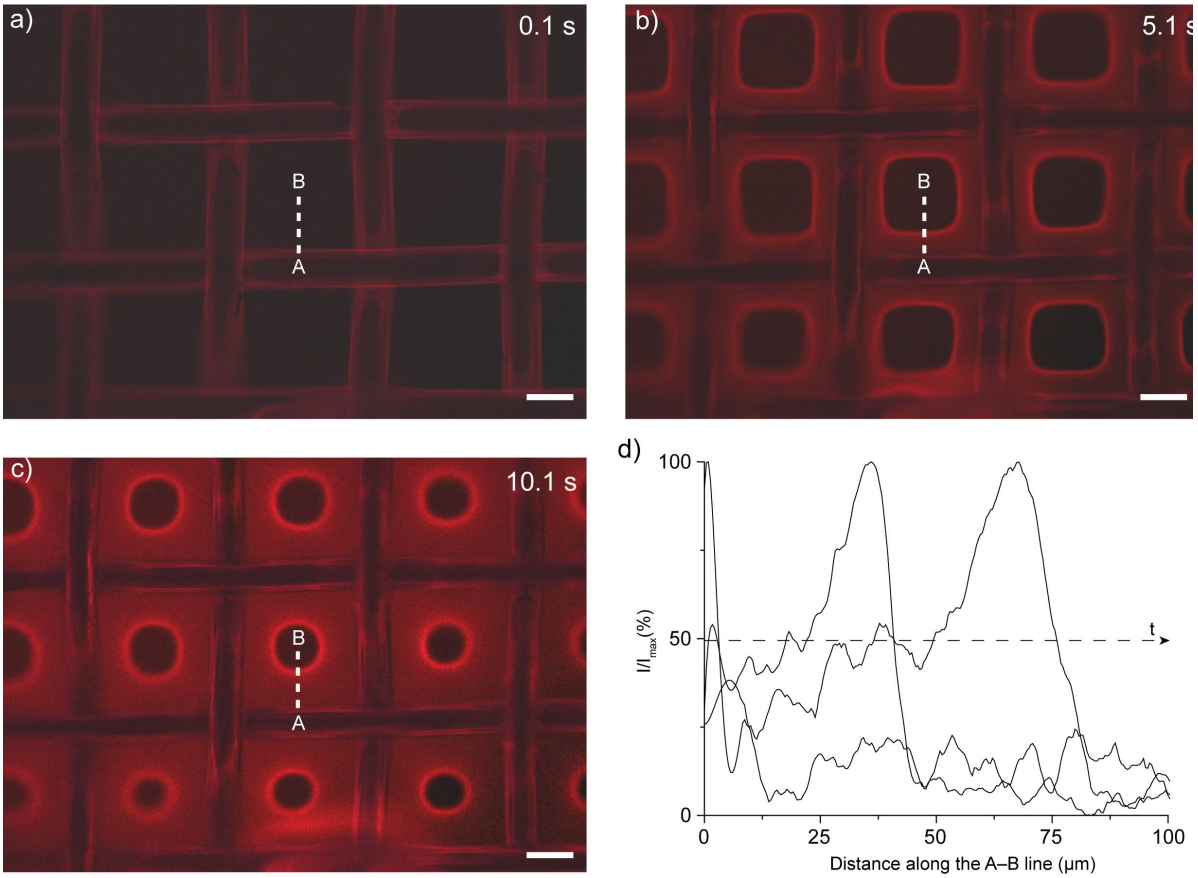

Figure S7. (a–c) Selected time-stamped micrographs (10× magnification, micrographs edited to maximise contrast, see Video S4) showing the movement of the **AMP–luc** electrochemiluminescent front (diffusion of superoxide away from the Pt mesh electrode where it forms). The electroluminescent reaction is triggered upon the cathodic electrolysis (−2.0 V) of an oxygen-saturated **AMP–luc** solution (0.4×10^{-3} M) in 2.0×10^{-1} M Bu_4NClO_4/DMSO. The video was recorded in a dark room and the time stamps (0.1 s (a), 5.1 s (b) and 10.1 s (c)) refer to the time that has elapsed after the working electrode potential is stepped from open circuit to −2.0 V (vs. reference). Scale bars in (a–c) are 100 μm. (d) Electrochemiluminescence profile sampled along the A–B line marked in (a–c), capturing the position of the diffusion front, from electrode's surface, (t) of 0.1, 5.1, and 10.1 s. The optically determined superoxide diffusion coefficient is 2.62×10^{-6} cm^2s^{-1}. Point A is placed approximately on the platinum wire edge (top view).

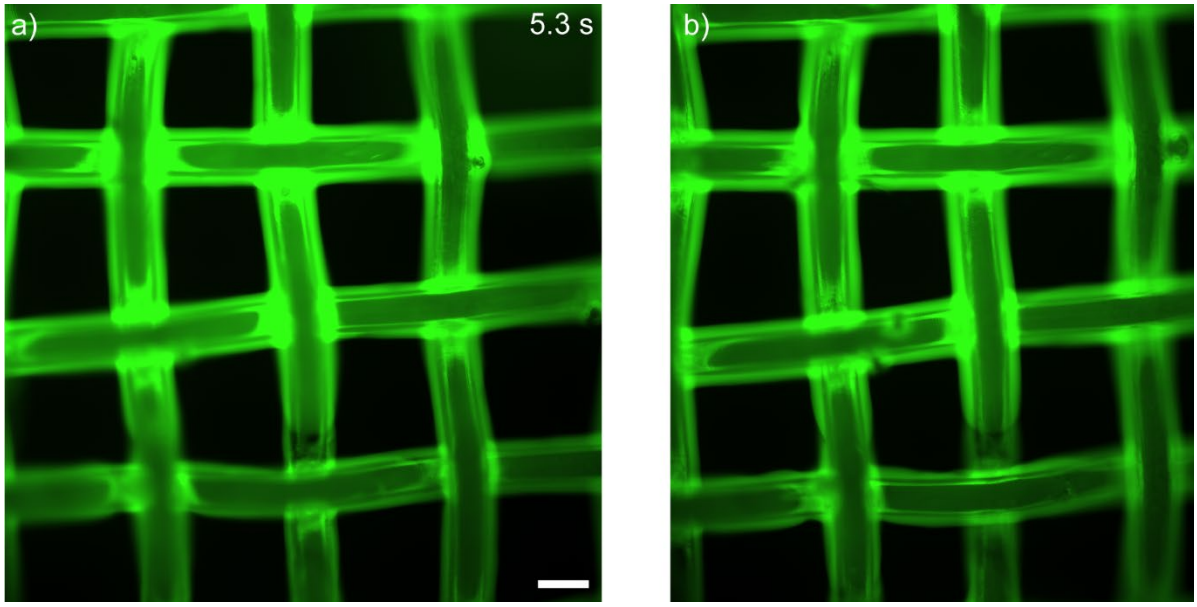

Figure S8. Fluorescence micrographs (10× magnification) recorded during the cathodic electrolysis (−2.0 V vs Ag/AgCl) of an oxygen-saturated **AMP–luc** solution (0.4×10^{-3} M in [EMIM][$EtSO_4$]) at a platinum mesh working electrode. The counter electrode (Pt coil) was placed either on the left (a) or on the right side (b) of the working electrode.

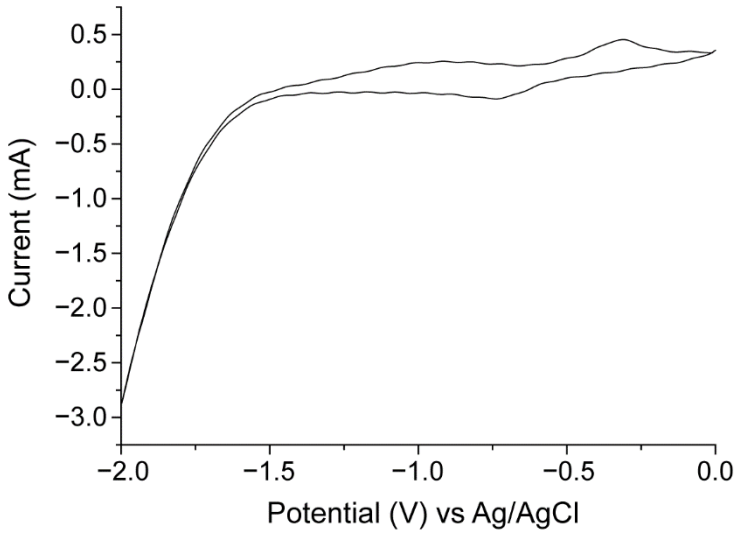

Figure S9. Representative cyclic voltammogram (CV) recorded at a platinum mesh electrode in oxygen-saturated [EMIM][$EtSO_4$], without **AMP–luc**. The voltage scan rate is 0.05 V/s. In the dynamic CV measurement the oxygen reduction peak is appearing at about −0.7 V vs Ag/AgCl (−1.15 vs Fc/Fc^+), a potential where overscreening should already be occurring (Fugure 2f, main text, onset of overscreening is at approximately −0.75 V vs Fc/Fc^+). These data suggest that the cation rich-structure effectively slows down inner-sphere reactions (such as hydrogen evolution) only at large negative potentials, where crowding sets in.

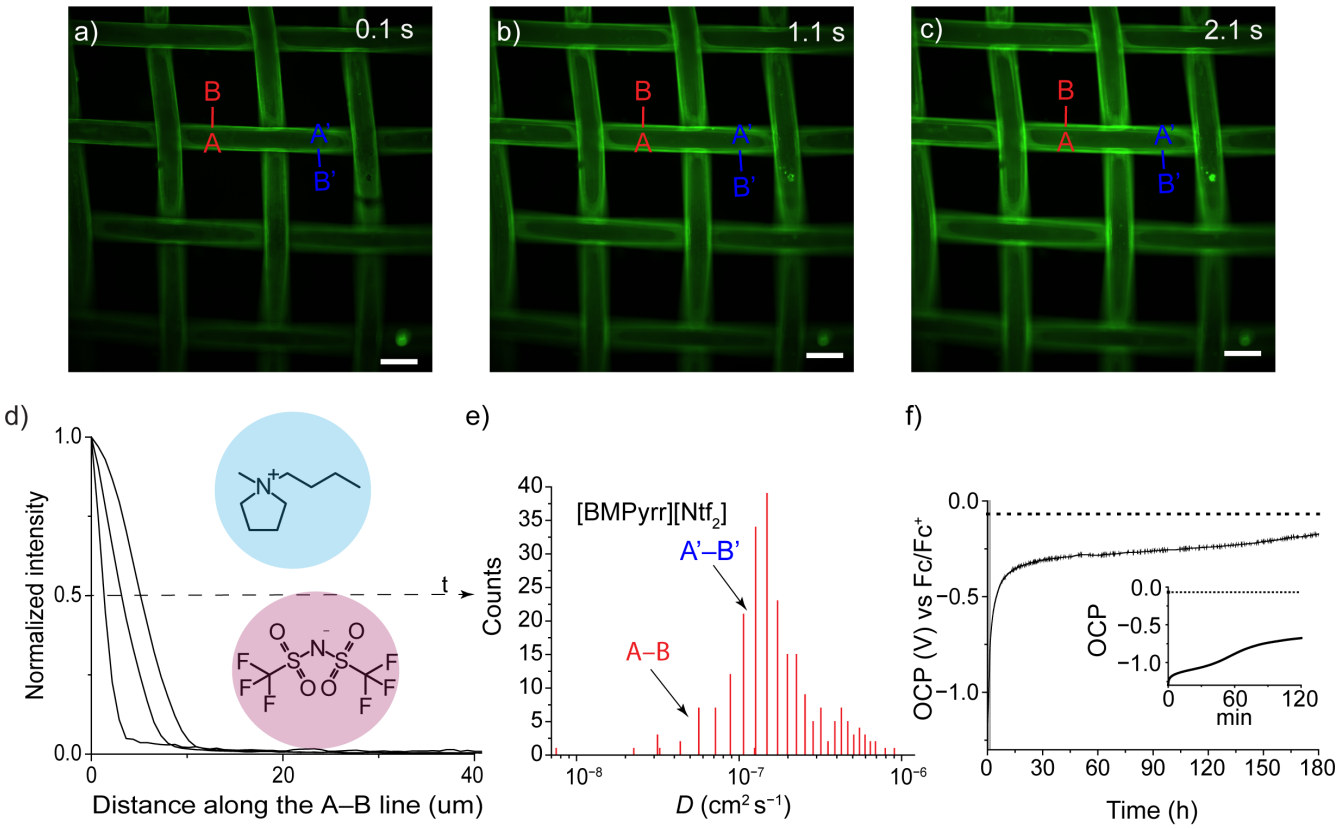

Figure S10. (a–c) Selected time-stamped fluorescence micrographs (10× magnification, 461.0–487.5 nm nm excitation, 502.5–547.5 nm emission, Video S5) capturing the movement of the electrochemically generated **ox–luc**. **ox–luc** if the product of the cathodic electrolysis of an oxygen-saturated **AMP–luc** solution (0.4×10^{-3} M in [BMPyrr][NTf_2]) at a platinum mesh electrode. The time stamps shown in panels (a–c) refer to the time that has elapsed after the working electrode potential is stepped from open circuit to −2.0 V (0.1 s (a), 1.1 s (b) and 2.1 s (d)). Representative fluorescence profiles, sampled along the A–B line, at electrolysis times of 0.1, 1.1 and 2.1 s. The procedure (tracking the movement of the diffusion front) was repeated in at least 20 different locations per experiment, and at least 10 independent experiments were performed. Approximately 200 values of diffusivity were calculated for each system, and the distribution of these values is shown by the histogram in (e). For example, by tracking superoxide diffusion along the A–B line, we obtained a diffusion coefficient (D) for superoxide of 0.40×10^{-7} cm^2 s^{-1}, while the same approach along the A'–B' line led to a D of 1.10×10^{-7} cm^2 s^{-1}. Scale bars in (a–c) are 100 µm. The mode of the optically determined superoxide D is 1.30×10^{-7} cm^2 s^{-1}. (f) Representative OCP–time measurement for a platinum mesh electrode immersed in [BMPyrr][NTf_2] (125 ppm water content). The OCP logging started after the end of a 60 s negative bias pulse (−2.0 V vs the initial OCP). The dotted line represents the initial OCP. The gray shaded area in (f) indicates the data plotted in the figure inset. This inset reveals the onset of crowding between −1.0 V and −1.2 V. The overscreening OCP signature (plateau in OCP) lays between −0.25 V and −0.35 V.

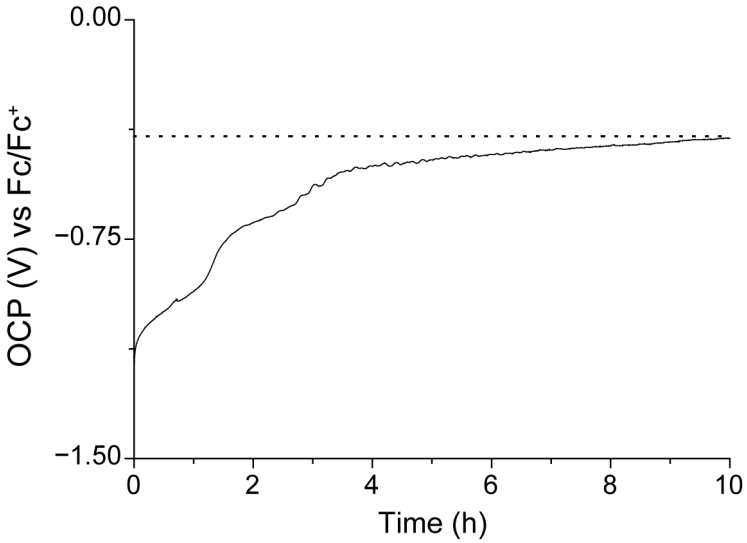

Figure S11. Representative OCP–time measurement of a platinum mesh electrode immersed in [EMIM][BF_4]. The OCP measurement was started after the end of a 60 s cathodic pulse (−2.0 V away from the system's initial OCP). The dotted horizontal line represents the initial OCP before the cathodic pulse.

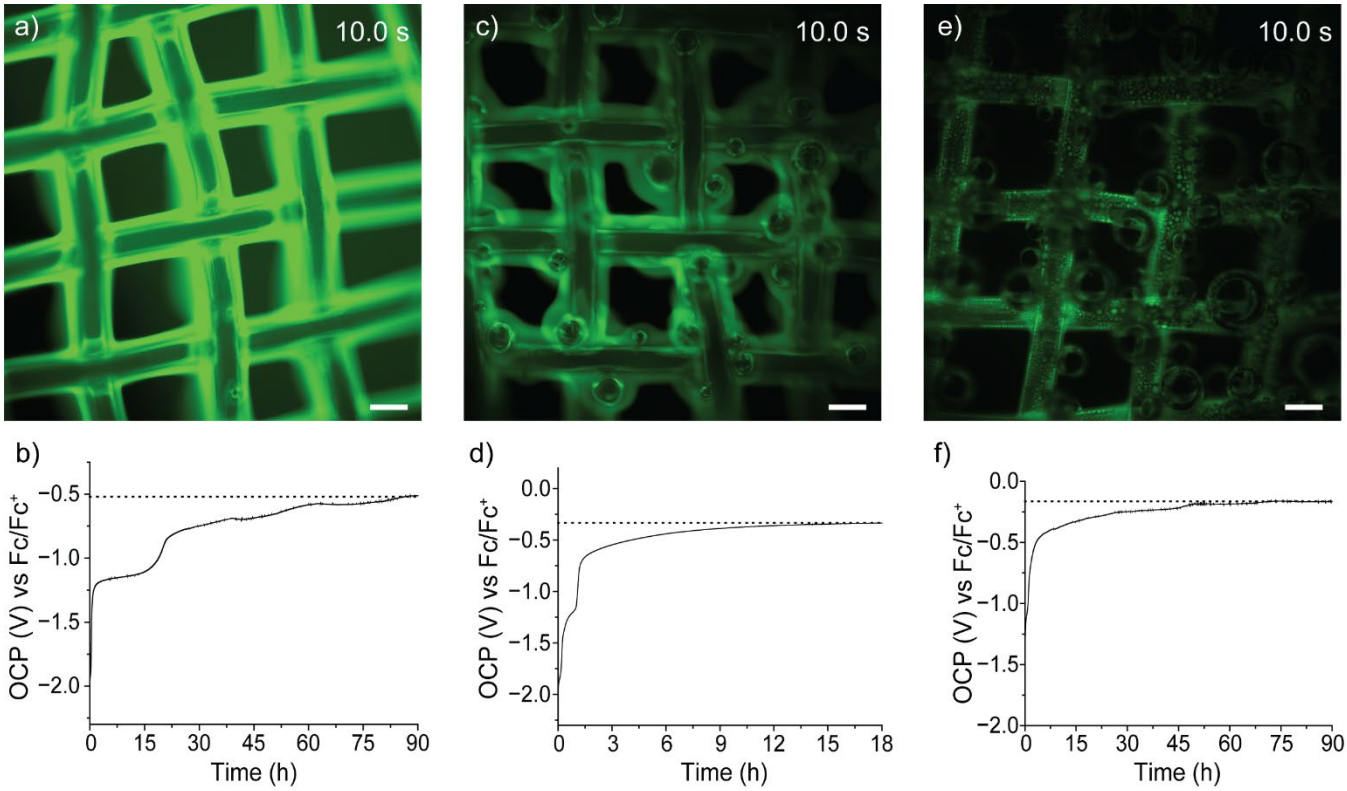

Figure S12. (a,c,e) Selected time-stamped fluorescence micrographs recorded 10 s after the working electrode potential is stepped cathodically (−2.0 V) away from open circuit (10× magnification 461.0–487.5 nm excitation, 502.5–547.5 nm emission). The fluorescence images capture the evolution of gases upon the electrolysis of oxygen-saturated **AMP–luc** solutions (0.4×10^{-3} M) in various RTILs. The RTIL in (a) and in (c) is [EMIM][$EtSO_4$], spiked respectively with either 2.0% (a) or 5% (c) of water (Videos S6–S7). The RTIL in (e) is [BMPyrr][NTf_2], spiked with 2.0% of water (Video S8). (b,d,f) OCP–time measurement for the mesh platinum electrode immersed in the RTIL systems of (a), (c) and (e). The OCP was recorded after the application of −2.0 V relative to the system's initial OCP.

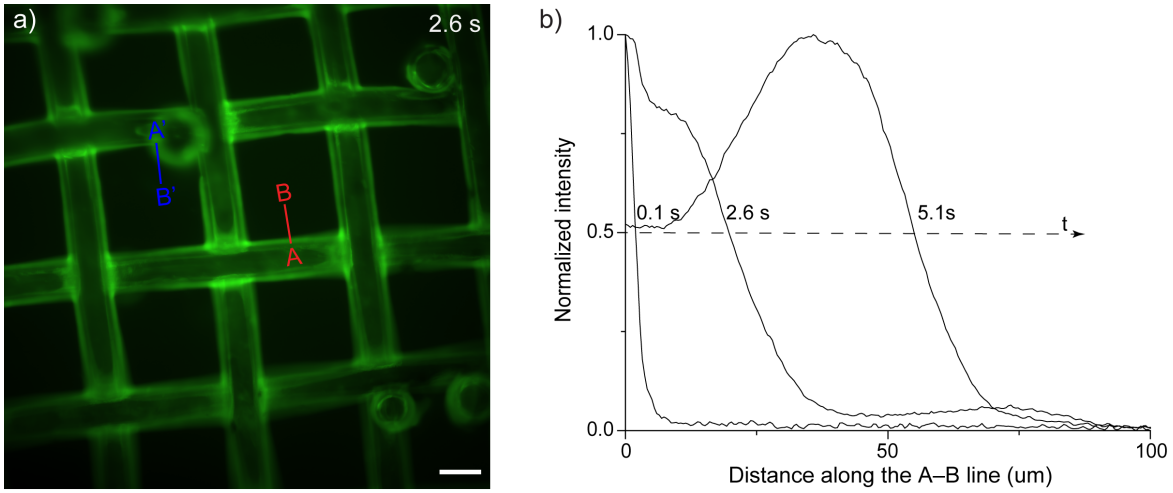

Figure S13. Selected time-stamped fluorescence micrograph (10× magnification) recorded during the cathodic electrolysis (−2.0 V vs Ag/AgCl) of an oxygen-saturated **AMP–luc** solution (0.4×10^{-3} M in [EMIM][BF_4]). (b) Representative fluorescence intensity plot profiles sampled along the A'–B' line marked in (a) and in Figure 3a–b, recorded 0.1, 2.6 and 5.1 s after the working electrode bias is stepped from open circuit to −2.0 V, used for the analysis of the movement over time of the superoxide diffusion front (triggering the **ox–luc** formation). The D values reported in the main text are calculated from the front distance travelled after 5.1 s, and are therefore and average apparent diffusivity during this time, but as data in (b) show, the apparent diffusion is not uniform over time, with the front progressing faster as the bubbles become larger.

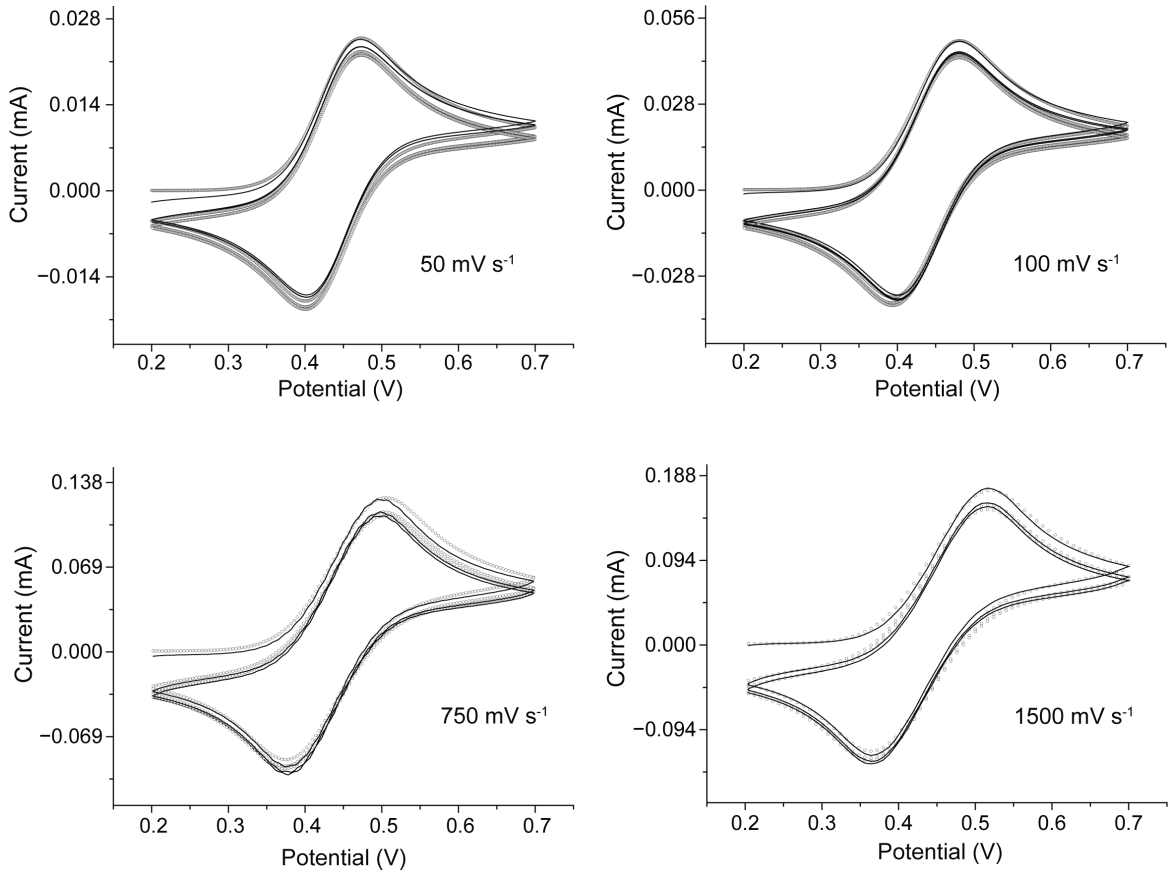

Figure S14. Representative experimental (solid line) and simulated (empty symbols) cyclic voltammograms recorded at a platinum disk electrode in an acetonitrile solution containing 1.0×10^{-3} M ferrocene and 1.0×10^{-1} Bu_4NPF_6. The voltage sweep rate is indicated as a label to the figures. The diffusivity (D) of ferrocene and ferricenium (Fc and Fc^+ hereafter) was set to 2.60×10^{-5} cm^2 s^{-1}.[1] The best-fit parameters (E mechanism) are E^0 (Fc/Fc^+) = 0.4371 V (vs. Ag/AgCl "leakless", upper limit 0.4374, lower limit 0.4368, 95.4% confidence level), and k_{et} = 0.040 cm s^{-1} (upper limit 0.043, lower limit 0.037, 95.4% confidence level). The electrochemically-determined effective area of the platinum disk is 0.08 cm^2.

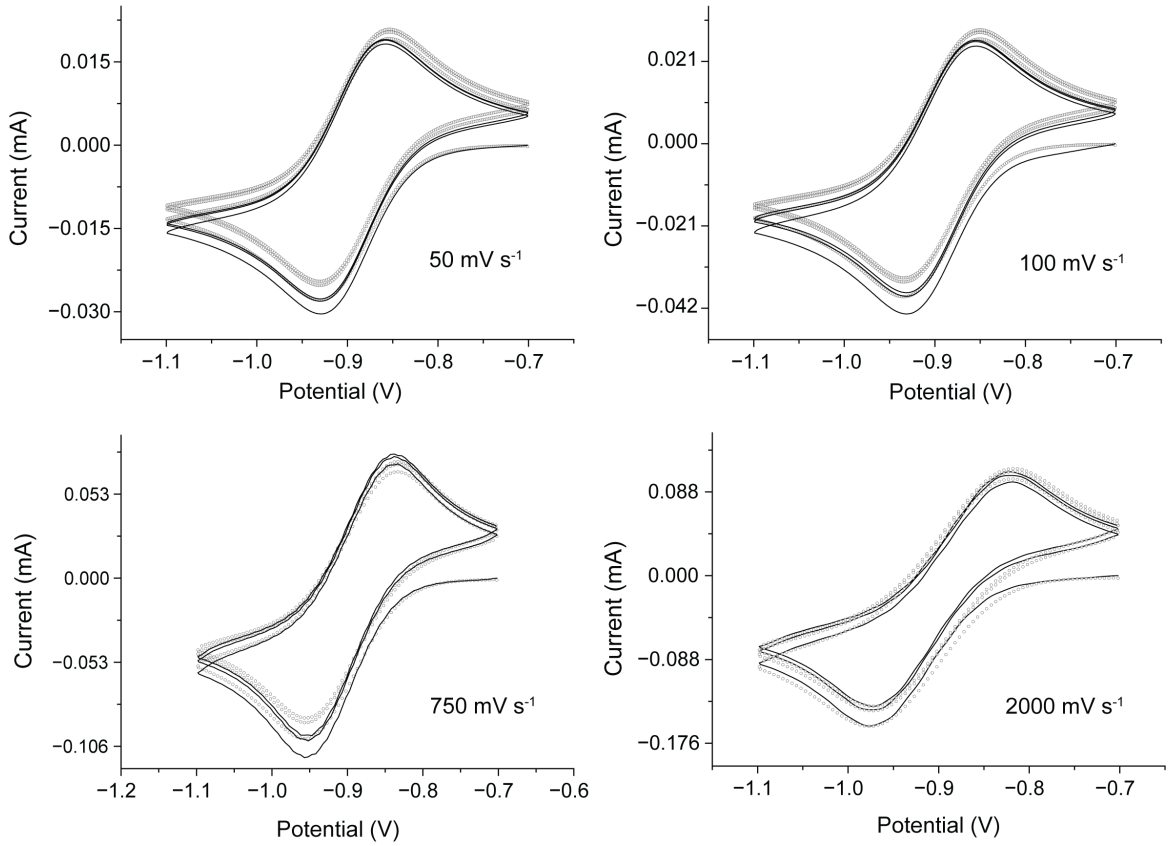

Figure S15. Representative experimental (solid line) and simulated (empty symbols) cyclic voltammograms recorded at a platinum disk electrode in an acetonitrile solution containing 1.0×10^{-3} M cobaltocenium hexafluorophosphate and 1.0×10^{-1} Bu_4NPF_6. The voltage sweep rate is indicated by labels to the figures. The D of cobaltocene and cobaltocenium (Cc and Cc^+ hereafter) was set to 3.25×10^{-5} cm^2 s^{-1}.[2] The best-fit parameters (E mechanism) are E^0 (Cc/Cc^+) −0.8824 V (vs. Ag/AgCl "leakless", upper limit −0.8919, lower limit −0.8929, 95.4% confidence level), and k_{et} = 0.044 cm s^{-1} (upper limit 0.049, lower limit 0.039, 95.4% confidence level). The electrochemically-determined effective area of the platinum disk is 0.08 cm^2.

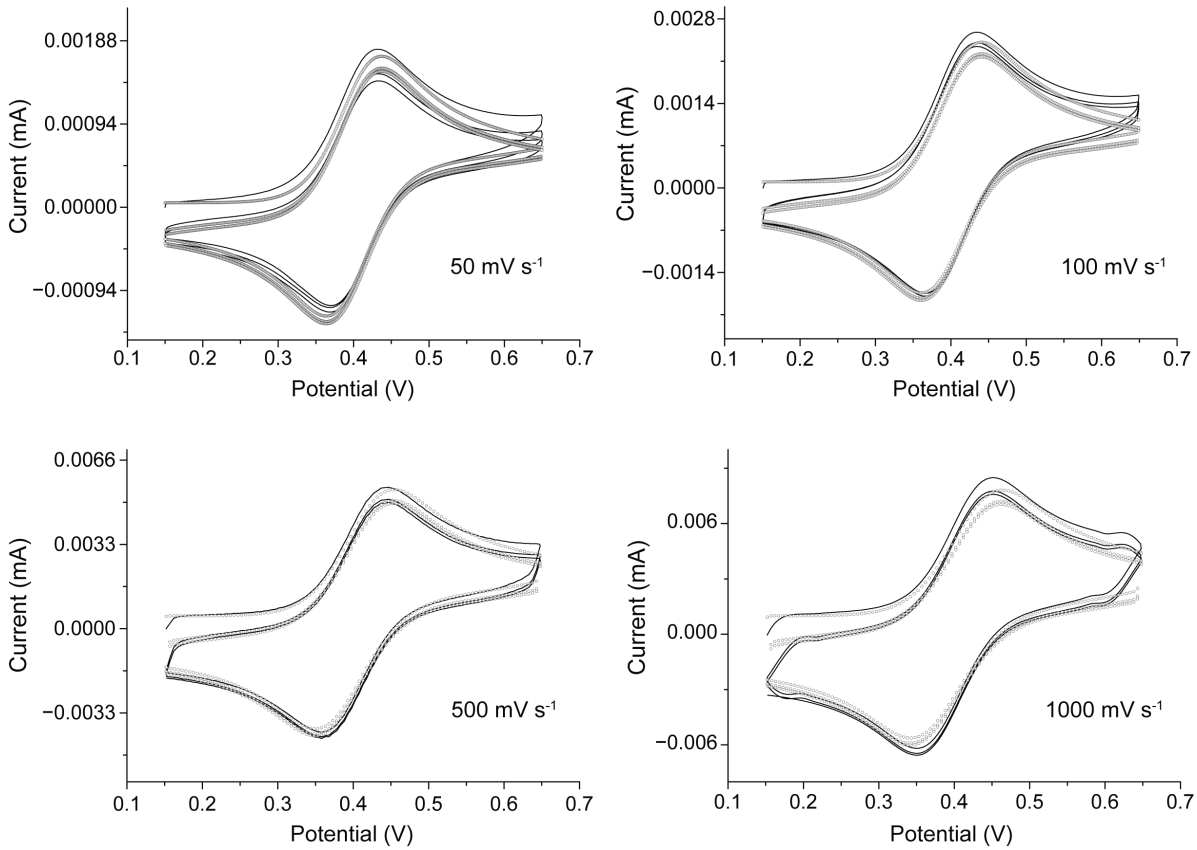

Figure S16. Representative experimental (solid line) and simulated (empty symbols) cyclic voltammograms at a platinum disk electrode in [EMIM][$EtSO_4$] containing 1.0×10^{-3} M ferrocene. The voltage sweep rate is indicated by the labels to the figures. The best-fit parameters (E mechanism) are E^0 (Fc/Fc^+) = 0.4001 V (vs. Ag/AgCl "leakless", upper limit 0.4000, lower limit 0.3998, 95.4% confidence level), k_{et} = 0.0011 cm s^{-1} (upper limit 0.0012, lower limit 0.0010, 95.4% confidence level), and $D = 0.608 \times 10^{-7}$ cm^2 s^{-1} (upper limit 0.611, lower limit 0.605, 95.4% confidence level). The electrochemically-determined effective area of the platinum disk is 0.08 cm^2.

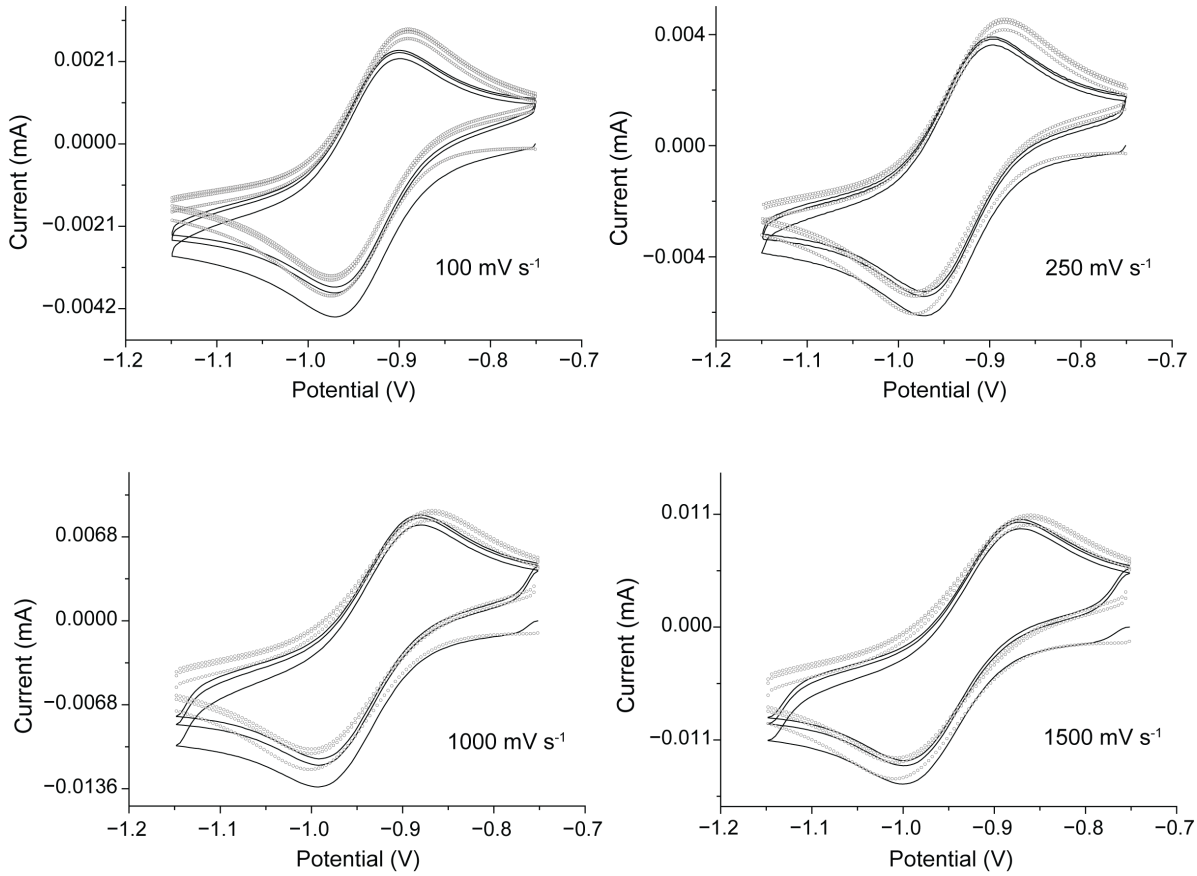

Figure S17. Representative experimental (solid line) and simulated (empty symbols) cyclic voltammograms at a platinum disk electrode in [EMIM][$EtSO_4$] containing 1.0×10^{-3} M cobaltocenium hexafluorophosphate. The voltage sweep rate is indicated by the labels to the figures. The best-fit parameters (E mechanism) are E^0 (Cc/Cc^+) = −0.9317 V (vs. Ag/AgCl "leakless", upper limit −0.9307, lower limit −0.9327, 95.4% confidence level), k_{et} = 0.0019 cm s^{-1} (upper limit 0.0021, lower limit 0.0018, 95.4% confidence level), and $D = 2.90 \times 10^{-7}$ cm^2 s (upper limit 2.93, lower limit 2.86, 95.4% confidence level). The electrochemically-determined effective area of the platinum disk is 0.08 cm^2.

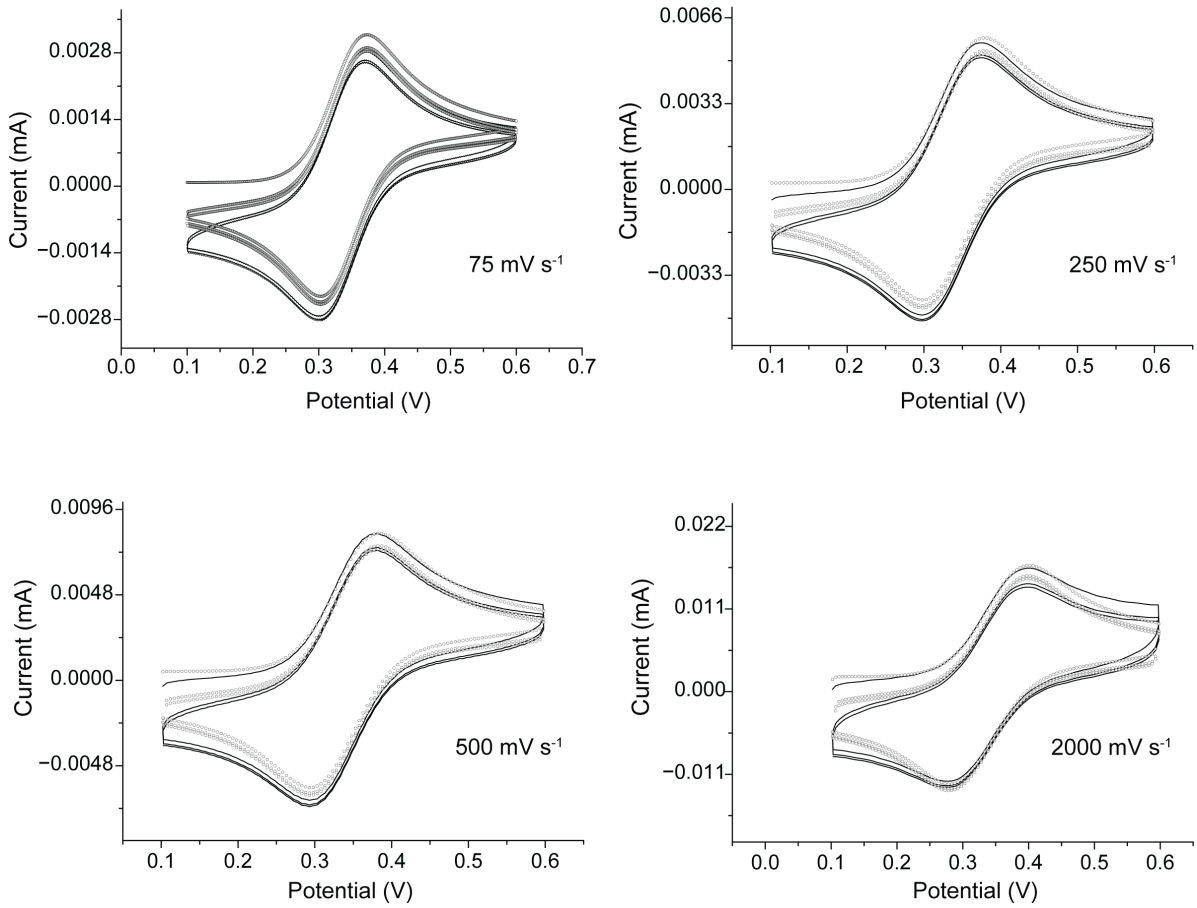

Figure S18. Representative experimental (solid line) and simulated (empty symbols) cyclic voltammograms at a platinum disk electrode in [BMPyrr][NTf_2] containing 1.0×10^{-3} M ferrocene. The voltage sweep rate is indicated by labels to the figures. The best-fit parameters are (E mechanism) E^0 (Fc/Fc^+) was 0.3377 V (vs. Ag/AgCl "leakless", upper limit 0.3382, lower limit 0.3373, 95.4% confidence level), k_{et} = 0.0046 cm s^{-1} (upper limit 0.0052, lower limit 0.0042, 95.4% confidence level), and $D = 2.37 \times 10^{-7}$ cm^2 s^{-1} (upper limit 2.41, lower limit 2.33, 95.4% confidence level). The electrochemically-determined effective area of the platinum disk is 0.08 cm^2

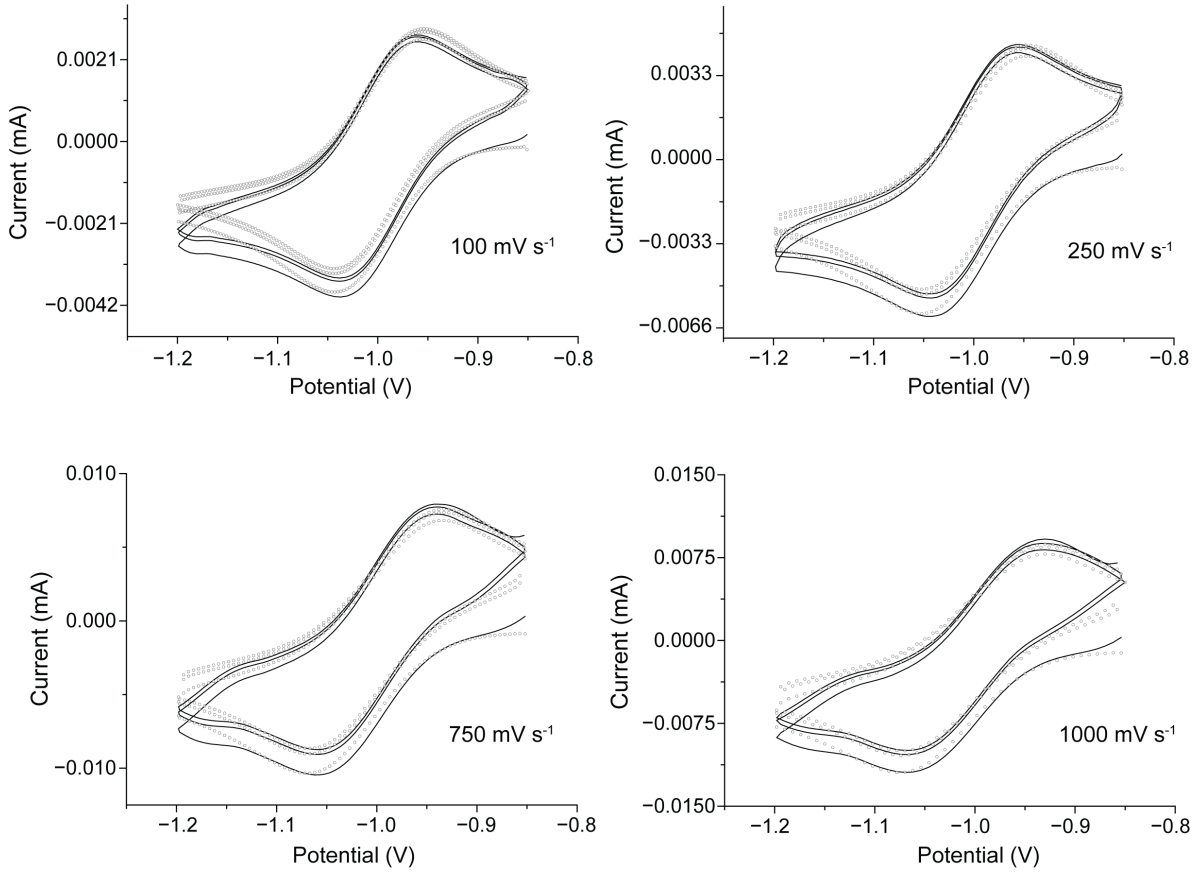

Figure S19. Representative experimental (solid line) and simulated (empty symbols) cyclic voltammograms at a platinum disk electrode in [BMPyrr][NTf_2] containing 1.0×10^{-3} M cobaltocenium hexafluorophosphate. The voltage sweep rate is indicated by labels to the figures. The voltage sweep rate is indicated as labels to the figures. The best-fit parameters (E mechanism) are E^0 (Cc/Cc^+) = −0.9978 V (vs. Ag/AgCl "leakless", upper limit −0.9973, lower limit −0.9983, 95.4% confidence level), k_{et} = 0.0131 cm s^{-1} (upper limit 0.0136, lower limit 0.0126, 95.4% confidence level), and $D = 1.92 \times 10^{-7}$ cm^2 s^{-1} (upper limit 1.94, lower limit 1.90, 95.4% confidence level). The electrochemically-determined effective area of the platinum disk is 0.08 cm^2.

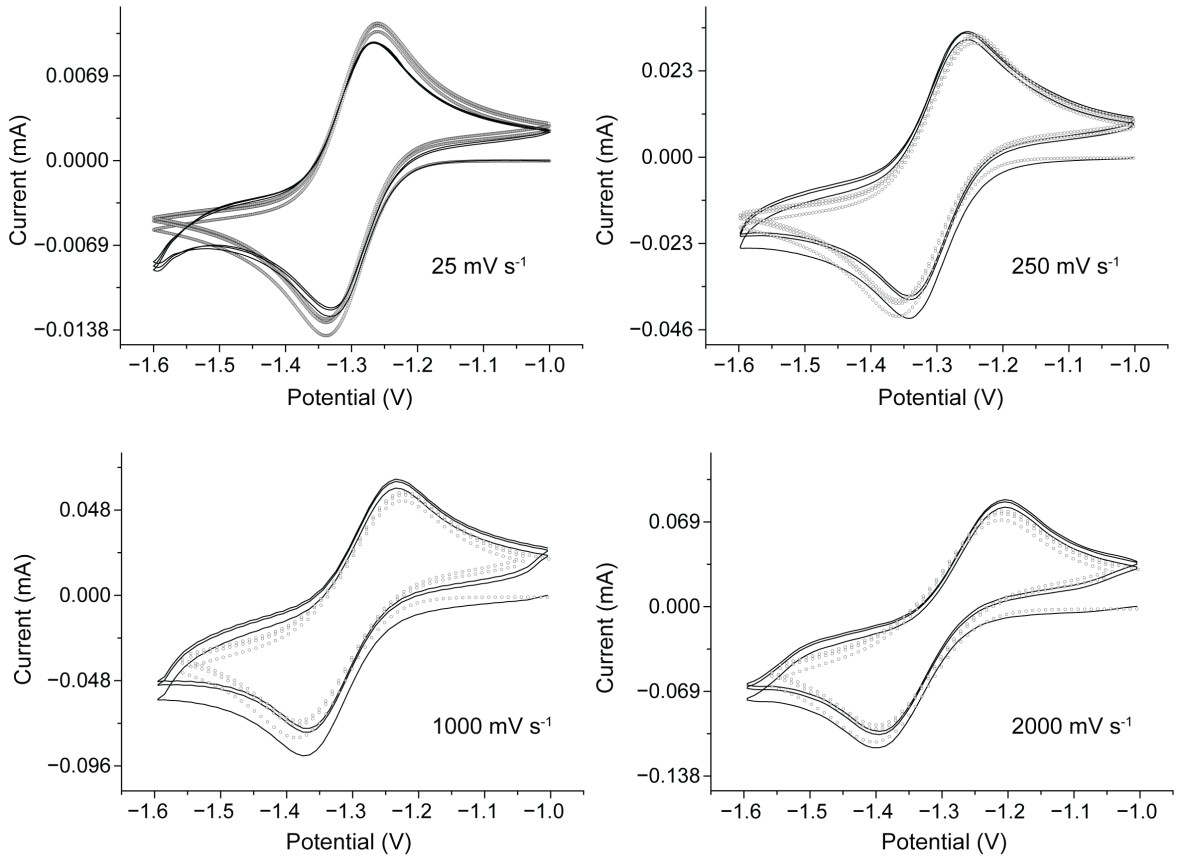

Figure S20. Representative experimental (solid line) and simulated (empty symbols) cyclic voltammograms at a platinum disk electrode in an acetonitrile solution containing 1.0×10^{-3} M decamethyl cobaltocenium hexafluorophosphate ($Me_{10}(Cc)^+$ hereafter) and 1.0×10^{-1} Bu_4NPF_6. The voltage sweep rate is indicated by labels to the figures. The best-fit parameters (E mechanism) are E^0 ($Me_{10}(Cc)/Me_{10}(Cc)^+$) = −1.300 V (vs. Ag/AgCl "leakless", upper limit −1.299, lower limit −1.301, 95.4% confidence level), k_{et} = 0.016 cm s^{-1} (upper limit 0.017, lower limit 0.014, 95.4% confidence level), and $D = 1.65 \times 10^{-5}$ cm^2 s^{-1}(upper limit 1.67, lower limit 1.63, 95.4% confidence level). The electrochemically-determined effective area of the platinum disk is 0.08 cm^2.

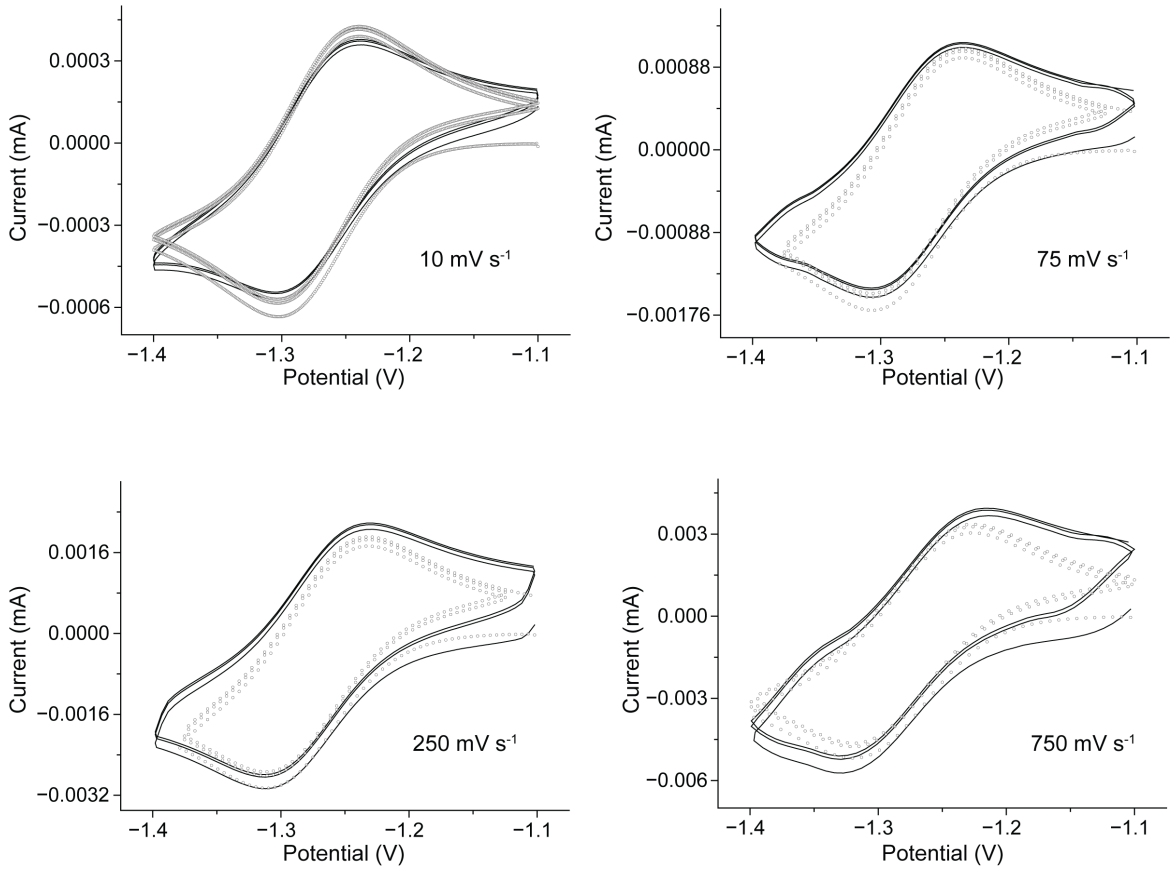

Figure S21. Representative experimental (solid line) and simulated (empty symbols) cyclic voltammograms at a platinum disk electrode in [EMIM][$EtSO_4$] containing 1.0×10^{-3} M $Me_{10}(Cc)^+$. The voltage sweep rate is indicated by labels to the figures. The best-fit parameters (E mechanism) are E^0 ($Me_{10}(Cc)/Me_{10}(Cc)^+$) = −1.2729 V (vs. Ag/AgCl "leakless", upper limit −1.214, lower limit −1.2724, 95.4% confidence level), k_{et} = 0.0023 cm s^{-1} (upper limit 0.0027, lower limit 0.0019, 95.4% confidence level), and $D = 0.805 \times 10^{-7}$ cm^2 s^{-1} (upper limit 0.816, lower limit 0.794, 95.4% confidence level). The electrochemically-determined effective area of the platinum disk is 0.08 cm^2.

Description of Supplementary Videos

File name: Video S1

Time-stamped ECL emission recorded with a Nikon Eclipse Ti2-U inverted microscope fitted with a Plan Apo λ 10×/0.45 objective (part 88-379, Nikon, CFI Plan Fluor) and setting a 500 ms exposure time. A −2.0 V bias was applied to the platinum mesh at the beginning of the video. The platinum mesh is immersed in an oxygen-saturated 0.4×10^{-3} M **AMP–luc** solution made in 0.2 M Bu_4NClO_4/DMSO. There was no emission filter. Selected video frames from this video are reproduced in Figure1b of the main text.

File name: Video S2

Time-stamped fluorescence recorded with a Nikon Eclipse Ti2-U inverted microscope fitted with a Plan Apo λ 10×/0.45 objective (part 88-379, Nikon, CFI Plan Fluor) and setting a 40 ms exposure time. A −2.0 V bias was applied to the platinum mesh working electrode. The platinum mesh working electrode is immersed in an oxygen-saturated 0.4×10^{-3} M **AMP–luc** solution in [EMIM][$EtSO_4$] (930 ppm). The microscope was fitted with a FITC filter/dichroic mirror cube (461.0–487.5 nm excitation filter, 502.5–547.5 nm emission filter) was used. Selected video frames from this video are reproduced in Figure 2a–c of the main text.

File name: Video S3

Time-stamped fluorescence recorded with a Nikon Eclipse Ti2-U inverted microscope fitted with a Plan Apo λ 10×/0.45 objective (part 88-379, Nikon, CFI Plan Fluor) and setting a 40 ms exposure time. A −2.0 V bias was applied to the platinum mesh. The platinum mesh working electrode is immersed in an oxygen-saturated 0.4×10^{-3} M **AMP–luc** solution in [EMIM][BF_4] (2400 ppm). The microscope was fitted with a FITC filter/dichroic mirror cube (461.0–487.5 nm excitation filter, 502.5–547.5 nm emission filter). Selected video frames from this video are reproduced in Figure 3a–b of the main text.

File name: Video S4

Time-stamped ECL emission recorded with a Nikon Eclipse Ti2-U inverted microscope fitted with a Plan Apo λ 10×/0.45 objective (part 88-379, Nikon, CFI Plan Fluor) and setting a 1 s exposure time. A −2.0 V bias was applied to the platinum mesh. The platinum mesh working electrode is immersed in an oxygen-saturated 0.4×10^{-3} M **AMP–luc** solution in 0.2 M Bu_4NClO_4/DMSO. No emission filter was used. Selected video frames from this video are reproduced in Figure S4a–c, Supporting Information.

File name: Video S5

Time-stamped fluorescence recorded with a Nikon Eclipse Ti2-U inverted microscope fitted with a Plan Apo λ 10×/0.45 objective (part 88-379, Nikon, CFI Plan Fluor) and setting a 40 ms

exposure time. A −2.0 V bias was applied to the platinum mesh at the beginning of the video. The platinum mesh working electrode is immersed in a 0.4×10^{-3} M **AMP–luc** solution in [BMPyrr][NTf_2] (125 ppm). A FITC filter/dichroic mirror cube (461.0–487.5 nm excitation filter, 502.5–547.5 nm emission filter) was used. Selected video frames from this video are reproduced in Figure S5a–c, Supporting Information.

File name: Video S6

Time-stamped fluorescence recorded with a Nikon Eclipse Ti2-U inverted microscope fitted with a Plan Apo λ 10×/0.45 objective (part 88-379, Nikon, CFI Plan Fluor) and setting a 40 ms exposure time. A −2.0 V bias was applied to the platinum mesh. The platinum mesh working electrode is immersed in an oxygen-saturated 0.4×10^{-3} M **AMP–luc** solution in [EMIM][$EtSO_4$] spiked with 2% of water. The microscope was fitted with a FITC filter/dichroic mirror cube (461.0–487.5 nm excitation filter, 502.5–547.5 nm emission filter). Selected video frames from this video are reproduced in Figure S7a, Supporting Information.

File name: Video S7

Time-stamped fluorescence recorded with a Nikon Eclipse Ti2-U inverted microscope fitted with a Plan Apo λ 10×/0.45 objective (part 88-379, Nikon, CFI Plan Fluor) and setting a 40 ms exposure time. A −2.0 V bias was applied to the platinum mesh. The platinum mesh working electrode is immersed in an oxygen-saturated 0.4×10^{-3} M **AMP–luc** solution in [EMIM][$EtSO_4$] spiked with 5% of water. A FITC filter/dichroic mirror cube (461.0–487.5 nm excitation filter, 502.5–547.5 nm emission filter) was used. Selected video frames from this video are reproduced in Figure S7c, Supporting Information.

File name: Video S8

Time-stamped fluorescence recorded with a Nikon Eclipse Ti2-U inverted microscope fitted with a Plan Apo λ 10×/0.45 objective (part 88-379, Nikon, CFI Plan Fluor) and setting a 40 ms exposure time. A −2.0 V bias was applied to the platinum mesh. The platinum mesh working electrode is immersed in a 0.4×10^{-3} M **AMP–luc** solution in [BMPyrr][NTf_2] spiked with 2% of water. The microscope was fitted with a FITC filter/dichroic mirror cube (461.0–487.5 nm excitation filter, 502.5–547.5 nm emission filter) was used. Selected video frames from this video are reproduced in Figure S7e, Supporting Information.

References

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