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Supplementary Information

Tuning the reduction potential of quinones by controlling the effects of hydrogen bonding, protonation and proton-coupled electron transfer reactions.

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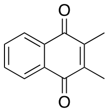
Experimental Procedures

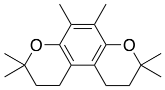
Chemicals

2,3-Dimethyl-1,4-napthoquinone (VKA),[S1,S2] pyrano[3,2-f]chromene (VEA),[16] and tetra-*n*-butylammonium hexafluorophosphate ($n\mathrm{Bu_4NPF_6}$)[S3] were synthesized according to literature procedures. 2,2,2-Trifluoroethanol (TFE, 99+%, Alfa Aesar), diethyl malonate (DEM) and trifluoroacetic acid (TFA, 99%, Alfa Aesar) and CH_3CN (AR grade, RCI Labscan Limited) were purchased from commercial sources and used as received.

NMR data for VKA: 1H NMR (300 MHz, $CDCl_3$): δ 2.18 (s, 6H), 7.69 (m, 2H), 8.09 (m, 2H).



NMR data for VEA: 1H NMR (300 MHz, $CDCl_3$): δ 1.29 (s, 12H), 1.78 (t, 4H, *J* = 6.9 Hz), 2.10 (s, 6H), 2.54 (t, 4H, *J* = 6.8 Hz).



Cyclic Voltammetry

Cyclic voltammetry experiments were performed with a computer-controlled Eco Chemie Autolab PGSTAT302N potentiostat in a three-electrode cell under an argon atmosphere inside a Faraday cage with a 1 mm diameter planar disk glassy carbon (Cypress Systems) working electrode, a platinum (Metrohm) auxiliary electrode, and a silver wire (Cypress Systems) miniature reference electrode connected to the solution via a salt bridge containing 0.5 M $n\mathrm{Bu_4NPF_6}$ in CH_3CN. The solution was deoxygenated by passing a steady stream of argon gas and the working electrode was systematically polished on a Buehler polishing pad before each scan. Accurate potentials were obtained by referencing to the ferrocene/ferrocenium redox couple (Fc/Fc^+) after adding ferrocene at the end of the experiments.

Controlled Potential Electrolysis

Controlled potential electrolysis experiments were performed in a two-compartment electrolysis cell separated by a sintered glass frit with porosity no. 5 (1.0-1.7 µm). Two identically sized glassy carbon cylinders were used as the working and counter electrodes and place symmetrically with respect to each other. The silver wire reference electrode was positioned to within 2 mm of the surface of the working electrode. 25 mL solutions were used both electrode compartments and simultaneously deoxygenated and stirred using bubbles of high purity argon gas. A 2 mM concentration of VKA (with specified amounts of TFE, DEM and TFA) was used for the electrolysis inside the working electrode compartment, and the number of electrons involved in the bulk conversion process was calculated using Faraday's law of electrolysis ($n = Q/NF$, where n is the no. of electrons transferred. Q is the amount of charge passed (C), N is the no. of moles of VKA (mol) and F being Faraday's constant (96485 C mol^{-1})).

Discussion of UV-vis data of VKA in presence of varying concentrations of acid.

UV-vis experiments were performed for VKA in the presence and absence of 50 and 500 equivalents of TFA, with the results shown in Figure S1. Collectively, these results suggest that almost no proton-transfer reaction had taken place between VKA and TFA at both concentrations of the acid, and that hydrogen bonding was more likely occurring between the neutral quinone and the acid instead. It is thus highly probable that the reduction of VKA follows an ECEC or ECCE mechanism in the presence of up to 5 M TFA.

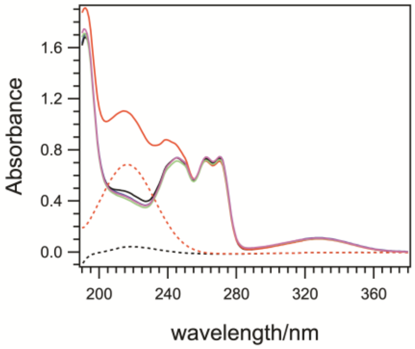


Figure S1. UV-vis spectra of VKA in the absence and presence of TFA. Legend: 1 mM VKA only (blue solid line), 1 mM VKA with 0.5 M (50 equivalents) TFA (black solid line - not corrected, green solid line - corrected), 0.5 M TFA only (black dashed line), 1 mM VKA with 5 M (500 equivalents) TFA (red solid line – not corrected, pink solid line - corrected), 5 M TFA only (red dashed line). The green and pink spectra were corrected by subtracting the UV-vis spectra of the acid only (black and red dashed lines) from those of VKA in the presence of the acids (black and red solid lines), respectively.

Discussion of Potentials Applied During the Electrolysis Experiments.

The applied potential for the reduction of VKA in the presence of the three additives decreases as follows: -1.269 V with TFE, -1.061 V with DEM and -0.420 V with TFA (with the potentials referenced to the Fc/Fc^+ redox couple). This arises because of the difference in stabilization imparted by the three hydrogen donors. A larger potential (i.e. higher energy) is needed with TFE because it is the least effective in stabilizing the reduced forms of the quinone (via hydrogen bonding), while a smaller potential (i.e. smaller energy) is required with TFA since it is best at stabilizing the charged species (through protonation). It has been reported that the extent of stabilization of the various quinone forms affects the electron affinity (and hence reduction potential) of Q and $Q^{\bullet-}$.[20]

The opposite trend was however seen for the re-oxidation of the reduced quinone forms: -0.899 V with TFE, -0.411 V with DEM and +0.012 V with TFA, where a larger potential was needed to oxidize $VKAH_2$ (formed through the reaction of VKA^{2-} with TFA) to VKA because of its greater stability. Being the least stable, the hydrogen bonded VKA^{2-} expectedly requires the least energy (i.e. least positive potential) for its conversion back to the neutral quinone.

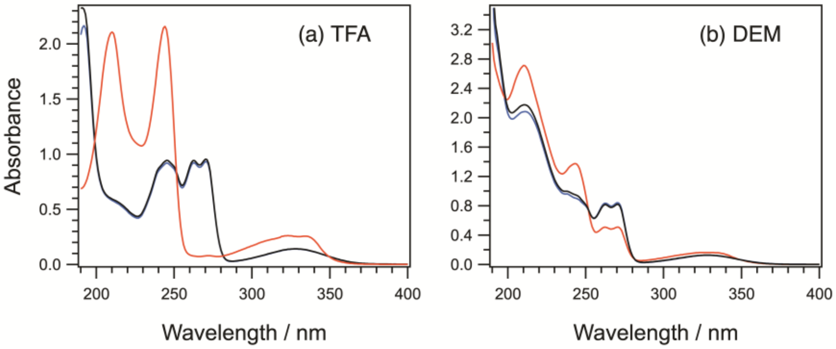


Figure S2. UV-vis spectra of 1 mM VKA/0.1 M *n*Bu$_4$NPF$_6$ in CH$_3$CN with (a) 50 mM of TFA and (b) 200 mM of DEM. Legend: blue line – at the start of the experiment before bulk electrolysis, red line – after 2-electron bulk reduction, black line – after 2-electron bulk re-oxidation.

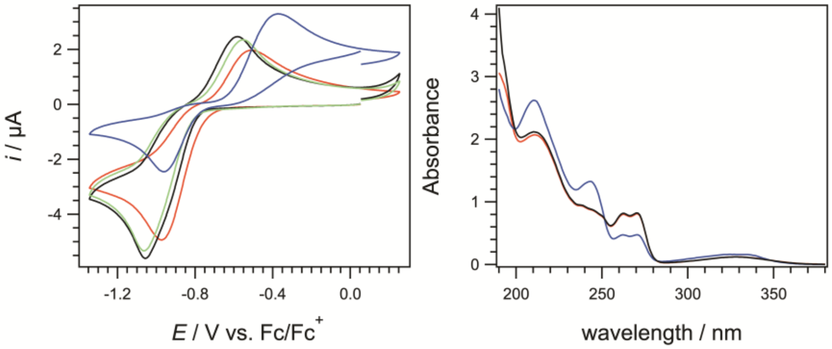


Figure S3. Cyclic voltammograms (left) and UV-vis spectra (right) of 1 mM VKA/0.1 M *n*Bu$_4$NPF$_6$ in CH$_3$CN with 200 mM of DEM. Voltammograms were recorded with a 1 mm diameter planar glassy carbon working electrode at 0.1 V s^{-1} at 25±2 °C. Legend: red line – at the start of the experiment before bulk electrolysis, blue line – at t = 0 after 2-electron bulk reduction, black line – at t = 24 h after 2-electron bulk reduction. The voltammogram in green line was recorded at the end of the experiment, after a 2-electron bulk re-oxidation CPE was performed to convert any reduced VKA back into VKA, to which the negligible amount of current measured indicate that the reduced VKA had undergone complete self-discharge over 24 h. The small difference in the currents (green vs. black) suggest good chemical reversibility of the process and long-term stability of the system.

Additional References

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