

## The unique properties of a perfluoroalkyl-modified 2,2'-bipyridyl ruthenium complex in a Nafion™ membrane: attenuated leaching of a potential biofuel cell redox mediator

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### Supplementary Information.

#### Solution Cyclic Voltammetry of Complex 3

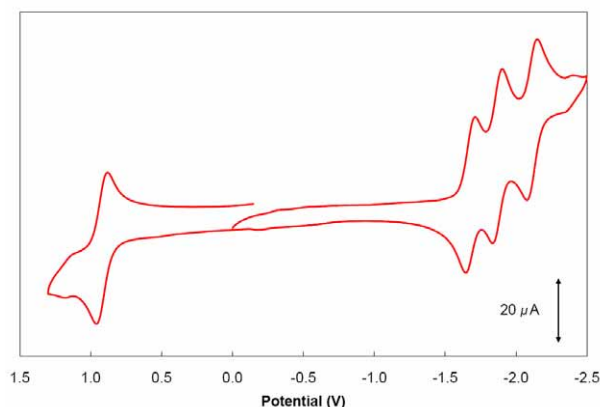


Figure S1. CV of complex 3, 1.0 mM solution in MeCN, glassy carbon disc working electrode, Ag/AgNO<sub>3</sub> (10 mM) solution in MeCN reference electrode, platinum counter electrode.

#### Complex 3/TBAB-modified-Nafion™ Loading Experiment

2 cm × 2 cm square glass microscope slips were each fully covered with applications of 150, 175, and 200 μL solutions of 5 wt% TBAB-modified-Nafion™ in EtOH, dried in a desiccator and then soaked in 5.00 mL of 200 μM CH<sub>2</sub>Cl<sub>2</sub> solutions of complex 3. UV-vis measurements were made prior to and following soakings and complex 3 molarities determined from a concentration-absorbance calibration plot (not shown). The decrease in molarity was used to compute the molar uptake of complex 3 by the 2 cm × 2 cm film. Based on a sulfonate group concentration of  $8.68 \times 10^{-6}$  mol SO<sub>3</sub><sup>-</sup>

/g TBAB-modified-Nafion™ and an accurately measured volume-mass conversion of 4.18 mg/100 μL TBAB-modified-Nafion™, the average Ru:SO<sub>3</sub><sup>-</sup> ratio could be calculated. Thus for a 200 μL (8.36 mg) TBAB-modified-Nafion™ deposit,  $2.29 \times 10^{-7}$  mol complex was absorbed, leading to a complex 3:sulfonate group ratio of 0.28:1.0.

The plot in Figure S2 was used to estimate the limiting absorbance corresponding to the maximum loading of complex 3 for this size of glass slip and sulfonate group concentration by applying a quadratic fit to the data. The estimated maximum concentration depletion from the solution (determined from the concentration-absorbance calibration plot (not shown)) was then converted into molar uptake of complex 3 as described above to afford a maximum average complex 3:sulfonate group ratio of 0.30:1.0.

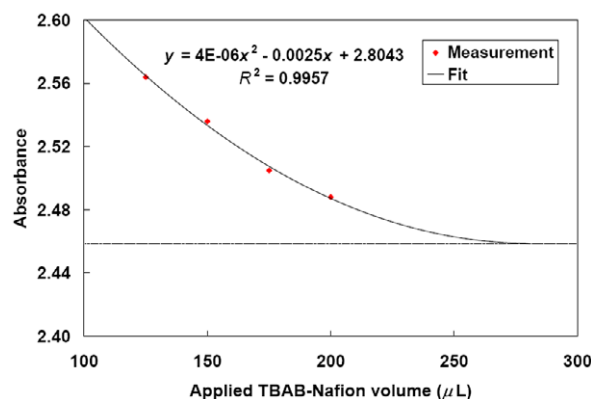


Figure S2. Plot of complex 3 CH<sub>2</sub>Cl<sub>2</sub> solution (200 μM, 5.00 mL) absorbance vs. volume of TBAB-modified-Nafion™ EtOH solution (5 wt%) applied to one side of a 2 cm × 2 cm glass microscope slip.