**Electronic Supplementary Information** for Goeltz, J. C. and Matsushima, L. N. *Metal Free Redox Active Deep Eutectic Solvents*

**General**
Solids were dried in a vacuum oven at 35 °C to a constant mass and stored in a desiccator. All other chemicals were used as received. Methyl viologen (98%) was obtained from Sigma Aldrich, Milwaukee, WI. Benzyl viologen (98%) was obtained from TCI, Portland, OR. Ethylene glycol (99%) was obtained from Alfa Aesar, Tewksbury, MA. Malonic acid (99%) was obtained from Sigma Aldrich. Choline chloride (high purity) was obtained from VWR, Radnor, PA. Generally, materials were mixed in the appropriate molar ratios and gently warmed on a sand bath until uniform mixtures were obtained. Melting points were determined with an Electrothermal melting point apparatus by manually increasing the set point to achieve a rate of increase of < 1 °C/min.

**Spectroelectrochemistry**
Spectroelectrochemistry was performed using a Perkin Elmer 13 UV-Vis/NIR with a cell holder thermostatted via water recirculating bath and a Pt mesh working electrode from BAS Inc., a Pt counter electrode, and a leak free Ag/AgCl reference electrode. Data, as presented in the manuscript, are show again here to facilitate discussion and are plotted again below in cm$^{-1}$ for readers who prefer to think in terms of energy.
The dimerisation constant $K_d$ for 1 mM benzyl viologen in a 2:1 eutectic of EG/ChCl is estimated by comparing the absorbances at 604 nm and the relative concentrations for the 1 mM solution versus the 66.4 $\mu$M solution in water (blue line, above). For aqueous solutions, a $K_d = [\text{mono}]^2/[\text{dim}] = 20 \mu$M is reported.\textsuperscript{1} The material in the deep eutectic is 15 times more concentrated (increases relative $K_d$, as formulated), and the absorbance at 604 nm is 1.4 times as large (also increases relative $K_d$, as formulated). $20 \mu$M $\times 15 \times 1.4 = 420 \mu$M, or 400 $\mu$M using one significant figure as is likely warranted here.

**Electrochemistry and Digital Simulation**

Voltammetry data were obtained with a 10 $\mu$m diameter Pt or a 2 mm diameter glassy carbon working electrode (CH Instruments), a Pt coil counter electrode (Alfa Aesar), a leak free Ag/AgCl reference electrode (Harvard Apparatus), and a CH Instruments 660e potentiostat.

Voltammetry for 1 mM benzyl viologen in 2:1 ethylene glycol choline chloride with a 2 mm diameter glassy carbon electrode, ferrocene as an internal standard and a scan rate of 100 mV/s are overlaid with voltammetry of the “blank” 2:1 EG/ChCl solvent.
Voltammetry of 4:1 EG/BVCl₂ (4.2 M in BV²⁺) at 40 °C with a 10 μm diameter Pt working electrode and varied scan rate is shown below. The electrode area was confirmed by analysis of peak currents obtained for a solution of ferrocyanide of known concentration and the Randles Sevcik equation before fitting. The same equation was then used with the peak currents to estimate the diffusion coefficients for BV²⁺ and BV¹⁺ as 3.4x10⁻⁹ cm²/s and 1.7x10⁻⁹ cm²/s, respectively. These were used as starting points for the digital simulation, *vide supra.*
Voltammetry results were simulated using DigiElch 8.0 from Gamry Instruments. A plot of the experimental data with simulated data including adsorption and dimerization (blue curve, well fit) and simulated data for just adsorption (gold, dashed line, less well fit).

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**DigiElch Parameters with dimerisation (blue, solid line above)**

Charge Transfer Reactions
BV²⁺ + e⁻ = BV¹⁺⁺ , Eₒ* (V) = -0.5663 , alfa* = 0.5 , ks* (1/s) = 1.5

Chemical Reactions
BV¹⁺ + BV¹⁺ = 2BV¹⁺ , Keq = 0.51917 , kf = 18.758 , kb = 36.131
Note: $K_{eq}$ for dimerisation here equals 0.5, but this fitting uses the inverse formalism (i.e., reactants over products) compared with that used in the literature: $K_d = [\text{mono}]^2/[\text{dim}]$. To make them conform, we take the inverse of this value and arrive at 2 M.

Adsorption Reactions

$BV2^+ = BV2^+*$, $Keq^* = 10000$, $kf^* = 10000$, $a^* = 0$

$BV1^+ = BV1^+*$, $Keq^* = 20000$, $kf^* = 10000$, $a^* = 0$

$\Gamma_{max} = 2.7E-8$

DigiElch Parameters without dimerisation (gold, dashed line above)

Charge Transfer Reactions

$BV2^+ + e = BV1^+*$, $Eo^* (V) = -0.5663$, $alfa^* = 0.5$, $ks^* (1/s) = 1.5$

Adsorption Reactions

$BV2^+ = BV2^+*$, $Keq^* = 10000$, $kf^* = 10000$, $a^* = 0$

$BV1^+ = BV1^+*$, $Keq^* = 20000$, $kf^* = 10000$, $a^* = 0$

$\Gamma_{max} = 2.7E-8$