Supporting information:

1. Experimental details

1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ($Pyr_{14}TFSI$, IoLiTec, 99 %, < 10 ppm water content) and lithium bis(trifluoromethylsulfonyl)imide (LiTFSI, 99.95%, trace metal basis, Aldrich) were dried under vacuum at 120 ˚C for 48h. Acetonitrile (anhydrous, 99.8%, Sigma-Aldrich) was purged with Ar gas for over 3 hours. Potassium dioxide (KO_2, Aldrich) was used as received. Ethyl viologen di-(trifluoromethanesulfonate), $EtV(OTf)_2$, was prepared by mixing solutions of ethyl viologen di-iodide ($EtVI_2$, 99%, Sigma-Aldrich) and silver trifluoromethanesulfonate (AgOTf, ≥99%, Aldrich). This formed a yellow precipitate, AgI, that was filtered off $EtV(OTf)_2$ was obtained by recrystallization from the filtrate. $EtV(OTf)_2$ was dried at 120 ˚C for 24 h, and then transferred to an argon filled glove box (< 1 ppm water content, < 10 ppm oxygen content). All solutions were prepared inside the argon filled glove box, by mixing the required salt in the respective solvent with vigorous stirring until all the salt was dissolved.

$Li_7Ti_5O_{12}$ was used to reduce the dication ethyl viologen, EtV^{2+}, to the monocation EtV^+. The reaction was followed by UV-vis spectroscopy. Figure S1 shows the spectrum of EtV^{2+}, as obtained by dissolving $EtV(OTf)_2$ in acetonitrile, and the spectrum of EtV^+ as obtained after addition of $Li_7Ti_5O_{12}$. These spectra are in agreement with previous studies.[1-3] It is possible to reduce EtV^+ further to neutral EtV by adding an excess of $Li_7Ti_5O_{12}$, and this produces a decrease in the intensity of the adsorption band at 600 nm, in agreement with previous work.[1, 3] Therefore, the full conversion of EtV^{2+} to EtV^+, without over-reduction to EtV, was identified as the point where the absorption band at 605 nm is at its maximum. The absorption cross section of EtV^+ at 605 nm is estimated to be 15200 M^{-1} cm^{-1}, which is in good agreement with previous studies.[1, 3]

$Li_7Ti_5O_{12}$ was prepared as follows. $Li_4Ti_5O_{12}$ spinel (Sigma Aldrich, >99%) was mixed in anhydrous hexane (Sigma Aldrich, 95%, dried with molecular sieves for 2 days before use) in a 3-neck round bottom flask under Ar atmosphere. Then, an excess of butyl lithium solution (Sigma Aldrich, 1.6 M in hexane) was injected into the flask through a syringe. The mixture was stirred under Ar atmosphere and the temperature was kept at 35 °C in an oil bath for 48 hours. At the end, the colour of solid powder had changed from white to dark blue. The solid was washed with anhydrous hexane twice and then dried under Ar atmosphere. Titration with I_2 indicated that around 2.7 Li were inserted per formula unit of $Li_4Ti_5O_{12}$. For simplicity, in the present study, the final reaction product is referred to as $Li_7Ti_5O_{12}$.

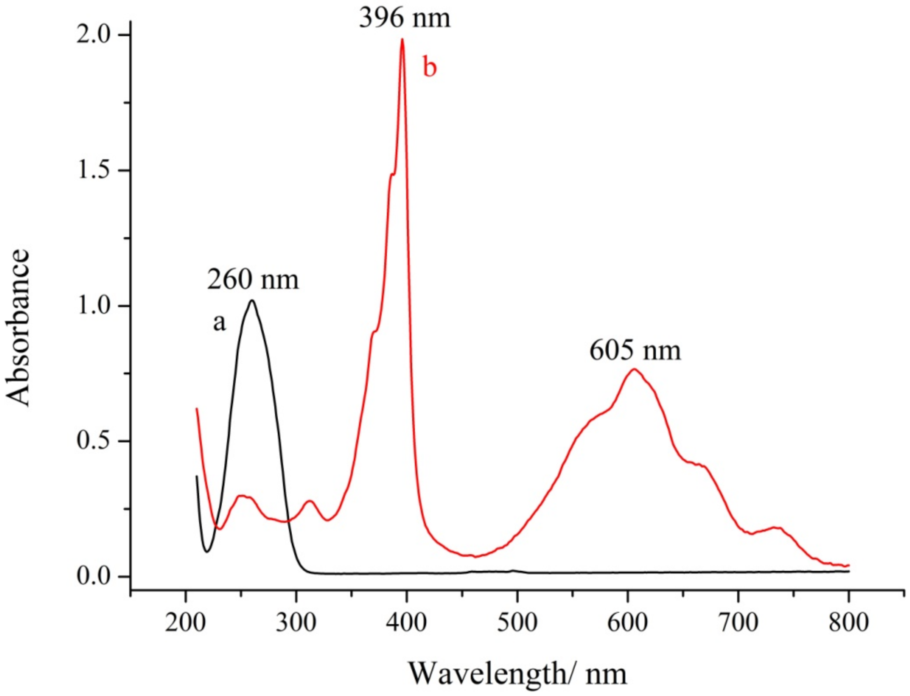

Figure S1. UV-Vis spectrum of 0.05 mM EtV^{2+} (a) and 0.05 mM EtV^{+} (b) in acetonitrile. The reduction of EtV^{2+} to EtV^{+} was done by adding $Li_7Ti_5O_{12}$ in a slight excess (0.4 moles of $Li_7Ti_5O_{12}$ were added per mol of EtV^{2+}), which was left to react overnight.

Electrochemical measurements were carried out using a 3 mm-diameter glassy carbon electrode as the working electrode, and lithium foil (99.99 %, Chemetall GmbH) pressed onto stainless steel gauze was used as the reference and counter electrode. Prior to each experiment, the working electrode was polished with 0.3 µm and 0.05 µm alumina powder (Buehler), rinsed and sonicated with acetone and water. The electrodes and the glass-made electrochemical cell were dried in an oven at 80 °C overnight, and then transferred to an argon filled glovebox, where the cell was assembled. Oxygen (BOC, 99.5%, dried through a bed of molecular sieves before use) was bubbled in the electrolytes for 40 minutes to achieve saturation.

2. Estimation of the standard potential of the reduction of EtV^{2+} to EtV^{+}

The standard potential of the EtV^{2+}/ EtV^{+}couple was estimated by comparing an experimental voltammogram measured with a glassy carbon electrode in a solution containing EtV^{2+} with computer simulations done with the program DigiSim (based on finite difference methods). The parameters of the simulation (standard redox potential, standard rate constant and diffusion coefficient) were tuned until a good agreement with the experimental data was achieved (figure S2). From, the position of the voltammetric peaks, it is concluded that $E^0(EtV^{2+}/ EtV^{+}) \approx$ 2.42 V vs. Li/Li^{+}. From the peak to peak separation, it is concluded that $k^0 \approx 3x10^{-4}$ cm/s, but this value of the standard rate constant is a lower limit, since IR drop effects will contribute to the peak to peak separation, and this effect has not been included in the simulation. From the height of the peak (peak current density), the value of the diffusion coefficient of ethyl viologen is obtained: $D(EtV^{2+}) \approx 1.4x10^{-7}$ cm^2/s.

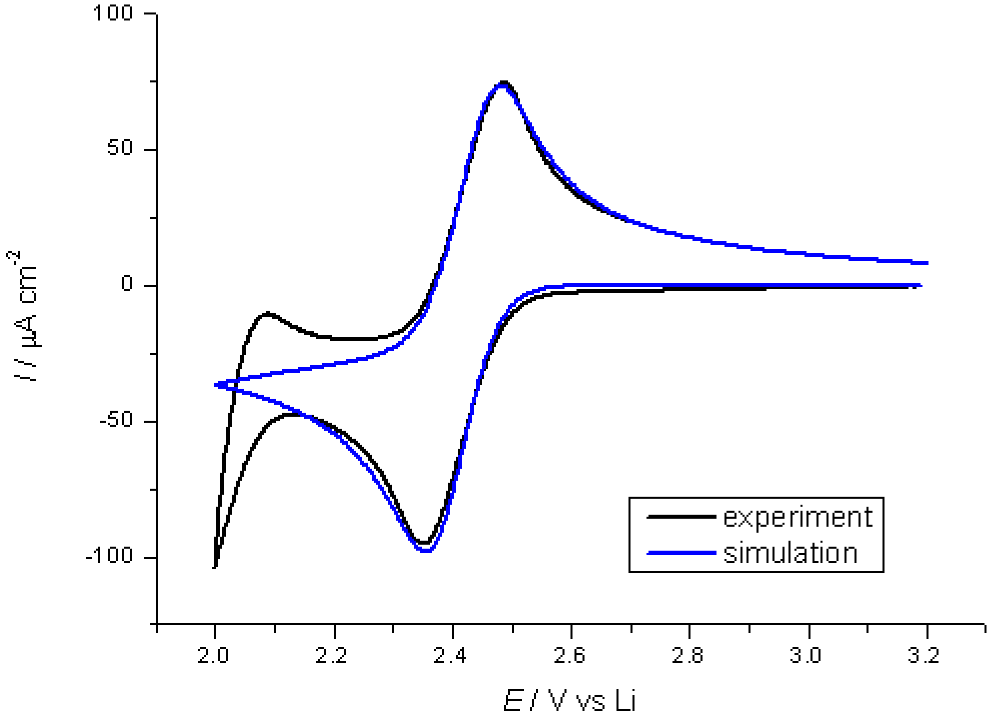

Figure S2. Comparison of the experimental voltammogram measured with a glassy carbon electrode in 5mM EtV(Tf)$_2$ in Py$_{14}$TFSI (Ar saturated) at 50 mV/s, with a simulated voltammogram obtained with the following parameters: E^0(EtV^{2+}/ EtV$^+$) = 2.42 V vs. Li/Li$^+$, k^0 = 3x10^{-4} cm/s, D(EtV^{2+})=D(EtV$^+$)=1.4x10^{-7} cm^2/s.

3. Stability of lithium superoxide against disproportionation

Figures S3 and S4 show the UV-vis spectra of a solution of KO$_2$ in acetonitrile and tetraglyme, respectively, before and after the addition of LiTFSI. It is observed that the spectra remain unchanged after 3 hours, demonstrating that the rate of disproportionation is very slow under these conditions.

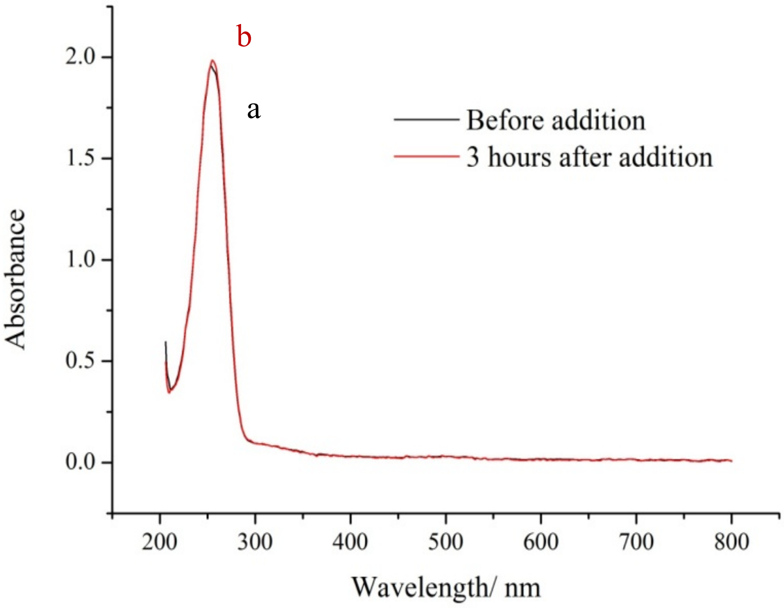

Figure S3. UV-vis spectra of a ca. 1 mM KO_2 solution in acetonitrile before (a) and after 3 hours (b) from the addition of 300 mM LiTFSI.

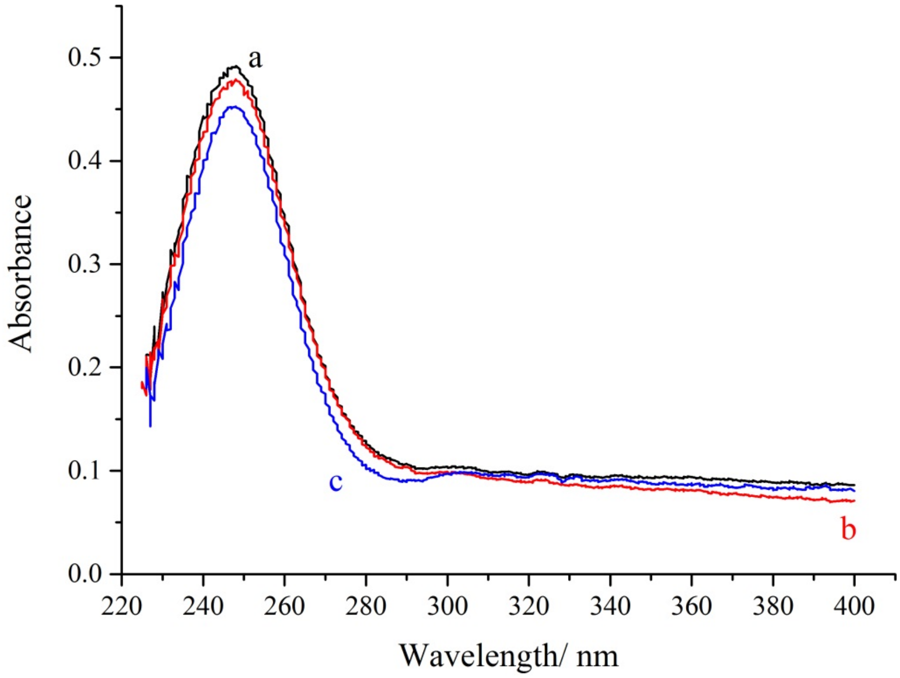

Figure S4. UV-vis spectra of a ca 0.5 mM KO_2 solution in tetraglyme before (a) and after 1 hour (b) and 3 hours (c) from the addition of 300 mM LiTFSI.

4. Reaction between EtV^+ and superoxide

Figure 3 in the main manuscript shows the reaction between EtV^+ and superoxide in acetonitrile. The quantification of the stoichiometry of the reaction has been done as follows. Taking into account the decrease in the absorption at 600 nm, it is concluded that the number of moles of EtV^+ that have reacted are:

$$\frac{076-0.32}{0.76} * 0.05mM * 60ml = 2.13\mu mol$$

Since the experiment was done with 60 ml of a 0.05mM EtV^{+} solution. The number of moles of KO_2 that have been added in total are

$$3 * 1.5mM * 0.5ml = 2.25\mu mol$$

In conclusion, nearly the same number of moles of EtV^{+} and superoxide are consumed during the reaction. The same conclusion can be reached by estimating the amount of EtV^{2+} formed during the reaction by looking at the change in the adsorption at 260 nm.

5. Reaction between EtV^{+} and oxygen

Figure S5 shows the UV spectra measured during the titration of EtV^{+} with oxygen in acetonitrile. The decrease in the bands at 600 and 400 nm demonstrate the consumption of EtV^{+}, while the increase in the band at 260 nm indicates the formation of EtV^{2+}. The number of moles of EtV^{+} consumed during the reaction can be estimated from the decrease in the absorption at 600 nm:

$$\frac{0787-0.413}{0.787} * 0.05mM * 60ml = 1.43\mu mol$$

Taking into account that the solubility of oxygen in acetonitrile is 8.1mM[4, 5], the number of moles of oxygen that have been added are

$$3 * 8.1mM * 0.03ml = 0.73\mu mol$$

In conclusion, one oxygen molecule reacts with ca two molecules of EtV^{+}.

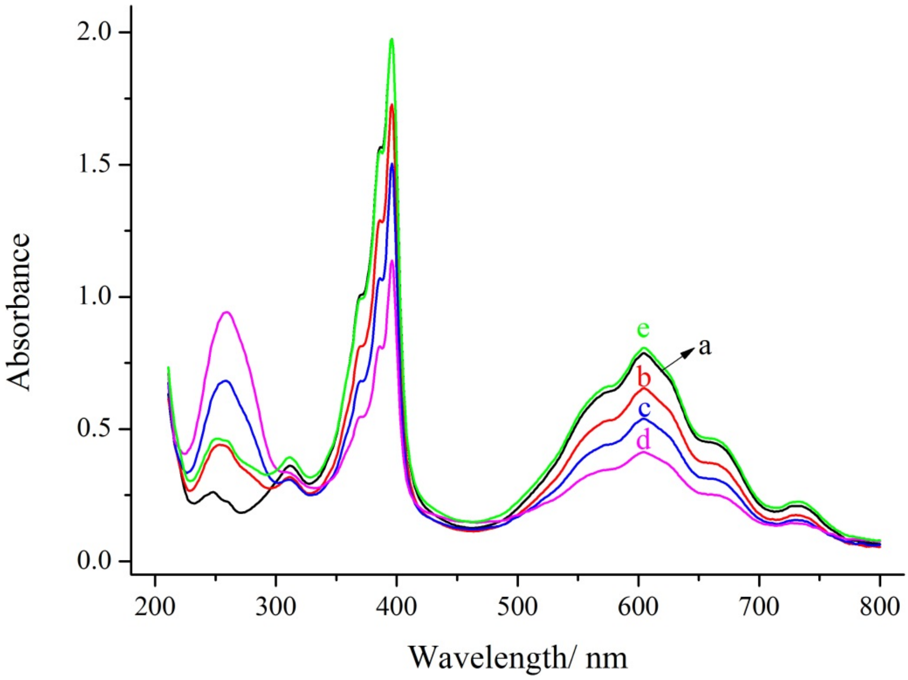

Figure S5. UV-vis spectra measured during the titration of 60 mL of 0.05 mM EtV^{+} + 0.15 M LiTFSI in acetonitrile with: a) zero, b) one, c) two, and d) three additions of 0.03 mL of oxygen-saturated acetonitrile. Curve e shows the UV-vis spectrum obtained after the titration with KO_2 followed by re-reduction with $Li_7Ti_5O_{12}$.

The reaction between EtV^+ and oxygen was then studied in $Py_{14}TFSI$ (figures S6-7). Taking into account the solubility of oxygen in $Py_{14}TFSI$ (3 mM)[6-8], it is concluded that ethyl viologen induces the 2-electron reduction of oxygen in this electrolyte. The number of moles of EtV^+ that have reacted at the end of the experiment are:

$$\frac{0731-0.36}{0.731}*0.05mM*60ml=1.52\mu mol$$

The number of moles of O_2 that have been added are:

$$3*3mM*0.08ml=0.72\mu mol$$

Absence of degradation reactions is also confirmed by the fact that EtV^+ can be recovered quantitatively via reduction of the EtV^{2+} reaction product with $Li_7Ti_5O_{12}$ (figure S7)

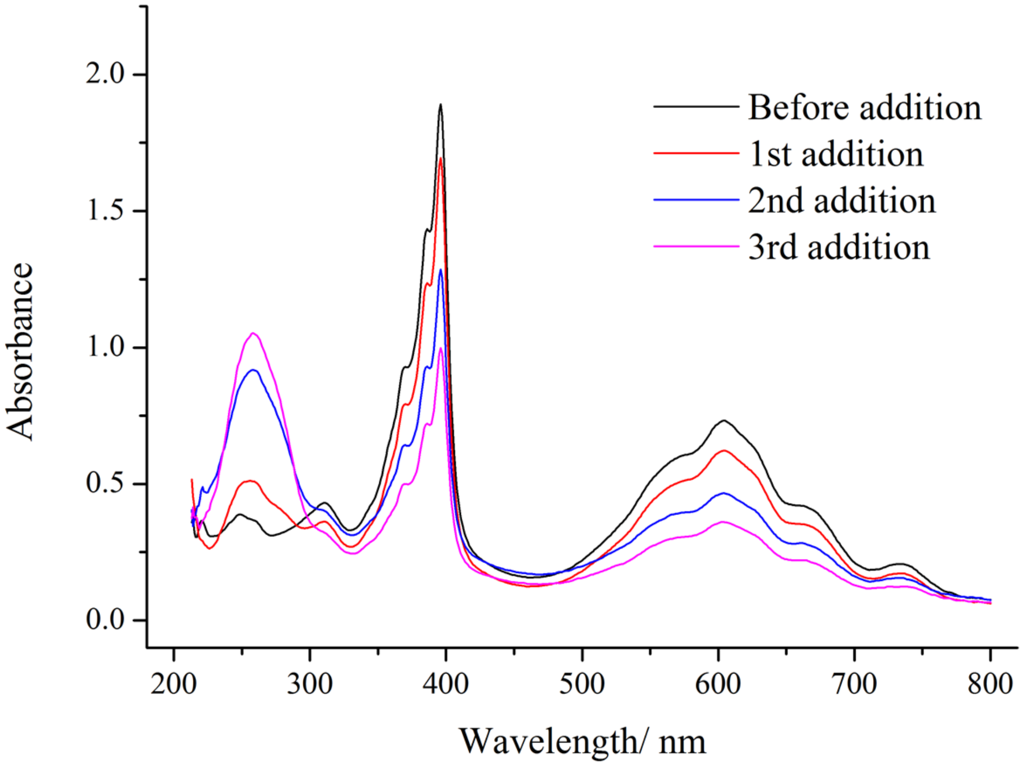

Figure S6. UV-vis spectra measured during the titration of 60 mL of 0.05 mM EtV^++ 0.15 M LiTFSI in $Py_{14}TFSI$ with several aliquots of 0.08 ml of oxygen-saturated $Py_{14}TFSI$.

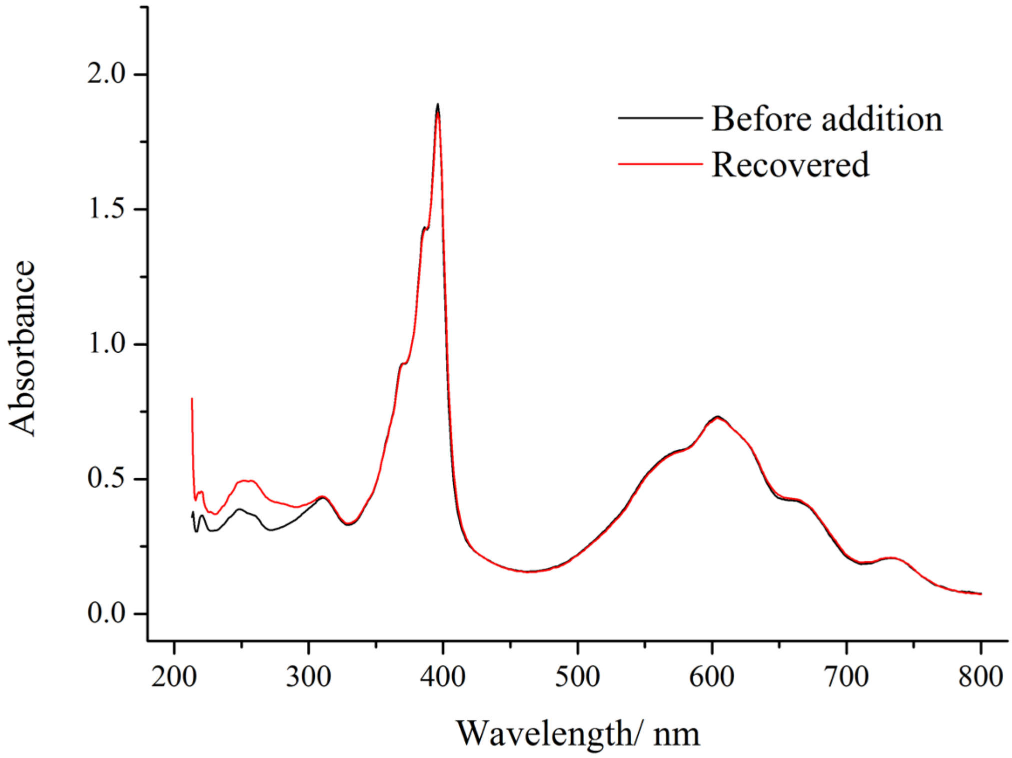

Figure S7. UV-vis spectra of 0.05 mM EtV^+ in $Py_{14}TFSI$ before and after the reaction with oxygen followed by re-reduction with $Li_7Ti_5O_{12}$.

2. Kinetic analysis of the reaction between EtV^+ and superoxide

The reaction between EtV^+ and superoxide was monitored by measuring the absorbance at 590 nm, which is proportional to the EtV^+ concentration, as a function of time. Solutions with an initial composition of 0.1 mM EtV^+ + 0.1 mM O_2^- with different concentrations of LiTFSI were prepared in acetonitrile. Since in all cases, the concentration of Li^+ is much higher than that of EtV^+ and superoxide, it can be regarded as constant. Therefore, it can be proposed that the reaction will follow pseudosecond-order reaction kinetics:

$d[EtV^+]/dt = k_{eff} [O_2^-][EtV^+]=k_{eff} [EtV^+]^2$

where the rate constant, k_{eff}, may depend on the Li^+ concentration. Integration of the equation above gives:

$[EtV^+]^{-1} = k_{eff}\, t + c$

where c is a constant. Figure S8 shows the plot of $[EtV^+]^{-1}$ vs. time, where $[EtV^+]$ has been calculated from the values of the absorbance taking into account the absorption cross-section. A liner relationship is observed, and the values of the slope are plotted vs. the Li^+ concentration in figure S9. From this, it is concluded that k_{eff} equals to ca. 90 $M^{-2}\ s^{-1}$ times the Li^+ concentration. The following reaction mechanism can be proposed, which is consistent with the experimental results:

$O_2^- + Li^+ \rightleftharpoons LiO_2$ (fast)

$EtV^+ + LiO_2 \rightarrow EtV^{2+} + LiO_2^-$ (rate determining step)

$LiO_2^- + Li^+ \rightleftharpoons Li_2O_2$ (fast)

The overall reaction would be reaction (10) proposed in the article as the third step in the viologen mediated reduction of oxygen.

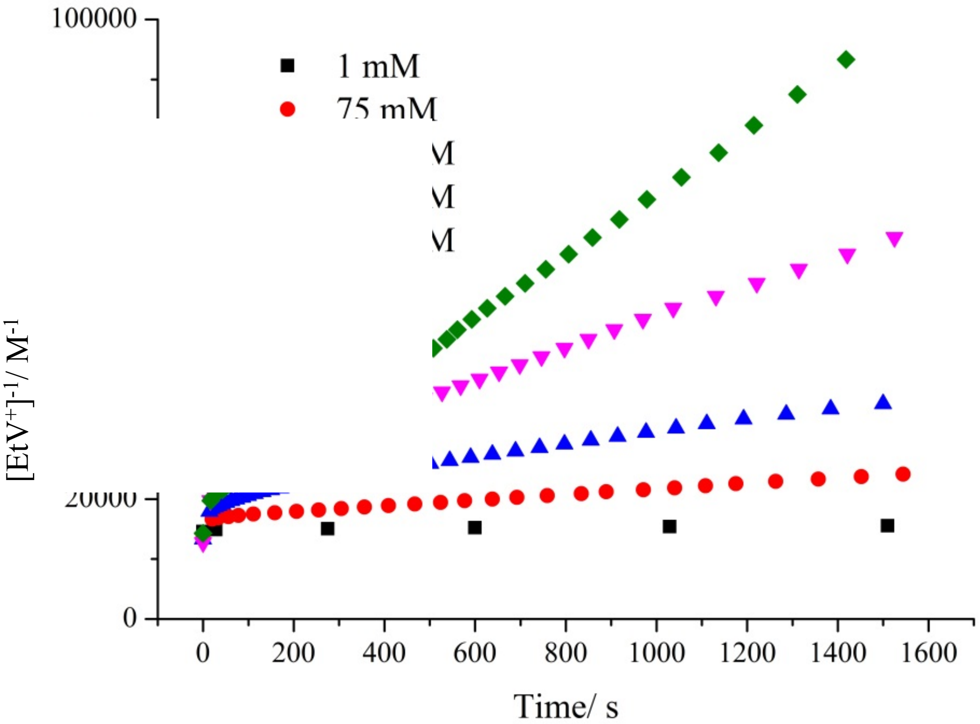

Figure S8. Plot of the reciprocal of the EtV^+ concentration vs. time. Note that the determination of the time when the reaction started (t=0) is difficult, but this uncertainty will not affect the evaluation of the value of the slope of this plot.

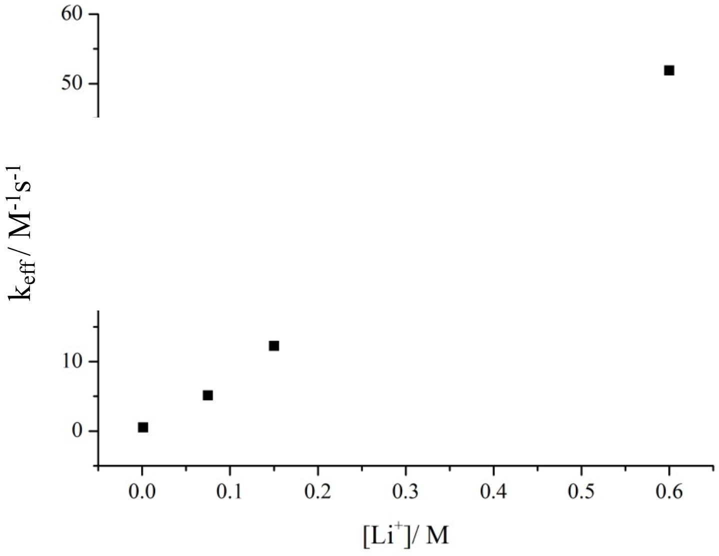

Figure S9. Plot of the values of slope in figure S8 vs. the Li^+ concentration.

Kinetic analysis of the reaction between EtV^+ and oxygen

In addition, the rate of reaction between oxygen and viologen was also measured. Since one mole of oxygen reacts with 2 moles of EtV^+, the experiments were done with a solution whose initial EtV^+ concentration was 0.1 mM and the initial oxygen concentration was 0.05 mM. The LiTFSI concentration was 300 mM. The results are shown in figure S10, and compared to the reaction between 0.1 mM KO_2 with 0.1 mM EtV^+ (at the same LiTFSI concentration, 300 mM). It can be observed that the decrease of $[EtV^+]$ was quicker with oxygen than with superoxide. This is because of the fast one electron reaction between oxygen and EtV^+:

$O_2 + EtV^{+} + Li^+ \rightarrow LiO_2 + EtV^{2+}$

Then, the decay in the absorbance is similar in both cases at longer times (>200 seconds), since in both cases the reaction is:

$LiO_2 + EtV^{+} + Li^{+} \rightarrow Li_2O_2 + EtV^{2+}$

The reactions above were proposed in the article (reactions 9 and 10) as the most likely pathway for the viologen mediated reduction of oxygen.

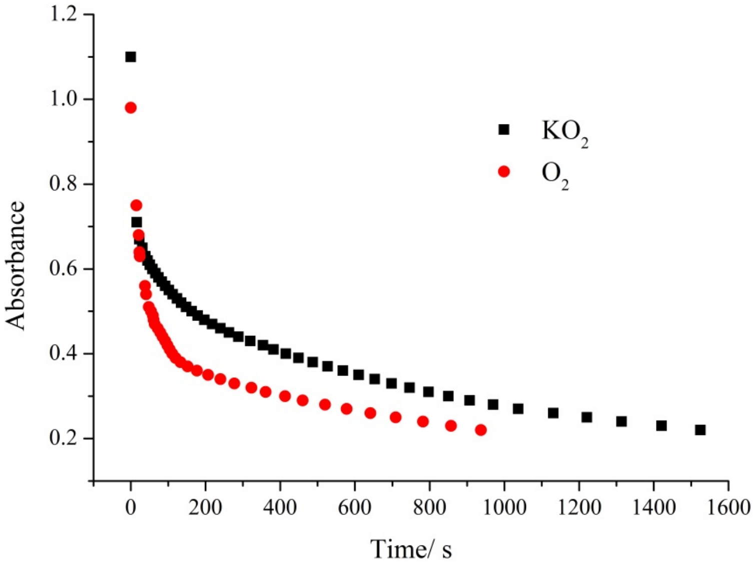

Figure S10. The absorbance of 0.1 mM EtV^{+} in acetonitrile after addition of KO_2 and O_2 with 300 mM of LiTFSI

References:

1. T. M. Bockman and J. K. Kochi, *J. Org. Chem.*, 1990, **55**, 4127-4135.
2. E. M. Kosower and J. L. Cotter, *J. Am. Chem. Soc.*, 1964, **86**, 5524-5527.
3. T. Watanabe and K. Honda, *J. Phys. Chem.*, 1982, **86**, 2617-2619.
4. J. M. Achord and C. L. Hussey, *Anal. Chem.*, 1980, **52**, 601-602.
5. D. T. Sawyer, G. Chlericato, C. T. Angelis, E. J. Nanni and T. Tsuchiya, *Anal. Chem.*, 1982, **54**, 1720-1724.
6. J. Herranz, A. Garsuch and H. A. Gasteiger, *J. Phys. Chem. C*, 2012, **116**, 19084-19094.
7. A. W. Lodge, M. J. Lacey, M. Fitt, N. Garcia-Araez and J. R. Owen, *Electrochim. Acta*, 2014, **140**, 168-173.
8. S. Monaco, A. M. Arangio, F. Soavi, M. Mastragostino, E. Paillard and S. Passerini, *Electrochim. Acta*, 2012, **83**, 94-104.