

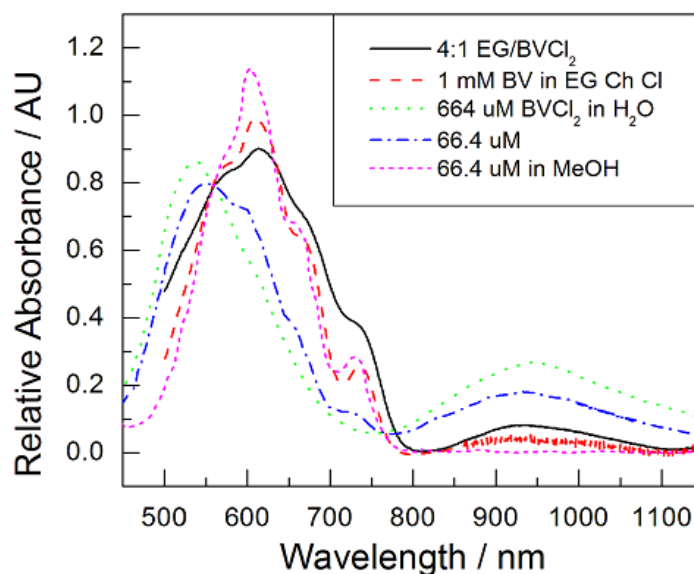
## Electronic Supplementary Information for Goeltz, J. C. and Matsushima, L. N. Metal Free Redox Active Deep Eutectic Solvents

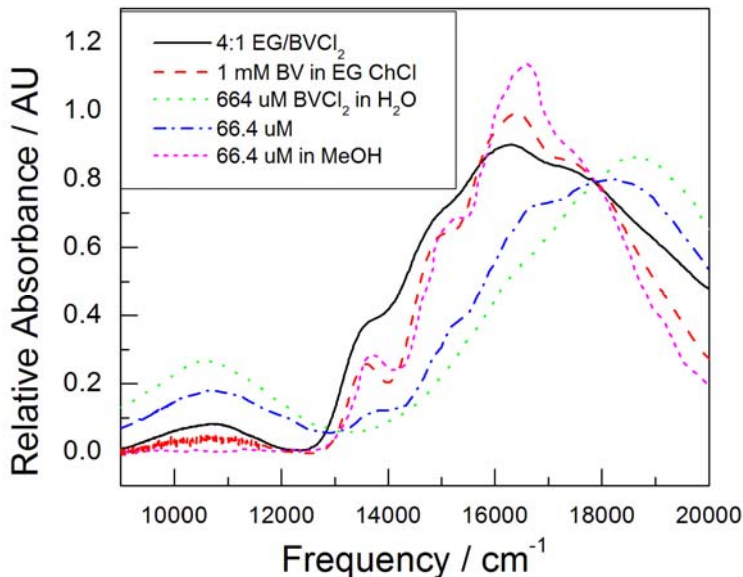
### General

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  $\text{cm}^{-1}$  for readers who prefer to think in terms of energy.



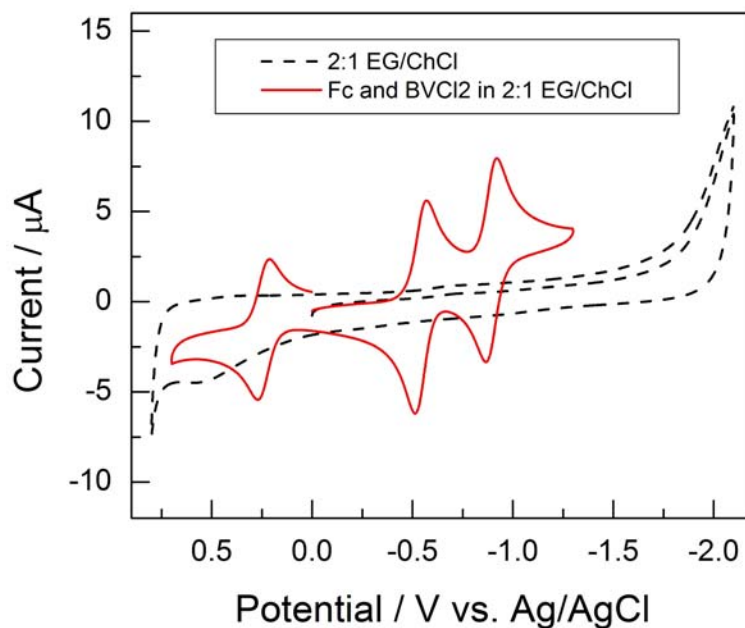


The dimerisation constant  $K_d$  for 1 mM benzyl viologen in a 2:1 eutectic of EG/ChCl is estimated by comparing the absorbances at 604 nm and the relative concentrations for the 1 mM solution versus the 66.4  $\mu\text{M}$  solution in water (blue line, above). For aqueous solutions, a  $K_d = [\text{mono}]^2/[\text{dim}] = 20 \mu\text{M}$  is reported.<sup>1</sup> 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).  $20 \mu\text{M} * 15 * 1.4 = 420 \mu\text{M}$ , or 400  $\mu\text{M}$  using one significant figure as is likely warranted here.

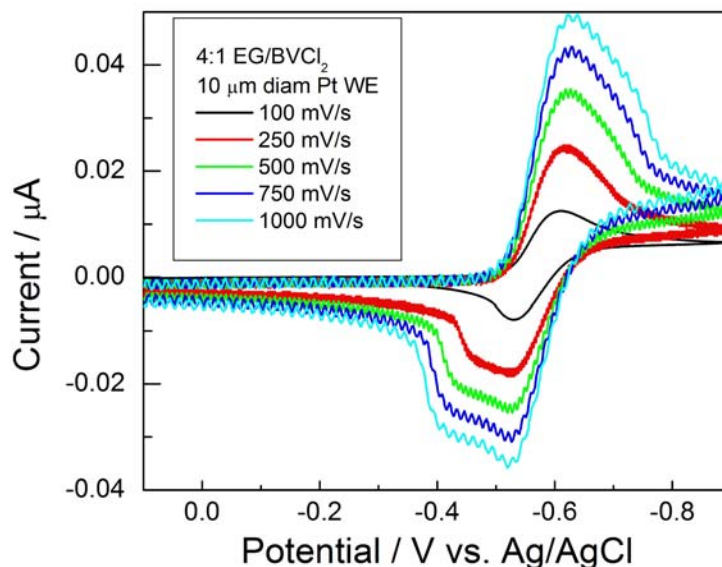
### Electrochemistry and Digital Simulation

Voltammetry data were obtained with a 10  $\mu\text{m}$  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.



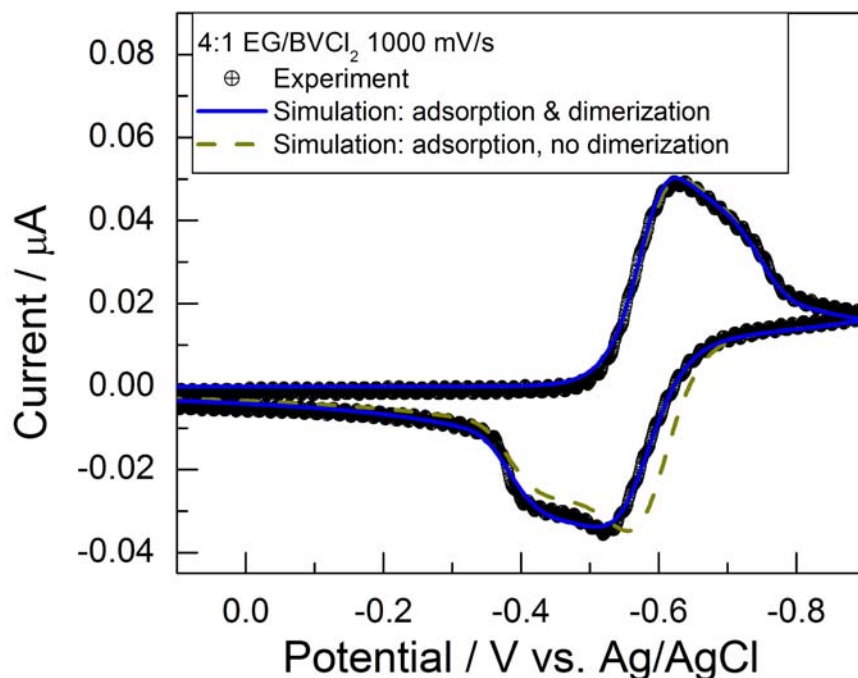
Voltammetry of 4:1 EG/BVCl<sub>2</sub> (4.2 M in BV<sup>2+</sup>) at 40 °C with a 10 μm diameter Pt working electrode and varied scan rate is shown below.



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 BV<sup>2+</sup> and BV<sup>1+</sup> as  $3.4 \times 10^{-9}$  cm<sup>2</sup>/s and  $1.7 \times 10^{-9}$  cm<sup>2</sup>/s, respectively. These were used as starting points for the digital simulation, *vide supra*.

EGBVCl <sub>2</sub>	Randles	Sevcik	Analysis				
scan rate V/s	i <sub>p</sub> red	D <sub>O</sub> / cm <sup>2</sup> /s	i <sub>p</sub> ox	D <sub>R</sub> / cm <sup>2</sup> /s	4.16 M		
0.1	1.24E-08	2.36E-09	7.89E-09	9.64E-10			units
0.25	2.39E-08	3.53E-09	1.78E-08	1.97E-09	n	1	e <sup>-</sup>
0.5	3.43E-08	3.64E-09	2.48E-08	1.91E-09	F	96485	C/mol e <sup>-</sup>
0.75	4.23E-08	3.69E-09	2.99E-08	1.84E-09	A	7.36E-07	cm <sup>2</sup>
1	4.86E-08	3.66E-09	3.49E-08	1.89E-09	R	8.314	J/molK
		<b>BV<sup>2+</sup></b>		<b>BV<sup>1+</sup></b>	T	313	K
	<b>avg</b>	<b>3.38E-09</b>		<b>1.71E-09</b>	C	0.00416	mol/cm <sup>3</sup>
	std dev	5.69E-10		4.23E-10			

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).



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

Charge Transfer Reactions

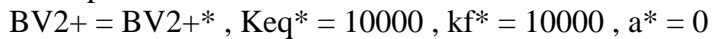
$BV^{2+} + e = BV^{1+*}$ ,  $E_{o^*}$  (V) = -0.5663,  $\alpha^* = 0.5$ ,  $k_{s^*}$  (1/s) = 1.5

Chemical Reactions

$BV^{1+} + BV^{1+} = 2BV^{1+}$ ,  $K_{eq} = 0.51917$ ,  $k_f = 18.758$ ,  $k_b = 36.131$

*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.

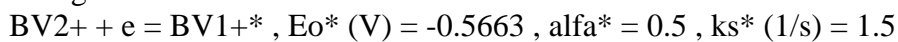
#### Adsorption Reactions



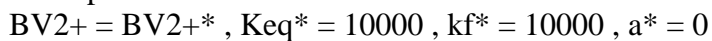
$$\Gamma_{\max} = 2.7\text{E-}8$$

#### **DigiElch Parameters without dimerisation (gold, dashed line above)**

#### Charge Transfer Reactions



#### Adsorption Reactions



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