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Electronic Supporting Information (ESI)

Surface Ligands Influence the Selectivity of Cation Uptake in Polyoxovanadate-alkoxide Clusters

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Experimental Methods

General Considerations. All manipulations, unless otherwise noted, were carried out in the absence of water and oxygen in a UniLab MBraun inert atmosphere glovebox under a nitrogen atmosphere. Glassware was oven-dried for a minimum of 4 h and cooled in an evacuated antechamber prior to use. 3 Å molecular sieves (Fisher Scientific) were dried in a Schlenk flask for 48 h at 125 °C under vacuum prior to use. Acetonitrile (MeCN) was dried and deoxygenated on a Glass Contour System (Pure Process Technology, LLC) and stored over 3 Å molecular sieves. Tetrabutylammonium triflate ($[^nBu_4N]OTf$) was purchased from Millipore Sigma, recrystallized three times by addition of pentane to a solution of the salt in ethyl acetate, and stored under dynamic vacuum for at least 24 h prior to use. Tetrabutylammonium borohydride, lithium triflate (LiOTf), sodium triflate (NaOTf), potassium triflate (KOTf), and lithium bis-(trifluoromethanesulfonyl)imide were purchased from Millipore Sigma and used as is. Complexes $[V_6O_7(OCH_3)_{12}]$,[1] $[V_6O_7(OC_3H_7)_{12}]$,[2] and $[V_6O_7(OC_5H_{11})_{12}]$[3] were synthesized according to reported procedures.

^1H NMR spectra were collected at 400 MHz on a Bruker DPX-400 instrument at 9.4 Telsa while locked on to deuterated solvent. CD_3CN was purchased from Cambridge Isotope Labs, degassed by three freeze-pump-thaw cycles, and stored over 3 Å molecular sieves prior to use. Single crystals of $[^nBu_4N]_2[V_6O_7(OC_3H_7)_{12}]$ and $[Li(pc)]_2[V_6O_7(OC_3H_7)_{12}]$ were mounted on the tip of a thin glass optical fiber (goniometer head) and mounted on a XtaLab Synergy-S Dualflex diffractometer equipped with a HyPix-6000HE HPC area detector for data collection at 100.00(10) K, respectively. The structures were solved using SHELXT-2018/2[4] and refined using SHELXL-2018/3.[5] Elemental analysis was performed on a PerkinElmer 2400 Series II analyzer, at the Elemental Analysis Facility located at the University of Rochester.

Synthesis of POV-Alkoxide Clusters

Synthesis of $[^nBu_4N][V_6O_7(OC_3H_7)_{12}]$ ***(2-propyl)***. A 25 mL Parr reactor was charged with $VO(OC_3H_7)_3$ (300 mg, 1.23 mmol), $[^nBu_4N]BH_4$ (262 mg, 1.02 mmol), and 10 mL of *n*-propanol. The reactor was sealed and heated at 125 °C for 24 h, after which the reactor was cooled to room temperature. The maroon reaction solution was removed from the reactor and added to a round bottom flask with a stir bar and 1 mL of deionized water and was allowed to stir until the solution turned green (~1 h). The solution was dried *in vacuo*, the product was extracted with ethyl acetate, filtered, and evaporated to dryness. The green solid was brought into a drybox, where it was extracted in diethyl ether, filtered, and evaporated to dryness to produce $[^nBu_4N][V_6O_7(OC_3H_7)_{12}]$ (**2-propyl**) in moderate yield (110 mg, 39 %) ^1H NMR (400 MHz, CD_3CN): δ = 26.26, 3.07, 1.59, 1.35, 0.97 ppm.

Synthesis of $[^nBu_4N]_2[V_6O_7(OR)_{12}]$($R = C_3H_7$, C_5H_{11}). A 48 mL pressure vessel was charged with 200 mg of neutral-charged POV-alkoxide $[V_6O_7(OR)_{12}]$ ($R=C_3H_7$, C_5H_{11}), 3 molar equivalents of $[^nBu_4N]BH_4$, a stir bar, and 20 mL MeCN. The vessel was sealed, removed from the drybox, and heated to 85 °C for 24 h with vigorous stirring. The brown-green solution was returned to the drybox, concentrated to 7 mL, and placed in a freezer at -30 °C, producing a teal green precipitate, identified as the dianionic, bis-$[^nBu_4N]^+$ salt in moderate yield (*vide infra*). The low temperature conditions produced crystals suitable for single crystal X-ray diffraction analysis for $[^nBu_4N]_2[V_6O_7(OC_3H_7)_{12}]$.

$[^nBu_4N]_2[V_6O_7(OC_3H_7)_{12}]$: yield = 97 mg, 0.060 mmol, 34 %; ^1H NMR (400 MHz, CD_3CN): δ = 27.10, 3.07, 1.59, 1.35, 0.97, 0.74 ppm.

$[^nBu_4N]_2[V_6O_7(OC_5H_{11})_{12}]$: yield = 82 mg, 0.042 mmol, 31 %; ^1H NMR (400 MHz, CD_3CN): δ = 26.26, 3.07, 1.59, 1.35, 0.97, 0.88 ppm.

Synthesis of $[Li(pc)]_2[V_6O_7(OC_3H_7)_{12}]$. A 20 mL scintillation vial was charged with $[^nBu_4N]_2[V_6O_7(OC_3H_7)_{12}]$ (100 mg, 0.062 mmol) and dissolved in 2 mL propylene carbonate. Li bis-(trifluoromethanesulfonyl)imide (180 mg, 0.63 mmol, 10 equiv.) was dissolved in 6 mL diethyl ether in a separate vial. The Li salt solution was added to the cluster solution, after which 6 mL of toluene and 4 mL of pentane were added. The cloudy solution was placed in a -30 °C freezer for 2 days, after which time crystals suitable for single crystal X-ray diffraction analysis were observed, and the compound was isolated in moderate yield (45.3 mg, 0.034 mmol, 54%). Crystals were crushed and dried for 48 h for elemental analysis. Elemental analysis for $C_{44}H_{96}O_{25}Li_2V_6$ (MW: 964.17 g/mol) Calc'd (%): C, 39.3; H, 7.2; Found (%): C, 39.522; H, 7.023; N, 0.053.

Electrochemistry. Electrochemical measurements were carried out using a Bio-Logic SP 150 potentiostat/galvanostat and the EC-Lab software suite. A 3 mm Glassy carbon disc electrode was used as the working electrode; a Pt wire was used as the counter electrode, and the reference electrode was a non-aqueous $Ag/AgNO_3$ cell filled with 1 mM silver nitrate ($AgNO_3$) in 0.1 M $[^nBu_4N]PF_6$ (BAS Inc). Cyclic voltammograms (CV) were measured at 100 mV s^{-1} with IR compensation accounted for by measuring the uncompensated resistance with a 100 kHz impedance measurement and correcting for 85% of the expected drop using the ZIR tool in the EC-Lab suite. Square wave voltammograms (SWV) were measured with a pulse height of 25 mV, a pulse width of 100 ms, and a step height of 10 mV.

Procedure for Metal Triflate Titration Experiments. An analyte solution consisting of 0.1 M $[^nBu_4N]OTf$ and 1 mM of selected cluster in 5 mL of MeCN or propylene carbonate was charged in an electrochemical cell. The second solution contained 10 mM MOTf (M = Li, Na, K) in 10 mL of MeCN or propylene carbonate. CV and SWV were recorded of the analyte solution prior to titration. Alkali salt solution was added to the cell to achieve specified MOTf : POV-alkoxide ratios and was allowed to stir for 10 s before a CV and SWV were taken. The process was repeated until 5 molar equivalents of MOTf was reached. After this point, where applicable, solid samples of MOTf salts were measured and added as a solid to access solutions with excess alkali salt (10-100 molar equivalents of MOTf versus POV-alkoxide).

Procedure for Cation Selectivity Studies. An electrochemical cell was charged with a solution containing 0.1 M MOTf (M = Na, K) and 1 mM of **1-methyl** or **3-pentyl** in MeCN and a stir bar. An initial CV and SWV were recorded of the cluster solution. A separate solution containing 10 mM LiOTf in 10 mL of MeCN and was added to the cluster solution in specified increments, stirring for 10 s before recording CV and SWV. The process was repeated until 5 molar equivalents of LiOTf (versus POV-alkoxide) was added.

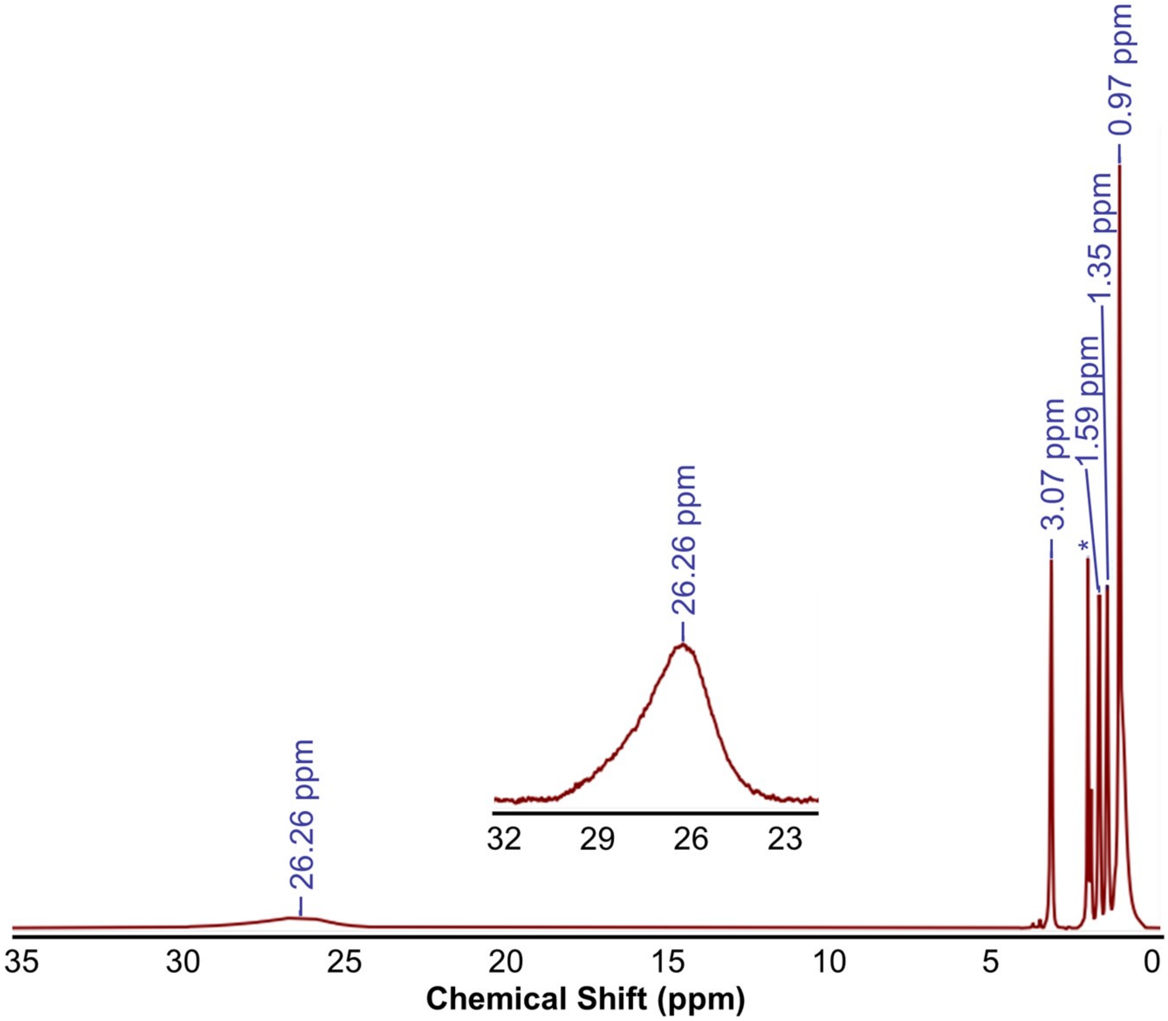

Figure S1. ^1H NMR of **2-propyl** in MeCN-d_3 at 21°C.

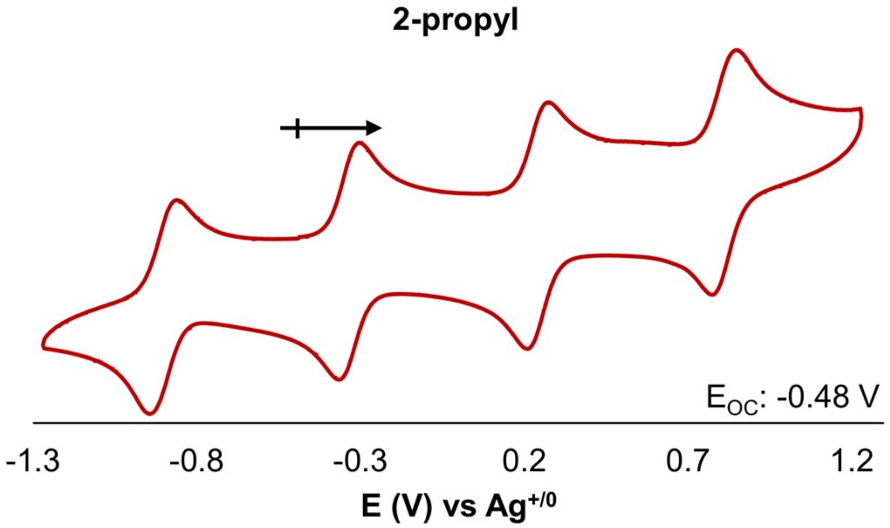

Figure S2. CV of a 0.5 mM solution of **2-propyl** at 100 mVs^{-1} in MeCN with 0.1 M [^{n}Bu$_4$N]OTf electrolyte.

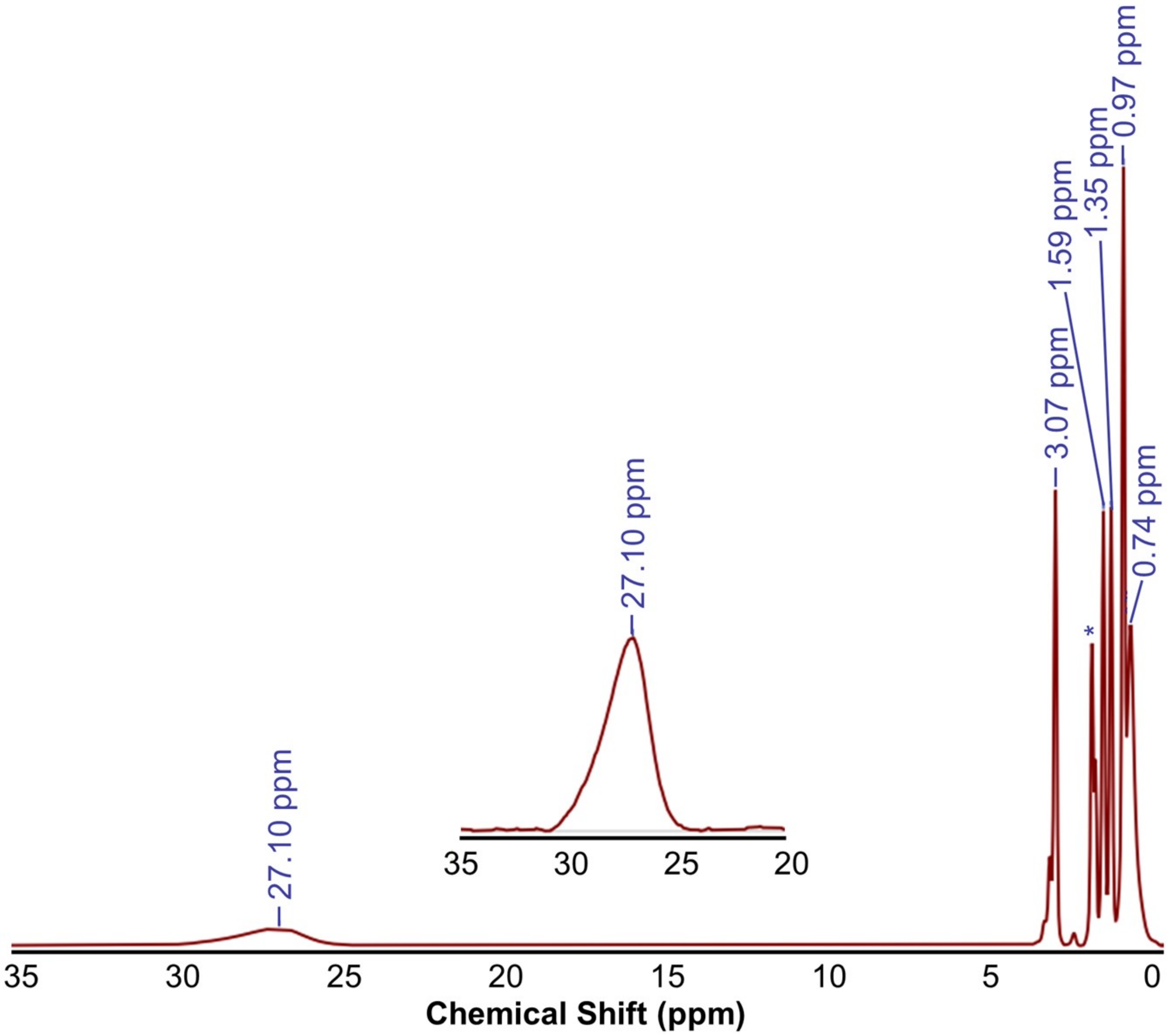

Figure S3. ^{1}H NMR of $[^nBu_4N]_2[V_6O_7(OC_3H_7)_{12}]$ in MeCN-d_3 at 21°C.

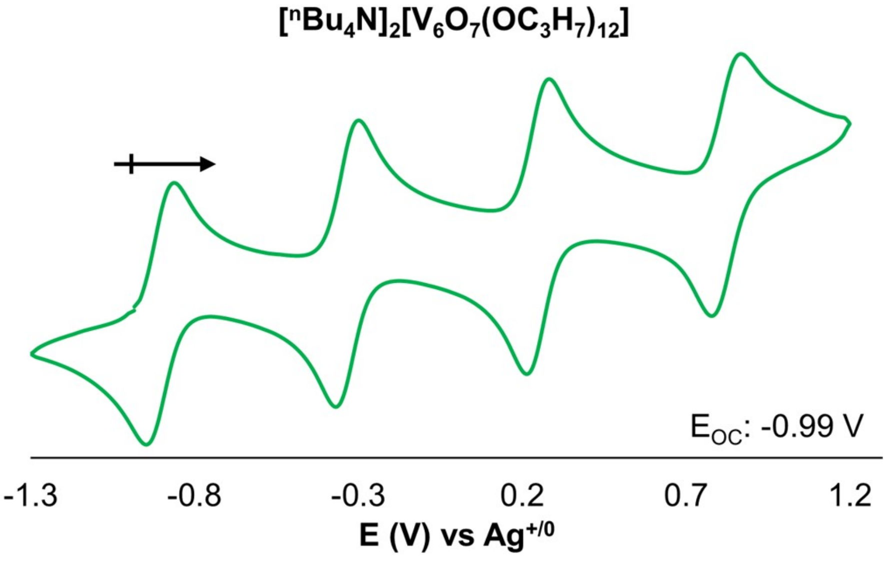

Figure S4. CV of a 1 mM solution of $[^nBu_4N]_2[V_6O_7(OC_3H_7)_{12}]$ at 100 mVs^{-1} in MeCN with 0.1 M $[^nBu_4N]OTf$ electrolyte.

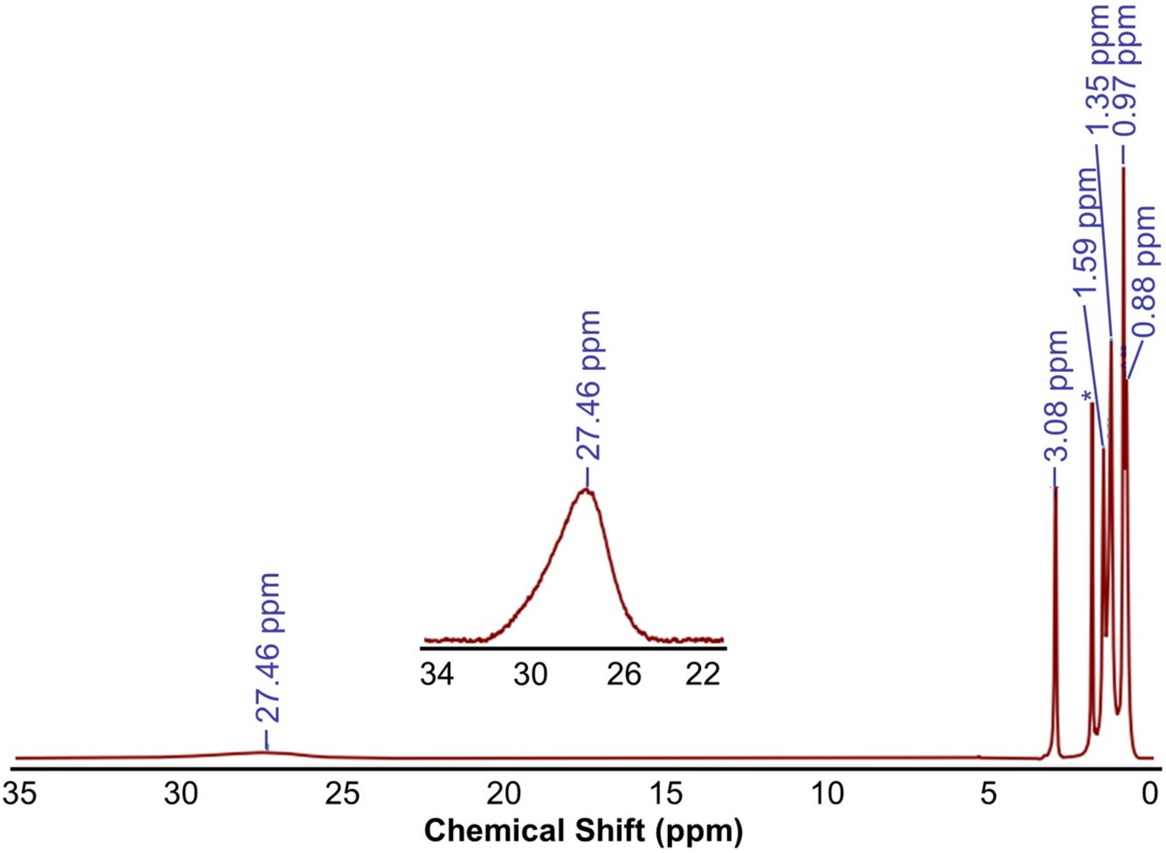

Figure S5. ^1H NMR of $[^nBu_4N]_2[V_6O_7(OC_5H_{11})_{12}]$ in MeCN-d_3 at 21°C.

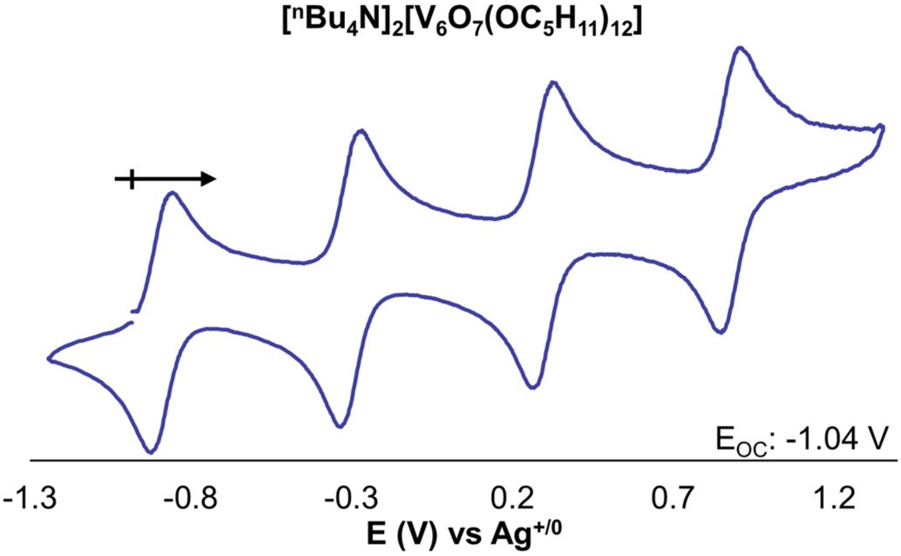

Figure S6. CV of a 1 mM solution of $[^nBu_4N]_2[V_6O_7(OC_5H_{11})_{12}]$ at 100 mVs^{-1} in MeCN with 0.1 M $[^nBu_4N]$OTf electrolyte.

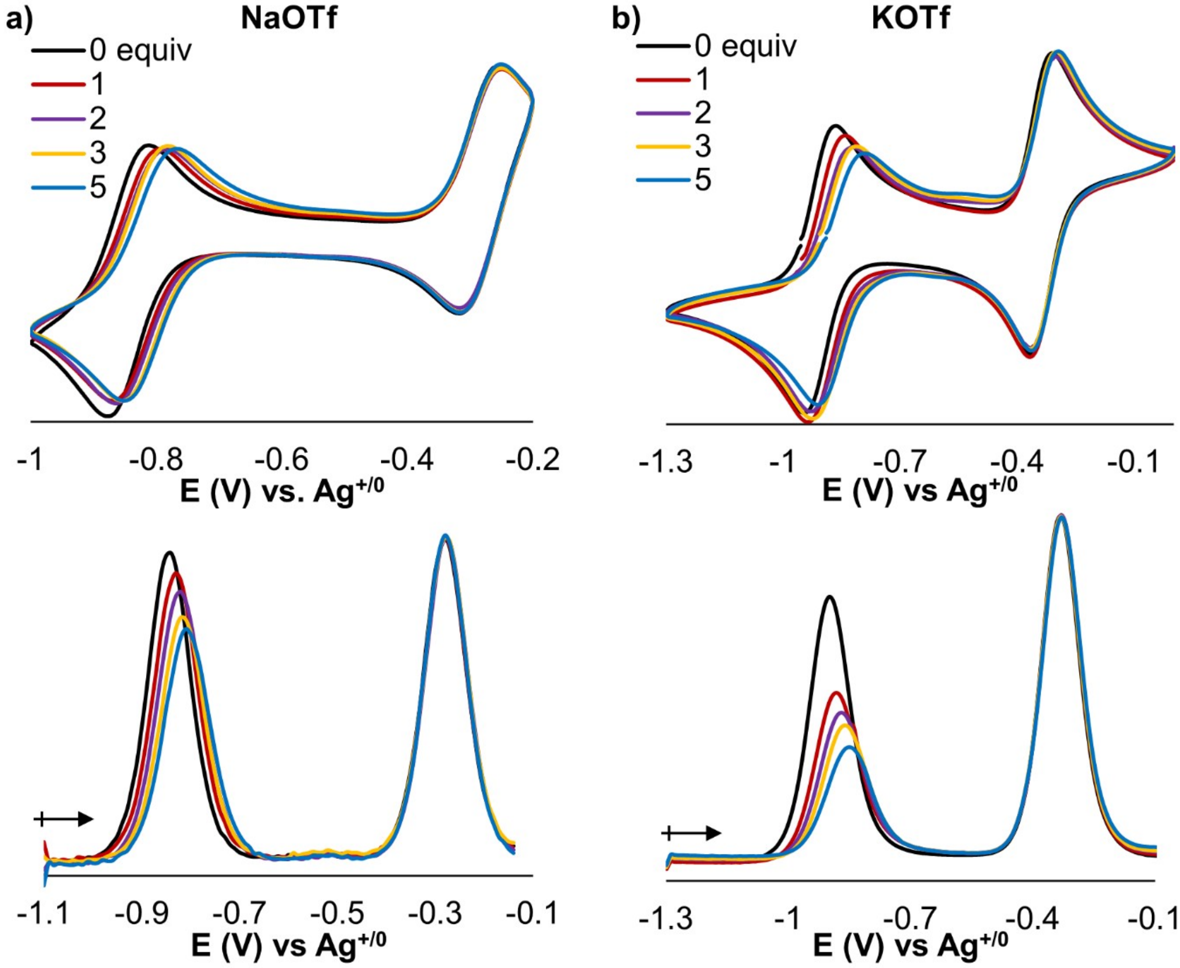

Figure S7. CV and SWV data for a) NaOTf and b) KOTf titration experiments for **2-propyl** in MeCN with 0.1 M [^{n}Bu$_4$N]OTf electrolyte.

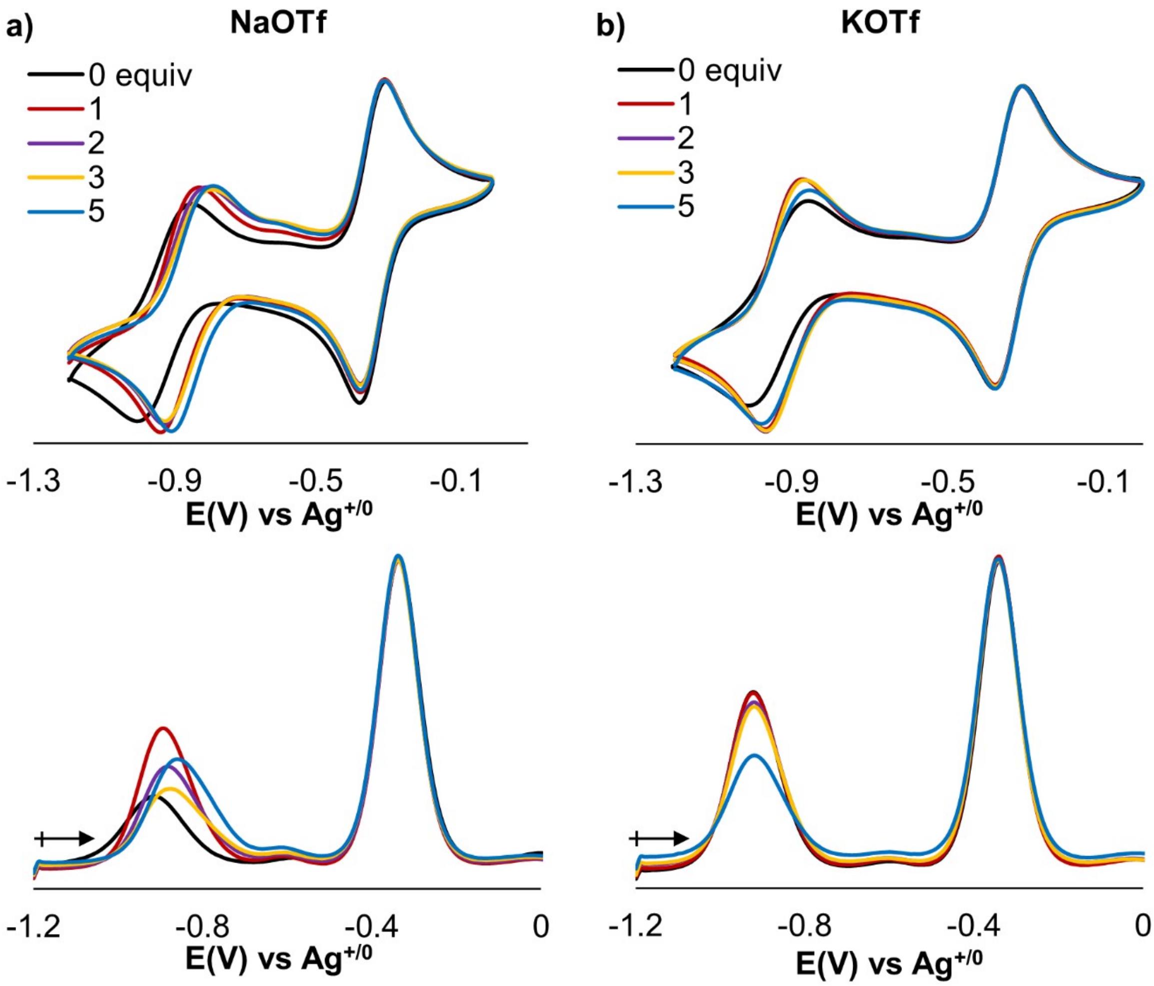

Figure S8. CV and SWV data for a) NaOTf and b) KOTf titration experiments for **3-pentyl** in MeCN with 0.1 M [^{n}Bu$_4$N]OTf electrolyte.

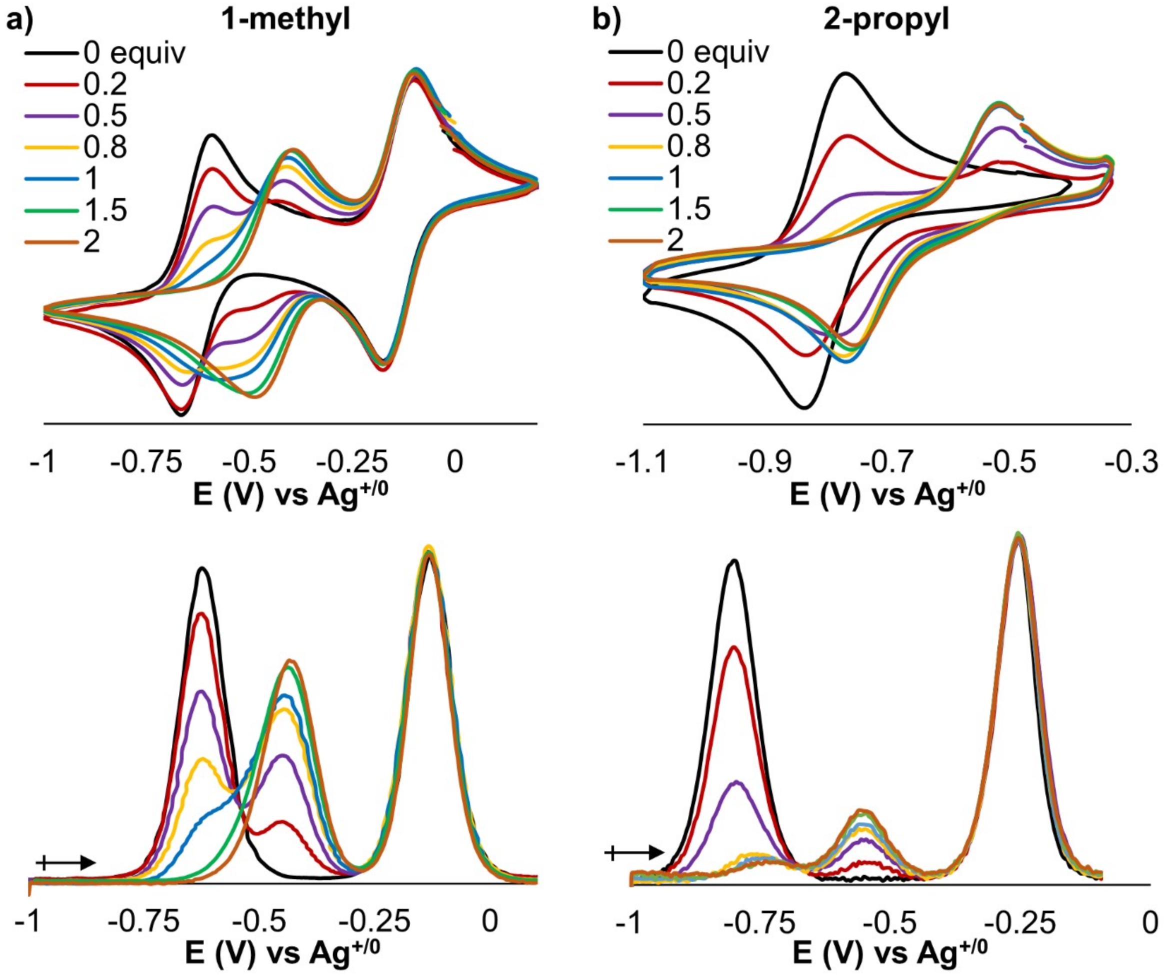

Figure S9. CV and SWV data for LiOTf titration experiments for a) **1-methyl** and b) **2-propyl** in propylene carbonate with 0.1 M [^{n}Bu$_4$N]OTf electrolyte.

Table S1. Crystallographic parameters for $[Li(pc)]_2[V_6O_7(OC_3H_7)_{12}]$ and $[^nBu_4N]_2[V_6O_7(OC_3H_7)_{12}]$.

Compound	**$[Li(pc)]_2[V_6O_7(OC_3H_7)_{12}]$**	**$[^nBu_4N]_2[V_6O_7(OC_3H_7)_{12}](CH_3CN)_4$**
CCDC	2145391	2145392
Empirical Formula	$C_{44}H_{96}Li_2O_{25}V_6$	$C_{76}H_{168}N_6O_{19}V_6$
Formula weight	1344.72	1775.79
Temperature/ K	100.00(10) K	100.00(10) K
Wavelength/ Å	1.54184 Å	1.54184 Å
Crystal system	monoclinic	monoclinic
Space group	C2/c	$P2_1/n$
Unit Cell Dimensions	a = 17.82370(10) Å b = 17.66670(10) Å c = 20.11890(10) Å α = 90° β = 91.2190(10)° γ = 90°	a = 13.85530(10) Å b = 18.3708(2) Å c = 18.6840(2) Å α = 90° β = 93.6200(10)° γ = 90°
Volume/ $Å^3$	6333.73(6) $Å^3$	4746.20(8) $Å^3$
Z	4	2
Reflections collected	54852	60860
Independent reflections	6854 [R(int) = 0.0297]	10232 [R(int) = 0.0513]
Completeness to theta =74.504°	99.9 %	99.9 %
Goodness-of-fit of F2	1.146	1.086
Final R indices [I>2sigma(I)]	R1 = 0.0277, wR2 = 0.0768	R1 = 0.0367, wR2 = 0.0988
Largest diff. peak and hole	0.419 and -0.440 $Å^{-3}$	0.468 and -0.596 $Å^{-3}$

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