

Supporting Information

An oxo-verdazyl radical for a symmetrical non-aqueous redox flow battery

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General synthetic information

All reactions involving air- or moisture-sensitive reagents were carried out in oven- or flame-dried glassware under dry argon atmosphere using standard Schlenk techniques. Dimethylformamide (DMF, 99.8%, Extra Dry) was purchased from Acros Organics. Methanol and dichloromethane were freshly distilled. Other solvents used in reactions, for extraction and for flash chromatography were either freshly distilled prior to use or purchased in high purity from Fisher Scientific. Deuterated chloroform for NMR was obtained from Eurisotop. Reagents and all other chemicals were purchased from ABCR, Acros Organics, Alfa Aesar, Sigma Aldrich, Fluorochem, or TCI, and were used as received. Unless specified otherwise, reactions were stirred with PTFE-coated magnetic stirrer bars over a stirring plate at 400–800 r.p.m..

Flash chromatography (FC) was performed on Merck silica gel 60 (40–63 μm) with an excess argon pressure up to 0.4 bar. Merck silica gel 60 F254 glass plates were used for thin layer chromatography (TLC) using UV light ($\lambda_{\text{max}} = 254 \text{ nm}$) or vanillin solution (5 g in 200 mL EtOH with 2 mL conc. H_2SO_4) for detection.

^1H NMR (300 MHz) spectra were measured at 298 K on a Bruker DPX 300 spectrometer. Abbreviation of signal multiplicity is as follows: s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). Broad signals are described with br. Chemical shifts (δ) are reported in ppm relative to TMS and were referenced to the residual peak of CDCl_3 (^1H NMR: $\delta = 7.26 \text{ ppm}$; ^{13}C NMR: $\delta = 77.16 \text{ ppm}$). Coupling constants (J) are given to the nearest 0.1 Hz. HRMS (ESI) was recorded on a Bruker Daltonics Micro-TOF or a Thermo Fisher Scientific LTQ Orbitrap XL and peaks are given in m/z .

General procedures for the synthesis of oxo-verdazyl radicals

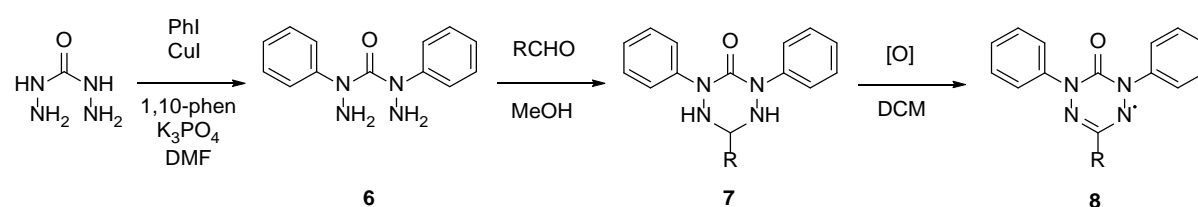


Figure S1. General synthetic route for oxo-verdazyl radicals

Tetrazinanone precursors

2,4-Diphenylcarbohydrazide **6** (1.0 equiv.) was dissolved in MeOH and stirred at 0–40 $^\circ\text{C}$, depending on the reaction. The respective aldehyde (1.0 equiv.) was dissolved in MeOH and this solution was added dropwise to the stirring carbohydrazide solution. The reaction was stirred at room temperature (for the methyl- and isopropyl-substituted tetrazinanones) or 60 $^\circ\text{C}$ (for all others) for 2–3 h. A precipitate formed, which was filtered off, washed with cold MeOH and dried *in vacuo* to afford the tetrazinanone **7** as a white solid. For further details, refer to the previously published procedures.^[1]

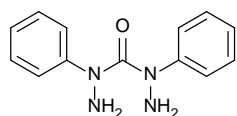
Verdazyl radicals

Tetrazinanone (1.0 equiv.) and 1,4-benzoquinone (1.7 equiv.) were dissolved in DCM and heated in a Schlenk pressure tube at 60 $^\circ\text{C}$ for 2–3 h. The solvent was then removed *in vacuo*

before purification of the product by FC, affording the verdazyl radical **8** as an intensely colored solid. For further details, refer to the previously published procedures.¹

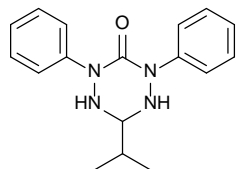
Synthesis of 1,5-diphenyl-3-isopropyl-6-oxo-verdazyl (*isoV*)

2,4-Diphenylcarbohydrazide (**6**)



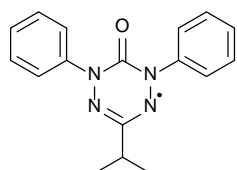
The reaction was performed based on a previously published procedure.¹ Copper (I) iodide (0.109 g, 0.572 mmol, 0.05 equiv.) and 1,10-phenanthroline (0.200 g, 3.30 mmol, 0.10 equiv.) were added to a flame-dried, argon-flushed 50 mL Schlenk pressure tube. Anhydrous K₃PO₄ (6.158 g, 29.0 mmol, 2.6 equiv.) and carbohydrazide (1.001 g, 11.1 mmol, 1.0 equiv.) were added to the reaction vessel against Ar flow, before the addition of dry DMF (14 mL). Finally, iodobenzene (3.0 mL, 27 mmol, 2.4 equiv.) was added. The reaction mixture was stirred vigorously at 90 °C under Ar for 46 h. After cooling to room temperature, the reaction mixture was vacuum filtered through silica gel and washed through with EtOAc (~200 mL) to give a bright yellow filtrate. H₂O (200 mL) was added to the filtrate, the phases separated, and the aqueous phase extracted with a further 2 × 50 mL EtOAc. The combined organic phases were dried over MgSO₄, filtered, and reduced *in vacuo* to afford a yellow-brown oil. The crude mixture was purified by FC (70%–100% Et₂O/pentane) to afford the product **6** as an orange oil (0.844 g, 31%). NMR data were in accordance with the literature. ¹H NMR (300 MHz, CDCl₃): δ = 7.17–7.11 (m, 8H, CH_{arom}), 7.02–6.95 (t, 2H, CH_{arom}), 4.49 (br s, 4H, NH₂).

6-Isopropyl-2,4-diphenyl-1,2,4,5-tetrazinan-3-one



The reaction was performed based on a previously published procedure.¹ 2,4-Diphenylcarbohydrazide (0.844 g, 3.48 mmol, 1.0 equiv.) was dissolved in MeOH (25 mL) in a 100 mL round-bottomed flask and stirred at room temperature. Isobutyraldehyde (0.35 mL, 3.8 mmol, 1.1 equiv.) was dissolved in 15 mL MeOH and this solution was added slowly to the stirring carbohydrazide solution. The reaction mixture was stirred for 18 h at room temperature, though the solution turned cloudy in under an hour and no further visible change was observed. The reaction mixture was then filtered through a glass fritted funnel to leave a white solid, which was then washed with cold MeOH and dried thoroughly to afford the product (0.481 g, 47%). Obtained NMR data are in accordance with literature. ¹H NMR (300 MHz, CDCl₃): δ = 7.65–7.61 (m, 4H, CH_{arom}), 7.36–7.29 (m, 4H, CH_{arom}), 7.10 (tt, *J* = 7.4, 1.1 Hz, 2H, CH_{arom}), 4.36 (d, *J* = 10.1 Hz, 2H, NH), 4.02 (td, *J* = 10.1, 7.1 Hz, 1H, N-CH-N), 1.84 (hextet, *J* = 1.8 Hz, 1H, CH), 1.11 (d, *J* = 6.8 Hz, 6H, CH₃).

3-Isopropyl-1,5-diphenyl-6-oxoverdazyl (*isoV*)



The reaction was performed based on a previously published procedure.¹ 6-Isopropyl-2,4-diphenyl-1,2,4,5-tetrazinan-3-one (0.481 g, 1.62 mmol, 1.0 equiv.) was dissolved in DCM (20 mL) in a 50 mL Schlenk pressure tube and stirred under air at room temperature to give a clear, colorless solution. 1,4-Benzoquinone (0.557 g, 5.15 mmol, 3.2 equiv.) was added to the reaction, upon which the colour changed to a brownish red. The reaction was sealed and heated to 60 °C while stirring. After 1 h the heat source was removed and the reaction allowed

to cool to room temperature while stirring for a further 19 h. Three spots were observed by TLC analysis (10% Et₂O/pentane), with the product being the first orange-red spot at $R_f \approx 0.40$. Purification by FC (10% Et₂O/pentane) afforded the product **isoV** as a crimson liquid that later solidified (0.410 g, 86%). HRMS (ESI): calculated for C₁₇H₁₇N₄ONa ([M+Na]⁺): 316.1295, found: 316.1305; calculated for (C₁₇H₁₇N₄O)₂Na ([2M+Na]⁺): 609.2697, found: 609.2727.

Preselection of promising candidate molecules based on cyclic voltammetry analysis

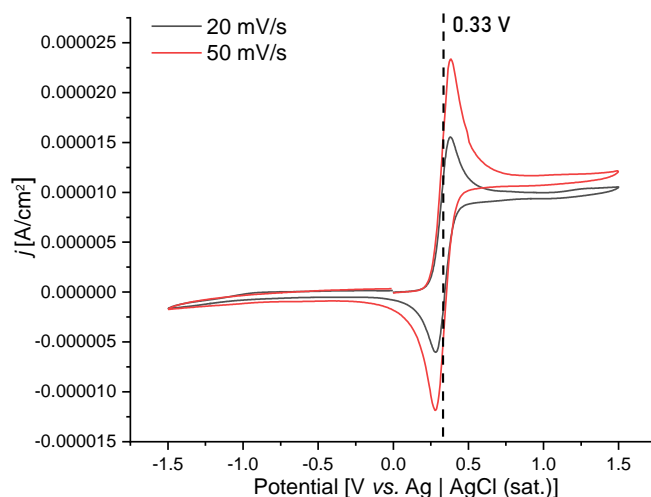


Figure S2. Calibration of Ag|AgCl (sat.) reference electrode with 10 mM ferrocene (acetonitrile, 0.1 M TBAP) within the potential range -1.5 V to 1.5 V vs. Ag|AgCl.

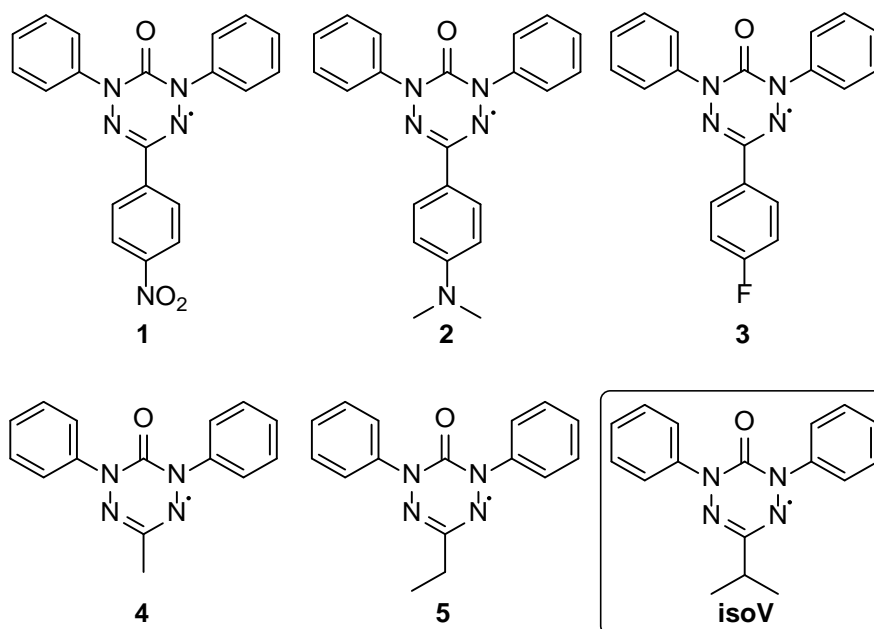
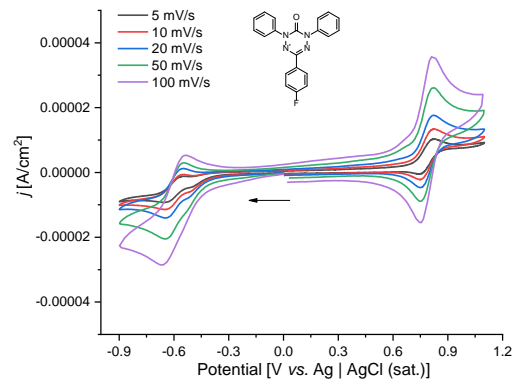
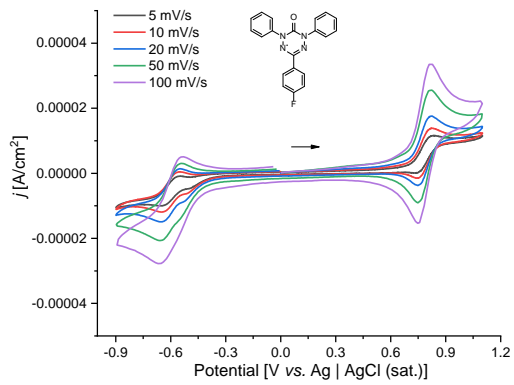
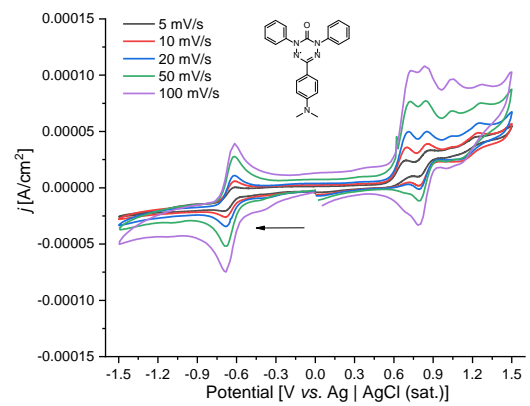
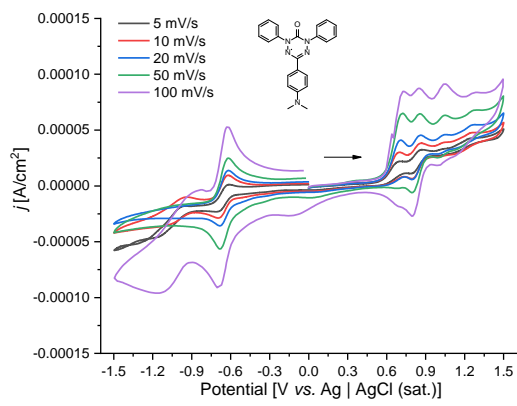
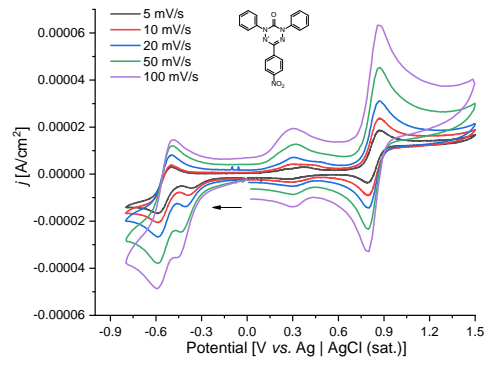
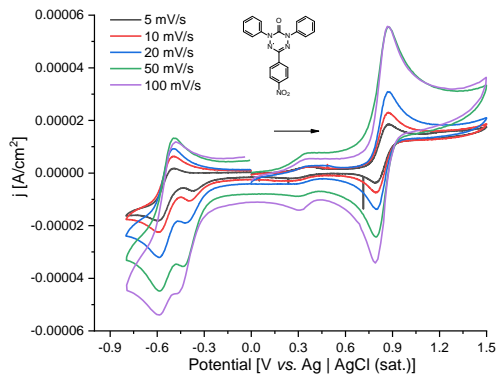


Figure S3. Chemical structures of screened oxo-verdazyl free radicals: 1,5-diphenyl-3-4-nitrophenyl-6-oxo-verdazyl (**1**), 1,5-diphenyl-3-4-*N,N'*-dimethylphenyl-6-oxo-verdazyl (**2**), 1,5-diphenyl-3-4-fluorophenyl-6-oxo-verdazyl (**3**), 1,5-diphenyl-3-methyl-6-oxo-verdazyl (**4**), 1,5-diphenyl-3-ethyl-6-oxo-verdazyl (**5**), 1,5-diphenyl-3-isopropyl-6-oxo-verdazyl (**isoV**).



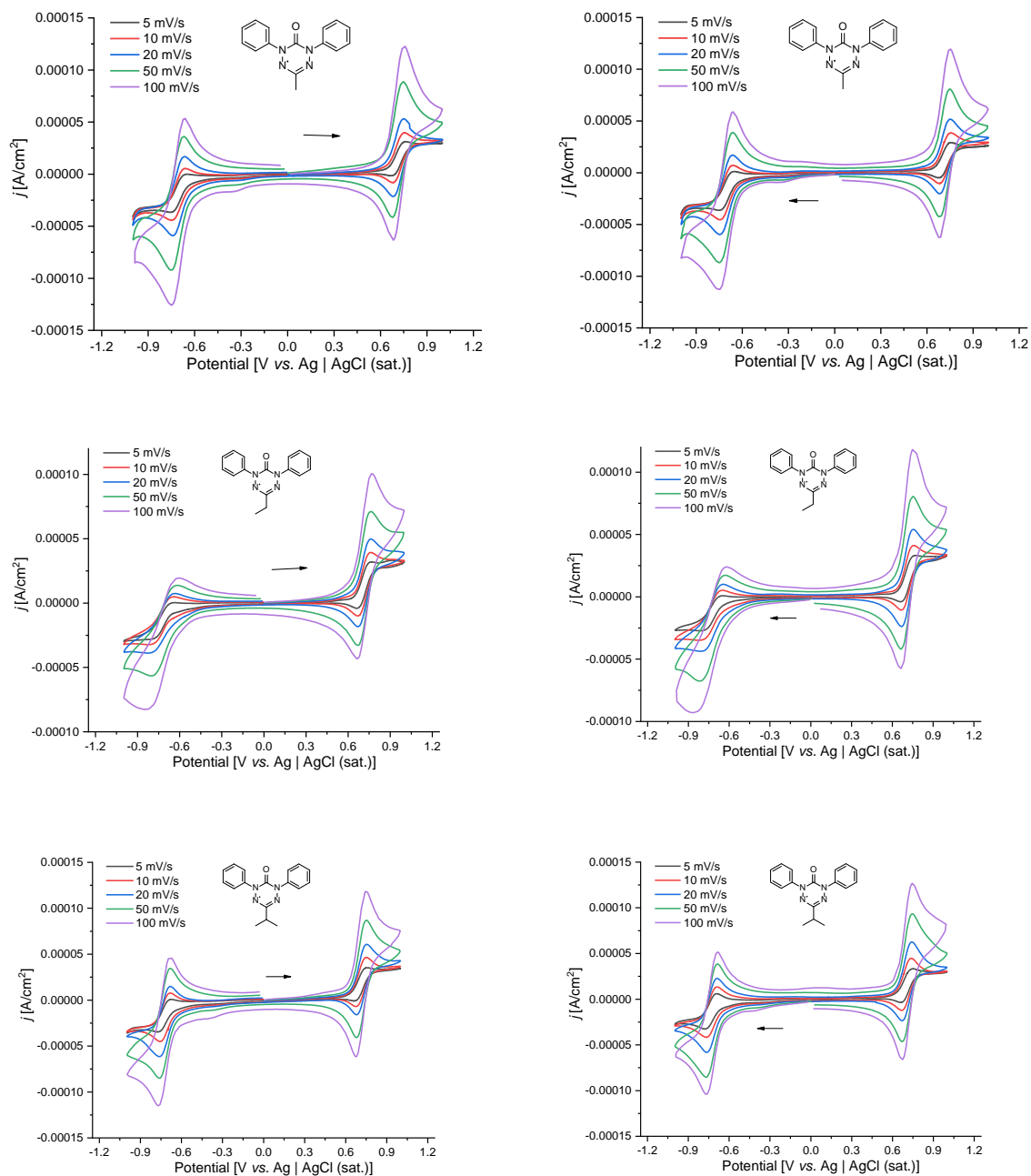


Figure S4. First cycle cyclic voltammograms for designated verdazyl radicals at different potential scan rates. Left column – backward potential sweep, right column – forward potential sweep. Pt disc electrodes were used as working and counter electrodes, and Ag|AgCl (sat.) electrode served as a reference electrode.

For aromatic substituents additional irreversible peaks were identified within the potential range of interest, in particular, between the half-reaction potential corresponding to the V/V^+ and V/V^- processes, immediately ruling out these compounds for a symmetrical electrolyte.

Regarding the other compounds (with aliphatic substituents), ethyl-substituted oxoverdazyl surprisingly demonstrated weak reversibility for V/V^- process in comparison to the others, visible directly from the measured CVs. The remaining two compounds were considered the best candidates for symmetrical NARFB studies and therefore required more in-depth assessment. Results of a comparative study (Table 1), mostly based on Randles-Sevcik analysis and potentiostatic electrochemical impedance spectroscopy (PEIS), slightly favored **isoV** over **4**.

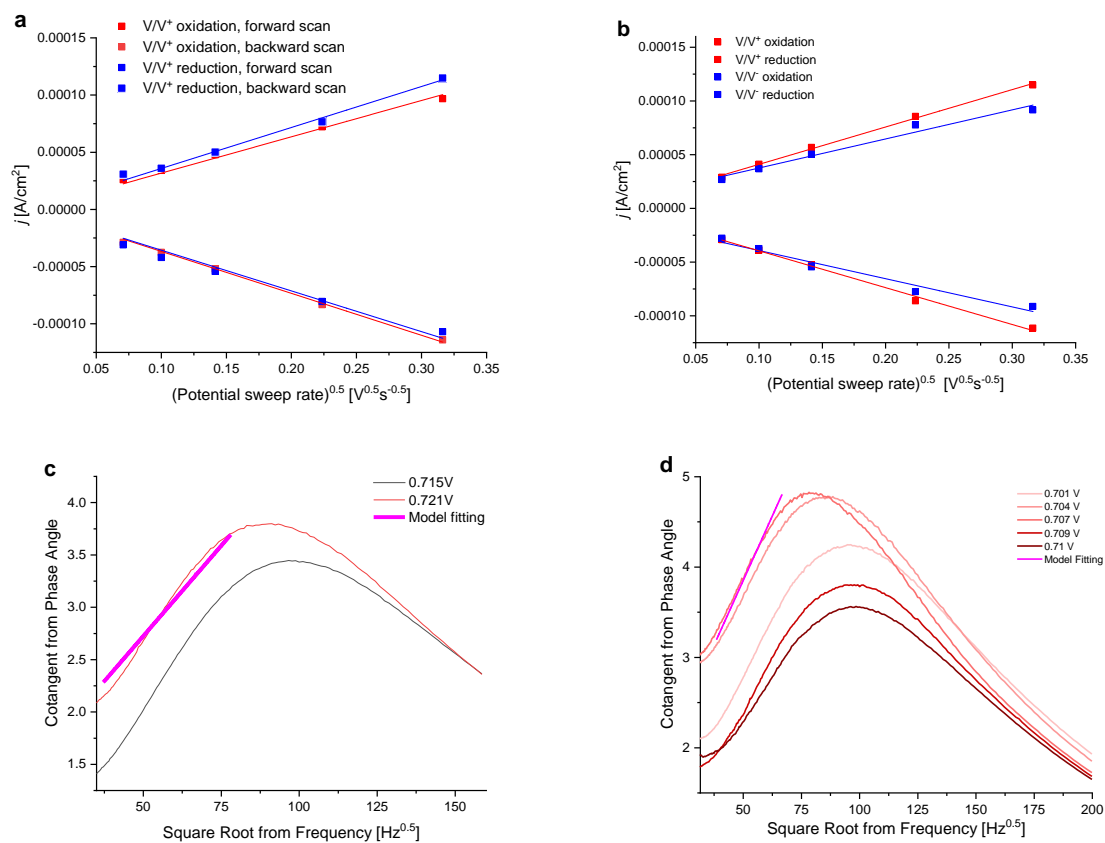


Figure S5. Randles-Sevcik analysis for A) 4, and B) isoV. Cotangent analysis (PEIS) for C) 4, and D) isoV.

Table S1. Relevant physicochemical properties of 4 and isoV

Compound	Diffusion coefficient V/V ⁺ (cm ² ·s ⁻¹)	Diffusion coefficient V/V ⁻ (cm ² ·s ⁻¹)	Standard electrochemical rate constant V/V ⁺ (cm·s ⁻¹) ¹	Qualitative solubility in acetonitrile
4	$2.5 \cdot 10^{-7}$	$2.3 \cdot 10^{-7}$	0.0100	Good
isoV	$2.8 \cdot 10^{-7}$	$1.8 \cdot 10^{-7}$	0.0081	Good

Solubility determination of *isoV* based on UV-Vis measurement

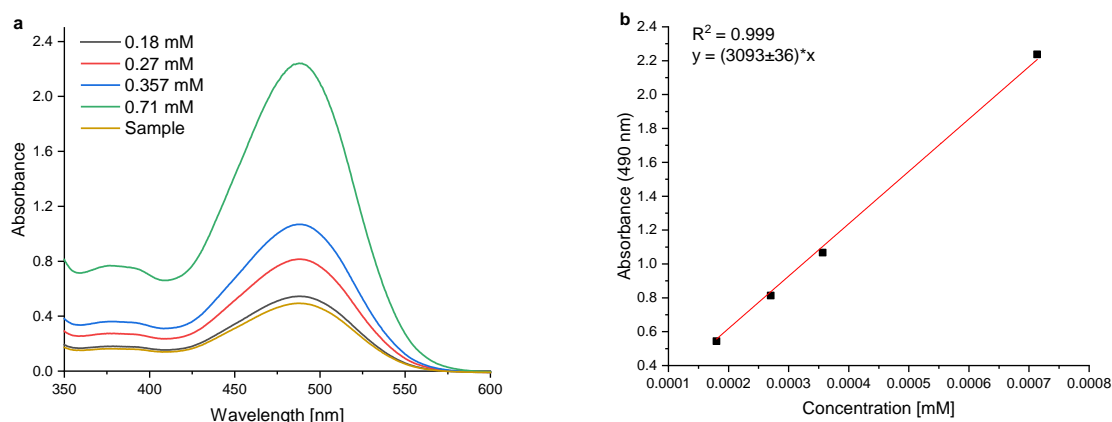


Figure S6. A) UV-Vis spectra of the *isoV* acetonitrile solutions with various concentrations (optical path length – 1 cm). B) A calibration curve based on the characteristic peak absorbance maximum at 490 nm.

Calibration curve:

In order to construct a calibration curve four acetonitrile *isoV* solutions of known concentrations (0.18 mM, 0.27 mM, 0.357 mM, 0.71 mM) were prepared. Spectra of the resulting samples were recorded in the 350-600 nm wavelength region (**Figure S6a**). The values of characteristic peak absorbance maximums at 490 nm and corresponding values of concentrations were subjected to linear fitting procedure to yield a linear calibration equation (**Figure S6b**).

A maximum solubility and a sample preparation:

To 10 mg of solid *isoV* 1 μL of acetonitrile was consecutively added four times. Before each new addition of the solvent a resulting composition was immersed in the ultrasonic bath for 5 min. After addition of the last acetonitrile portion the majority of appeared to be dissolved. 1 μL of the saturated *isoV* solution was gently isolated and diluted with 14.999 mL of acetonitrile. Spectrum of the resulting sample was recorded in the 350-600 nm wavelength region (**Figure S6a**). According to the calibration linear equation the maximum solubility of *isoV* was determined as (2.40 ± 0.02) M.

State of the charge determination based on UV-Vis monitoring

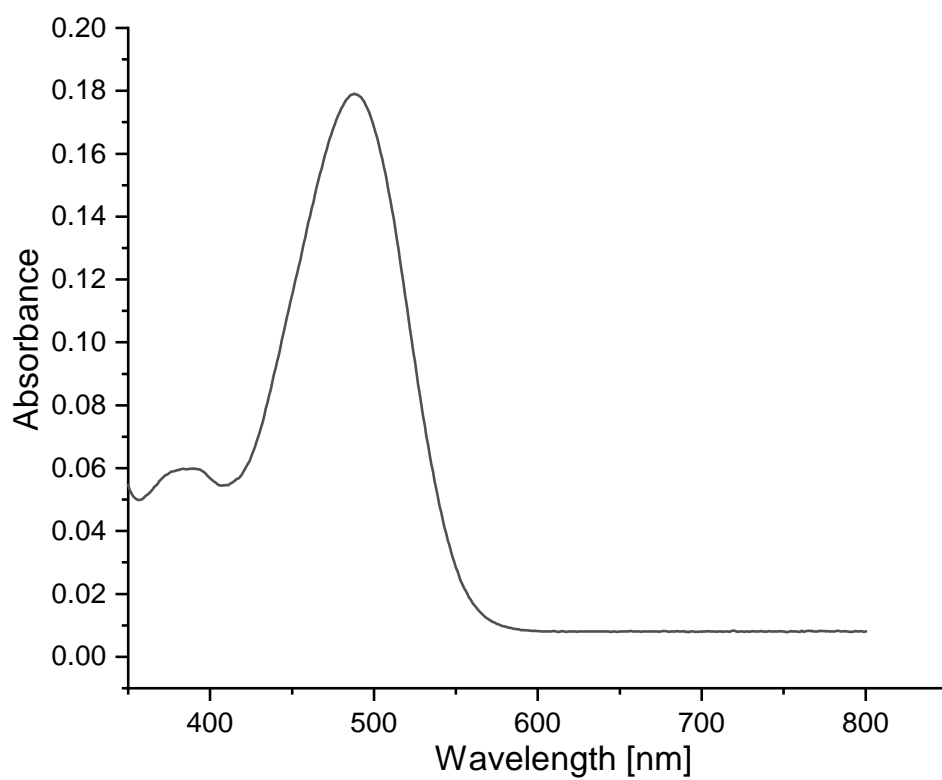


Figure S7. UV-Vis spectrum of 0.06 mM isoV solution.



Figure S8, UV-Vis samples ordered as follows (from left to right): negolyte 100%, 80%, 60%, 40%, 20%, original electrolyte solution, posolyte 20%, 40%, 60%, 80%, 100%.



Figure S9. Fumasep®FAP-375-PP AEM after galvanostatic battery cycling.

References

- 1 S. Eusterwiemann, D. Matuschek, L. Stegemann, S. Klabunde, C.C. Doerenkamp, C.G. Daniliuc, N.L. Doltsinis, C.A. Strassert, H. Eckert and A. Studer, *Chimia*, 2016, **70**, 172–176.