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Supporting Information

for

[4]Helicenium late-stage functionalization for significant Symmetric

high-voltage Organic Redox Flow Batteries improvement

Jules Moutet, David Mills, Md Mubarak Hossain and Thomas L. Gianetti*

University of Arizona, Department of Chemistry and Biochemistry, Tucson, AZ, United States

*E-mail: tgianetti@arizona.edu

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I. General informations

All solvents were purified by SPS or distillation over the drying agents indicated. Dried solvents and liquid reagents were transferred by oven-dried syringes or hypodermic syringes. The supporting electrolyte tetrabutylammonium hexafluorophosphate (TBAPF₆) was recrystallized three times from ethanol, then dried at 80 °C for three days prior to use. The racemic- 1,13dimethoxy-6-nitro-5,9-dipropyl-9,13b-dihydro-5H-quinolino[2,3,4-kl]acridinium tetrafluoroborate salt (compound ^{NO2}C⁺) was prepared according to Lacour *et al.* report and was purified by crystallization by slow vapor diffusion of Et₂O in concentrated ACN solution.¹ Electrochemical analyses were conducted inside a N₂-filled glovebox using a BioLogic SP-200 potentiostat/galvanostat. For convenience, all potentials are given *vs.* the reference electrode AgNO₃/Ag (reference electrode).

Cyclic voltammograms (CV) were measured in a three-electrode electrochemical cell, consisting of a platinum wire counter electrode, a AgNO₃/Ag reference electrode (0.01 M AgNO₃ in 0.1 M TBAPF₆ in CH₃CN), and a Pt working electrode (0.031 cm², CH Instrument, Inc.). The Pt working electrode was polished using aluminum oxide polishing paper and anhydrous CH₃CN. CVs were recorded at different scan rates (10, 25, 75, 100, 250, 400, and 500 mV/s) in an CH₃CN electrolyte containing ~1mM active species and 0.1M TBAPF₆.

Charge/discharge measurements were carried out in a custom-made glass H-cell with a 2 mm fine porous glass frit (4-5.5 μ m holes diameter) was used as the separator^{2,3} and a reference electrode (0.01 M AgNO₃/Ag 0.01 M in 0.1 M TBAPF₆ in CH₃CN). 10mL of a 1 mM solution (0.1 M TBAPF₆) of C⁺ was used to study the cycling in the cell. Reticulated vitreous carbon (RVC) electrodes (100 ppi Duocel[®]) were cut into rods of the dimensions 0.5 cm x 0.5cm x 4cm and positioned about 2 cm deep in solution (active surface ~ 33 cm² per electrode). To rule out contamination processes, the electrodes were singly-used. Then a Constant Current following by a Constant Voltage galvanostatic charging (CCCV GCPL protocol) at 151 mA current was applied *via* RVC electrodes. For the mono-electronic cycling potentials boundaries were set at -1.49 V and -0.49 V whereas the double-reduction cycling potentials boundaries were set -2.07 V and -0.49 V vs E_{ref} for both 90% State-Of-Charge (SOC) maximum loading. Along the the stress-test experience the voltage was limited between 1.55 V and -1.49 V vs E_{ref} for a 100% SOC loading. During charge-discharge experiments both cells were continuously stirred at 1000 rpm. Throughout this paper, the numbers reported in parentheses indicate the standard deviation in the last reported digit.

The saturation concentration of the $^{NO2}C^+$ and $^{NO2}C^-$ salt in pure acetonitrile were evaluated by UV-Visible via a calibration curve, at 154.1 mM and 110.0 mM respectively.



Figure S1. Cyclic voltammogram of $^{NO2}C^+$ 1 mM in 0.1M TBAPF₆ ACN. Recorded at a scan rate of 100 mV/s.



Figure S2. Differential pulse voltammetry (DPV) of ^{NO2}C⁺ 1 mM in 0.1M TBAPF₆ ACN.



Figure S3. Cyclic voltammogram of ^{NO2}C⁺ 1 mM in 0.1M TBAPF₆ ACN.at different scan rates.

III. Determination of ^{NO2}C⁺ kinetics parameters

Table S1. Values used to determine kinetics parameters D and k^0 .

n	1	electrons transfered
Α	0.031415927	cm ²
С	1.17E-06	mol.cm ³
Т	298	K

Table S2. Current values (i_p) recorded for processes at at -1.67 V (left), -0.89 V (middle) and1.34V (right) at different scan rates v.

	-1.6	4 V	-0.8	9 V	1.3	5 V
v (V/s)	I _{min} (A)	I _{max} (A)	I _{min} (A)	I _{max} (A)	I _{min} (A)	I _{max} (A)
0.010	-3.67E-06	-1.87E-07	-2.44E-06	1.08E-06	1.01E-06	5.17E-06
0.025	-4.94E-06	8.18E-07	-3.57E-06	2.24E-06	3.25E-07	7.14E-06
0.075	-7.79E-06	2.33E-06	-5.67E-06	4.66E-06	-8.59E-08	1.03E-05
0.100	-8.81E-06	2.84E-06	-6.40E-06	5.53E-06	-2.84E-07	1.11E-05
0.250	-1.30E-05	5.00E-06	-9.70E-06	9.27E-06	-1.17E-06	1.41E-05
0.400	-1.60E-05	6.51E-06	-1.20E-05	1.20E-05	-1.78E-06	1.66E-05
0.500	-1.80E-05	7.35E-06	-1.30E-05	1.30E-05	-1.79E-06	2.00E-05



Figure S4. Peak current *vs* square root of scan rate v and linear fits for processes at -1.67 V (left), -0.89 V (middle) and 1.34V (right).

$$i_p = 0.4463 n FAC \sqrt{\frac{n F \nu D}{RT}}$$
(1)

Equation S1. Randles-Sevcik equation, with i_p the peak current in Amperes, *n* equals the number of electrons transferred, *F* equals Faraday's constant, *A* is the area of the electrode in cm², *C* the concentration of redox active species in mol cm⁻³, *D* the diffusion coefficient in cm² s⁻¹, *v* the scan rate in V s⁻¹, *R* the ideal gas constant, and *T* the temperature in Kelvin.

 Table S3. Randles-Sevcik equation numerical application from the slopes for diffusion

 coefficients (D) determination in Figure S5

D (cm².s ⁻¹)			
-1.67 V	-0.89 V	1.34 V	
4.3 × 10 ⁻⁶	5.6 × 10⁻ ⁶	9.9 × 10⁻ ⁶	

$$\psi = \frac{(-0.6288 + 0.0021\Delta E_p)}{(1 - 0.017\Delta E_p)}$$
(2)
$$\psi = \frac{k^0}{\sqrt{\frac{\pi DnFv}{RT}}}$$
(3)
Where:
$$\Delta E_p = (E_p^{max} - E_p^{min})$$

Equation S2-S3. Nicholson's method⁴ and the more recent work of reported by Lavagnini et al.⁵ were used to determine the electron transfer rate constant (k^0) by relating it with the dimensionless kinetic parameter (Ψ). With *n* the number of electrons transferred, *F* equals Faraday's constant, *v* the scan rate, *R* the ideal gas constant and *T* the temperature in Kelvin. *D* diffusion coefficient at the corresponding scan rate.

Table S4. Lavagnini's method numerical application of Equation S2 and S3 for electron transfer rate constant (k^0) determination.

k ⁰ (cm.s ⁻¹)			
-1.67 V	-0.89 V	1.34 V	
1.2 × 10 ⁻²	3.7 × 10 ⁻²	7.9 × 10 ⁻³	



IV. Electronic spectrum and calibration curve for $^{NO2}C^{\bullet/+}$

Figure S5: UV-Visible absorption spectrum of $^{\rm NO2}C^+$ in acetonitrile at different concentration in mol/L



Figure S6: UV-Visible spectroscopy calibration curve for $^{NO2}C^+$ in acetonitrile at the absorbance of 421 nm and 573 nm.



Figure S7: UV-Visible absorption spectrum of ${}^{NO2}C^{\bullet}$ in acetonitrile at different concentration in mol/L



Figure S8: UV-Visible spectroscopy calibration curve for $^{NO2}C^{\bullet}$ in acetonitrile at the absorbance of 393 nm and 503 nm.

V. Density functional theory (DFT) calculations

Initial structures were built using Spartan Student v8.0.3.⁶ Density functional theory (DFT)^{7,8} calculations were carried out using a long-range corrected Perdew–Burke–Ernzerhof (LC-wPBE) functional⁹ with a 6-311G(d,p) basis set applied to all atoms. The optimized structures were determined to be energy minima by lack of imaginary vibrations in the frequency calculations. Solvated models were calculated with the polarizable continuum model (PCM) using the integral equation formalism variant (IEFPCM) as the SCRF method, with acetonitrile as the solvent. The molecular orbitals and spin densities for each model were calculated using cubegen and drawn using VMD 1.9.3.¹⁰ All calculations were performed on the High Performance Computing (HPC) system at the University of Arizona using G16.¹¹

Table S5: Energy minima for $^{NO2}C^+$ different states of oxidation in Gas Phase and solvated in acetonitrile

Energy (Kcal/mol)			
Molecule	Gas Phase	Solvated	
$^{NO2}C^{\dots}(S=3)$	-947598.88	-947659.45	
$^{NO2}C^{-}(S = 1)$	-947602.69	-947651.46	
NO2C·	-947582.71	-947593.01	
NO2C+	-947463.13	-947500.55	
^{NO2} C*++	-947220.80	-947348.87	

Table S6: Relative solubility of the different species was determined using the ΔG_{solv} . Consistent with experimental results, ^{NO2}C[•] was found to be less soluble than NO2C+. These calculations also suggest that both ^{NO2}C^{•++} and the anion are more soluble than the cation, though this could not be confirmed experimentally due to the aforementioned challenges in isolation of the desired species.

Model	∆Gsolv (kcal/mol)
$^{NO2}C^{\dots}$ (S = 3)	-60.50
$^{NO2}C^{-}(S = 1)$	-48.27
NO2C.	-10.56
NO2C+	-37.89
^{NO2} C•++	-127.43



Figure S9: SCRF spin density plots for ^{NO2}C^{••}, ^{NO2}C[•], ^{NO2}C[•], ^{NO2}C⁺, and ^{NO2}C^{++•} models. Isosurfaces were plotted at a 0.02 value.



Figure S10: Comparison of frontier molecular orbital (MO) isosurfaces and energies for solvated (CH₃CN) ^{NO2}C[•], ^{NO2}C[•], ^{NO2}C[•], ^{NO2}C⁺, and ^{NO2}C⁺⁺⁺ models. Isosurfaces were plotted at a 0.04 value. MO energy levels correspond to alpha electrons and color representations are as follows: black are core MOs, blue are HOMOs, green are SOMOs, and red are unoccupied orbitals. Gas phase isosurfaces and MO energies were observed to be nearly identical.



Figure S11: (a) MO energies for $^{NO2}C^{\bullet\bullet-}$ and $^{NO2}C^{\bullet}$. MO energy levels correspond to alpha electrons and color representations are as follows: black are core MOs, blue are HOMOs, green are SOMOs, and red are unoccupied orbitals. (b) Frontier molecular orbital (MO) isosurfaces plotted at a 0.04 value. Relative energies between $^{NO2}C^{\bullet\bullet-}$ and $^{NO2}C^{\bullet}$ are similar, which suggests both spin states are likely contributing to the anion redox state.

VI. Pictures of the H-cell used.



Figure S12. Picture of the empty H-Cell used with the two RVC electrodes, the AgNO₃/Ag reference electrode, and a magnetic stirrer on either side.

VII. Monitoring of GCPL CCCV experiments

GCPL CCCV mono-polarization



Figure S13. Coulombic Efficiency and Initial Capacity monitoring along GCPL CCCV monopolarization cycling at 90% SOC. Decay started at 186th cycle.



Figure S14. Plot of E_{we} potential and current (I) at the working electrode over 10 cycles of GCPL CCCV mono-polarization cycling.



Figure S15. Zoom-in of E_{we} during the 25th and 26th cycle of along GCPL CCCV monopolarization cycling and species formation in E_{ref} compartment.



Figure S16. Cyclic voltammogram analysis at 100mV/s of the respective contents of each side of the cell after 400 cycles of GCPL CCCV mono-polarization cycling on $^{NO2}C^+$.

GCPL CCCV double reduction



Figure S17. Coulombic Efficiency and Initial Capacity monitoring along GCPL CCCV double reduction cycling at 90% SOC.



Figure S18. Plot of E_{we} potential and current (I) at the working electrode over 10 cycles of GCPL CCCV double reduction cycling at 90% SOC.



Figure S19. Cyclic voltammogram analysis at 100mV/s of the respective contents of each side of the cell after 150 cycles of GCPL CCCV double-reduction experiments on $^{NO2}C^+$.

GCPL CCCV bi-polarization cycling stress-test



Figure S20. Capacity (Q) and Coulombic efficiency over 100 cycles GCPL CCCV bi-polarization cycling stress-test.



Figure S21. Plot of E_{we} potential and current (I) at the working electrode over 90 cycles of GCPL CCCV bi-polarization cycling stress-test (ca. 42400. s).



Figure S22. Zoom-in of E_{we} during the 9th and 10th cycles along GCPL CCCV bi-polarization cycling stress-test.

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