Electronic Supporting Information (ESI)

Polyoxovanadate-alkoxide Clusters as Multi-electron Charge Carriers for Symmetric Non-aqueous Redox Flow Batteries.

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Experimental Details

General considerations.

All manipulations were carried out in the absence of water and oxygen in a UniLab MBraun inert atmosphere glovebox under a dinitrogen atmosphere. Glassware was oven dried for a minimum of 4 hours and cooled in an evacuated antechamber prior to use in the drybox. Anhydrous methanol was purchased from Sigma-Aldrich and stored over activated 4 Å molecular sieves purchased from Fisher Scientific. All other solvents were dried and deoxygenated on a Glass Contour System (Pure Process Technology, LLC) and stored over activated 3 Å molecular sieves purchased from Fisher Scientific. [NBu₄][BH₄] and VO(OPr)₃ were purchased from Sigma-Aldrich and used as received. VO(OCH₃)₃ was synthesized according to previous literature. [NBu₄][PF₆] was purchased from Sigma-Aldrich, recrystallized thrice using hot methanol, and stored under dynamic vacuum for a minimum of two days prior to use. ¹H NMR spectra were recorded at 500 on Bruker DPX-500 spectrometer locked on the signal of deuterated solvents. All chemical shifts were reported relative to the peak of residual ¹H signal in deuterated solvents. CD₃CN was purchased from Cambridge Isotope Laboratories, degassed by three freeze−pump−thaw cycles, and stored over activated 4 Å molecular sieves. Infrared (FT-IR, ATR) spectra of complexes were recorded on a Shimadzu IRAffinity-1 Fourier Transform Infrared Spectrophotometer and are reported in wavenumbers (cm⁻¹). Electronic absorption measurements were recorded at room temperature in anhydrous acetonitrile in a sealed 1 cm quartz cuvette with an Agilent Cary 60 UV-Vis spectrophotometer.

POV-alkoxide Syntheses.

The active species, 1-V₆O₇(OMe)₁₂, was accessed from one of two methods. The first is the previous synthetic route established by Hartl and coworkers, and the second is a modified procedure designed to access the molecule directly from commercially available reagents.

Synthesis of 1-V₆O₇(OMe)₁₂ from commercial starting materials.

In the glovebox, VO(OCH(CH₃))₃ (510 mg, 2.08 mmol), [NBu₄][BH₄] (53.7 mg, 0.208 mmol) and 14 mL methanol were charged in a 25 mL Teflon-lined Parr reactor. The Parr reactor was sealed, and the mixture heated in an oil bath at 125 °C for 24 hours. The Parr reactor was allowed to cool to room temperature. Subsequent workup was conducted on the bench top. The resulting dark green solution was rotary evaporated to reduce the volume by half, then placed in a freezer at −35 °C for 24 hours. The resulting dark green crystals were spectroscopically pure 1-V₆O₇(OMe)₁₂ (231.289 mg, 0.293 mmol, 70.1%). The crystallization procedure was repeated twice to improve the yield (294.710 g, 0.373 mmol, 89.3 %). Characterization matches the previously reported synthesis.

Complexes 2-V₆O₇(OMe)₁₂²⁻ and 3-V₆O₇(OMe)₁₂²⁻ were prepared and characterized according to the literature. The monocationic complex, 4-V₆O₇(OMe)₁₂¹⁺, has been reported previously, however was prepared here using an alternate method:

Synthesis of 4-V₆O₇(OMe)₁₂¹⁺.

In the glovebox, silver hexafluorophosphate (AgPF₆, 66 mg, 0.260 mmol) was added to a solution of 1-V₆O₇(OMe)₁₂ (200 mg, 0.253 mmol) in dichloromethane (10 mL). This solution was stirred for 1 hour, after which it was filtered and then evaporated to dryness. The green solid 4-V₆O₇(OMe)₁₂¹⁺ was obtained in
good yield (184 mg, 0.196 mmol, 77.4%). Characterization of this product matches that for the previously reported synthesis.  

Complex $6\text{-V}_6\text{O}_7(\text{OEt})_{12}^+$ was prepared and characterized according to the previous literature. Complexes $7\text{-V}_6\text{O}_7(\text{OEt})_{12}^{2-}$ and $8\text{-V}_6\text{O}_7(\text{OEt})_{12}^{-}$ had not been reported previously, and were prepared and characterized as follows:

**Synthesis of $7\text{-V}_6\text{O}_7(\text{OEt})_{12}^{2-}$**

In the glove box, $[\text{NBu}_4][\text{BH}_4]$ (108 mg, 0.420 mmol) was added to a solution of $6\text{-V}_6\text{O}_7(\text{OEt})_{12}$ (200 mg, 0.209 mmol) in acetonitrile (10 mL). This solution was allowed to stir for 1.5 hours, at which time the color had changed from dark green to teal blue. This solution was evaporated to half of its original volume and placed in the freezer. After 24 hours, dark blue-green crystals of $7\text{-V}_6\text{O}_7(\text{OEt})_{12}^{2-}$ precipitated from the solution (125 mg, 0.087 mmol, 41.6%). $^1\text{H}$ NMR (400 MHz, CD$_2$Cl$_2$): $\delta = 1.00$ (s) 1.49 (s) 1.64 (s), 3.37 (s) 26.34 (br). FT-IR (ATR, cm$^{-1}$) 737, 889, 922, 1063, 1170, 1183, 1474,1622,1673. UV-Vis (CH$_3$CN) [$\varepsilon$ (M$^{-1}$cm$^{-1}$): 324 nm (5.150 x 10$^3$)

**Synthesis of $8\text{-V}_6\text{O}_7(\text{OEt})_{12}^{-}$**

In the glovebox, VO(OCH$_3$)$_3$ (392 mg, 1.939 mmol), $[\text{NBu}_4][\text{BH}_4]$ (105 mg, 0.408 mmol) and 14 mL methanol were charged in a 25 mL Teflon-lined Parr reactor. The Parr reactor was sealed, and the mixture heated in an oven at 125 °C for 24 hours. The Parr reactor was allowed to cool to room temperature, and returned to the glove box. The resulting solution was evaporated to dryness, and washed with hexanes until the washes were colorless. The dark green solid $8\text{-V}_6\text{O}_7(\text{OEt})_{12}^{-}$ was obtained in good yield (295 mg, 0.246 mmol, 76.0%). $^1\text{H}$ NMR (400 MHz, CD$_2$Cl$_2$): $\delta = -1.59$ (s) 1.01 (s) 1.64 (s), 3.43 (s) 23.42 (br). FT-IR (ATR, cm$^{-1}$) 734, 883, 951, 1028, 1169, 1379, 1460. UV-Vis (CH$_3$CN) [$\varepsilon$ (M$^{-1}$cm$^{-1}$): 318 nm (5.877 x 10$^3$)

The syntheses of complexes $9\text{-V}_6\text{O}_7(\text{OEt})_{12}^{2+}$ and $10\text{-V}_6\text{O}_7(\text{OEt})_{12}^{2+}$ were reported previously, however were prepared here using alternate synthetic routes:

**Synthesis of $9\text{-V}_6\text{O}_7(\text{OEt})_{12}^{2+}$**

In the glovebox, silver hexafluorophosphate (AgPF$_6$, 53 mg, 0.210 mmol), was added to a solution of $6\text{-V}_6\text{O}_7(\text{OEt})_{12}$ (200 mg, 0.209 mmol) in dichloromethane (10 mL). The solution was allowed to stir for 1 hour, after which it was filtered and evaporated to dryness. This crude product was washed with hexanes (3x 10mL) leaving the green solid $9\text{-V}_6\text{O}_7(\text{OEt})_{12}^{2+}$ (168 mg, 0.152 mmol, 72.7 %). Characterization of this product matches that for the previously reported synthesis.  

**Synthesis of $10\text{-V}_6\text{O}_7(\text{OEt})_{12}^{2+}$**

In the glovebox, nitrosonium hexafluorophosphate (NOPF$_6$, 74 mg, 0.420 mmol) was added to a solution of $6\text{-V}_6\text{O}_7(\text{OEt})_{12}$ (200 mg, 0.209 mmol) in dichloromethane (10 mL). The solution was allowed to stir for one hour, after which a solid green precipitate formed. This precipitate was collected via filtration and washed with ether (3x 10mL). The resulting light green solid $10\text{-V}_6\text{O}_7(\text{OEt})_{12}^{2+}$ was formed in moderate yield (59 mg, 0.047 mmol, 22.4 %). Characterization of this product matches that for the previously reported synthesis.
Electrochemistry.

Cyclic voltammetry experiments.

Concentrations of POV-alkoxide and [NBu$_4$][PF$_6$] used were 1 mM and 100 mM, respectively. CV measurements were carried out inside a nitrogen filled glove box (Vigor Tech, USA) using a Bio-Logic SP 200 potentiostat/galvanostat and the EC-Lab software suite. Cyclic voltammograms were recorded using a 3 mm diameter glassy carbon working electrode (CH Instruments, USA), a Pt wire auxiliary electrode (CH Instruments, USA), and a Ag/Ag$^+$ non-aqueous reference electrode with 0.01 M AgNO$_3$ in 0.05 M [NBu$_4$][PF$_6$] in CH$_3$CN (BASi, USA). Cyclic voltammograms were $iR$ compensated at 85% with impedance taken at 100 kHz using the ZIR tool included within the EC-Lab software.

Diffusion coefficients associated with each redox couple was determined by using the slope of the peak current ($i_p$) versus the square root of scan rate $\nu^{1/2}$. The Randles-Sevcik equation was used to estimate the diffusion coefficients from CV data. For a reversible redox couple, the peak current is given by the eq. S1:

$$i_p = 2.69 \times 10^5 n^{3/2} A c D_0^{1/2} \nu^{1/2} \quad \text{Eq. S1}$$

In eq. S1, $n$ is the number of electrons transferred; $A$ is the electrode area (0.0707 cm$^2$ for the glassy carbon working electrode); $c$ is the bulk concentration of the active species; $D_0$ is the diffusion coefficient of the active species; $\nu$ is the scan rate. For an irreversible redox couple, the peak current, is given by the eq. S2:

$$i_p = 2.99 \times 10^5 n^{3/2} \alpha^{1/2} A c D_0^{1/2} \nu^{1/2} \quad \text{Eq. S2}$$

where $\alpha$ is the charge transfer coefficient ($\alpha \sim 0.5$).

For the redox couples that show quasi-reversible kinetics, relationships for both reversible and irreversible redox reaction are usually employed to determine the diffusion coefficients of such redox processes. Therefore, an average value of diffusion coefficient was approximated for a quasi-reversible redox couple using both equations S1 and S2.$^4$

The Heterogeneous Electron-Transfer (ET) Rate Constants were calculated using the Nicholson method.$^5$ The potential difference ($\Delta Ep$) of oxidation and reduction peaks were obtained at different scan rates. The transfer parameter, $\psi$, was extracted from the working curve constructed by Nicholson using $\Delta Ep$ values. The standard heterogeneous charge transfers rate constant, $k_0$, for the electron transfer process was determined using the following equation:

$$\psi = \frac{k_0}{(\pi n F D v)^{1/2}} \quad \text{Eq. S3}$$

where $n$ is the number of electrons transferred, $F$ is the Faraday constant, $D$ is the diffusion coefficient, $\nu$ is the scan rate, $R$ is the ideal gas constant and $T$ is the temperature.$^5$
**Chronoamperometry/bulk electrolysis experiments**

Bulk electrolysis experiments were performed in a H-cell with a glass frit separator (Porosity =10-16 µm, Adams and Chittenden, USA) using a Bio-Logic SP 200 potentiostat/galvanostat. An active species concentration of 1 mM was used. Working electrode compartment contained 5 mL of the active species with 100 mM [NBu₄][PF₆] in CH₂CN and counter electrode compartment had 5 mL of 100 mM [NBu₄][PF₆] in CH₂CN. A Pt mesh working electrode and a Pt wire counter electrode were used. Bulk electrolysis experiments were carried out using the chronoamperometry techniques available in EC lab software suite at constant potentials, selected from the CV data.

**Charge-discharge experiments**

Charge-discharge testing was done in a nitrogen filled glove box using a glass H-cell (Adams and Chittenden, USA) and a Bio-Logic SP 150 potentiostat/galvanostat. The electrolyte solutions used in charge-discharge experiments were 0.01 M active species in 0.5 M [NBu₄][PF₆] in CH₂CN. Each compartment of the H-cell was filled with 15.0 mL of the electrolyte solution. The compartments of the H-cell were separated by an AMI-7001 anion exchange membrane (~0.05 cm², Membrane International Inc., USA). Two graphite felt electrodes (2 × 1 × 0.5 cm, Fuel Cell Store, USA) were placed in the posolyte and negolyte chambers. Electrodes attached to Pt wire current collectors submerged in the electrolyte solutions (~0.5 cm). Membranes and graphite felt electrodes were soaked in electrolyte solutions for 24 hours before each experiment. A galvanostatic charge-discharge method was adopted using a charging current of 0.2 mA and a discharging current of 0.02 mA for each experiment. The charge voltage cut offs were 2.0 V for the two separate experiments, both involving all four redox couples. The discharge cutoff voltage was 0.5 V for 1-V₆O₇(OCH₃)₁₂ and 0.6 V for 6-V₆O₇(OCH₃)₁₂. For the duration of the charge-discharge experiments, both half cells were stirring at approximately 1,000 rpm.
Figure S1. CV cycling of 1.0 mM $\text{1-V}_2\text{O}_7(\text{OMe})_{12}$ in MeCN with 0.1 M $[\text{NBu}_4][\text{PF}_6]$ supporting electrolyte. Scan rate 100mV/s. Duration of cycling approximately one hour.
Figure S2. (a) CV of 1 mM 1-V₆O₇ in MeCN with 0.1 M [NBu₄][PF₆] supporting electrolyte at various scan rates. (b) CV of only the most reducing redox-event (R2) of 1-V₆O₇. Each redox event is isolated to determine $i_p$ and $\Delta E$ values for use in diffusion coefficient ($D_0$) and heterogeneous electron transfer rate constant ($k_0$) calculations.
Figure S3. (a) Plots of $i_p$ vs. $(v)^{1/2}$ and (b) $\Delta E$ vs. $(v)^{1/2}$ for the second reduction event ($E_{1/2} = -0.72\text{V}$) of $1-V_6\text{O}_7(\text{OMe})_{12}$
Figure S4. (a) Plots of $i_p$ vs. $(v)^{1/2}$ and (b) $\Delta E$ vs. $(v)^{1/2}$ for the first reduction event ($E_{1/2} = -0.22$ V) of $1$-$V_6O_7(OMe)_{12}$
Figure S5. (a) Plots of $i_p$ vs. $(v)^{1/2}$ and (b) $\Delta E$ vs. $(v)^{1/2}$ for the first oxidation event ($E_{1/2} = +0.30$ V) of 1-V$_6$O$_7$(OMe)$_{12}$
Figure S6. (a) Plots of $i_p$ vs. $(v)^{1/2}$ and (b) $\Delta E$ vs. $(v)^{1/2}$ for second oxidation event ($E_{1/2} = +0.85$ V) of 1-V$_6$O$_7$(OMe)$_{12}$
Figure S7. (a) Cyclic voltammograms at 100 mV/s and (b) absorption spectra of a 1 mM solution of $2-\text{V}_6\text{O}_7(\text{OMe})_{12}^{2-}$ with 0.1 M [NBu$_4$][PF$_6$] in acetonitrile over the course of a week.
Figure S8. (a) Cyclic voltammograms at 100 mV/s and (b) absorption spectra of a 1 mM solution of $3\text{-V}_6\text{O}_7\text{(OMe)}_{12}^-$ with 0.1 M [NBu$_4$][PF$_6$] in acetonitrile over the course of a week.
Figure S9. (a) Cyclic voltammograms at 100 mV/s and (b) absorption spectra of a 1 mM solution of 1-V₆O₇(OMe)₁₂ with 0.1 M [NBu₄][PF₆] in acetonitrile over the course of a week.
Figure S10. (a) Cyclic voltammograms at 100 mV/s and (b) absorption spectra of a 1 mM solution of $4\text{-V}_6\text{O}_7(\text{OMe})_{12}^+$ with 0.1 M $\text{NBu}_4\text{PF}_6$ in acetonitrile over the course of a week.
Figure S11. Bulk oxidation (+1.1 V) of 1-V₅O₇(OMe)₁₂ in MeCN
Figure S12. (a) absorbance spectra of $\text{2-V}_6\text{O}_7\text{(OMe)}_{12}^{2-}$ at various concentrations in MeCN with 0.1 M $[\text{NBu}_4][\text{PF}_6]$ (b) Beer’s Law plot of absorbance at 626 nm for $\text{2-V}_6\text{O}_7\text{(OMe)}_{12}^{2-}$ in MeCN.

Molar Absorptivity at 626nm : $50.3 \text{ M}^{-1}\text{cm}^{-1}$

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<th>Saturated Solution 1:</th>
<th>Saturated Solution 2:</th>
<th>Saturated Solution 3:</th>
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<tbody>
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<td>Diluted 200uL to 5mL MeCN</td>
<td>Diluted 200uL to 5mL MeCN</td>
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<tr>
<td>$A = 0.222605$</td>
<td>$A = 0.22048$</td>
<td>$A = 0.20776$</td>
</tr>
<tr>
<td>$C = 4.2001 E-3 \text{ M}$</td>
<td>$C = 4.16 E-3 \text{ M}$</td>
<td>$C = 3.9218 E-3 \text{ M}$</td>
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<tr>
<td>$5\text{mL}(\text{M}) = .200 \text{ mL} \times \text{ M}$</td>
<td>$5\text{mL}(\text{M}) = .200 \text{ mL} \times \text{ M}$</td>
<td>$5\text{mL}(3.9218 \text{ E-3 M}) = .200 \text{ mL} \times \text{ M}$</td>
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<tr>
<td>$X = 0.105 \text{ M}$</td>
<td>$X = 0.104 \text{ M}$</td>
<td>$X = 0.098 \text{ M}$</td>
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<tr>
<td></td>
<td></td>
<td>Average solubility = 102 mM</td>
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Figure S13. (a) absorbance spectra of $\text{3-V}_6\text{O}_7(\text{OMe})_{12}^-$ at various concentrations in MeCN with 0.1 M $[\text{NBu}_4][\text{PF}_6]$ (b) Beer’s Law plot of absorbance at 378 nm for $\text{3-V}_6\text{O}_7(\text{OMe})_{12}^-$ in MeCN.

Molar Absorptivity at 378nm : 3,668.7 M$^{-1}$cm$^{-1}$

saturated solution 1: Diluted 5uL to 5mL MeCN
A = .684129
C = 1.865 E-4

saturated solution 2: Diluted 5uL to 5mL MeCN
A = .693158
C = 1.889 E-4

saturated solution 3: Diluted 5uL to 5mL MeCN
A = .715259
C = 1.950 E-4

5mL(1.865 E-4 M) = .005 mL X M
5mL(1.889 E-4 M) = .005 mL X M
5mL(1.950 E-4 M) = .005 mL X M

X = 0.1865 M
X = 0.1889 M
X = 0.1950 M

Average solubility = 190 mM
Figure S14. (a) absorbance spectra of 1-V₆O₇(OMe)₁₂ at various concentrations in MeCN with 0.1 M [NBu₄][PF₆] (b) Beer’s Law plot of absorbance at 382 for 1-V₆O₇(OMe)₁₂ in MeCN.

Molar Absorptivity at 382 nm : 9001.1 M⁻¹ cm⁻¹

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<th>Solution</th>
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<th>Concentration</th>
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<tr>
<td>Saturated 1</td>
<td>A = 0.918122</td>
<td>C = 1.02 E-4 M</td>
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<tr>
<td>Saturated 2</td>
<td>A = 0.927113</td>
<td>C = 1.03 E-4 M</td>
</tr>
<tr>
<td>Saturated 3</td>
<td>A = 0.882108</td>
<td>C = 1.96 E-5 M</td>
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10mL (1.02 E-4 M) = .005 mL X M  
10mL (1.03 E-4 M) = .005 mL X M  
10mL (1.96 E-5 M) = .005 mL X M

X = .204 M  
X = .206 M  
X = .196 M

Average solubility = 202 mM
Figure S15. (a) absorbance spectra of \(4\text{-V}_6\text{O}_7\text{(OMe)}_{12}^+\) at various concentrations in MeCN with 0.1 M \([\text{NBu}_4][\text{PF}_6]\) (b) Beer’s Law plot of absorbance at 382 for \(4\text{-V}_6\text{O}_7\text{(OMe)}_{12}^+\) in MeCN.

Molar Absorptivity at 382 nm: 14,632 M\(^{-1}\)cm\(^{-1}\)

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<th>Saturated Solution 1:</th>
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<th>Saturated Solution 3:</th>
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<td>Diluted 2.5uL to 10mL MeCN</td>
<td>Diluted 2.5uL to 10mL MeCN</td>
<td>Diluted 2.5uL to 10mL MeCN</td>
</tr>
<tr>
<td>(A = 0.68404)</td>
<td>(A = 0.691362)</td>
<td>(A = 0.643808)</td>
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<tr>
<td>(C = 4.675 \text{ E-5})</td>
<td>(C = 4.725 \text{ E-5} \text{ M})</td>
<td>(C = 4.4 \text{ E-5} \text{ M})</td>
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<td>10mL(4.675 \text{ E-5} \text{ M}) = .0025 mL X M</td>
<td>10mL(4.725 \text{ E-5} \text{ M}) = .0025 mL X M</td>
<td>10mL(4.4 \text{ E-5} \text{ M}) = .0025 mL X M</td>
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<tr>
<td>(X = 0.187 \text{ M})</td>
<td>(X = 0.189 \text{ M})</td>
<td>(X = 0.176 \text{ M})</td>
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Average solubility = 184 mM
Figure S16. CV of catholyte solution of 1-V₆O₇(ΟCH₃)₁₂ before and after charge discharge cycling at 2 V cutoff potential.

Figure S17. CV cycling of 1 mM 6-V₆O₇(OEt)₁₂ in acetonitrile with 0.1 M [NBu₄][PF₆] supporting electrolyte.
Figure S18. (a) Plots of $i_p$ vs. $(v)^{1/2}$ and (b) $\Delta E$ vs. $(v)^{1/2}$ for the second reduction event ($E_{1/2} = -0.88$ V) of 6-$V_2O_5$($OEt$)$_{12}$.
Figure S19. (a) Plots of $i_p$ vs. $(v)^{1/2}$ and (b) $\Delta E$ vs. $(v)^{1/2}$ for the first reduction event ($E_{1/2} = -0.34$ V) of 6-V$_2$O$_5$(OEt)$_{12}$
Figure S20. (a) Plots of $i_p$ vs. $(v)^{1/2}$ and (b) $\Delta E$ vs. $(v)^{1/2}$ for the first oxidation event ($E_{1/2} = +0.22$ V) of $6\text{V}_2\text{O}_5(\text{OEt})_{12}$.
Figure S21. (a) Plots of $i_p$ vs. $(v)^{1/2}$ and (b) $\Delta E$ vs. $(v)^{1/2}$ for the second oxidation event ($E_{1/2} = +0.79$ V) of $6\cdot V_2O_5(OEt)_{12}$
Figure S22. (a) absorbance spectra of $7\text{-V}_6\text{O}_7\text{(OEt)}_{12}^{2-}$ at various concentrations in MeCN with 0.1 M $[\text{NBu}_4][\text{PF}_6]$ (b) Beer’s Law plot of absorbance at 626 nm for $7\text{-V}_6\text{O}_7\text{(OEt)}_{12}^{2-}$ in MeCN.

Molar Absorptivity at 323 nm: 5,069 M\(^{-1}\)cm\(^{-1}\)

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<th>Saturated Solution 2:</th>
<th>Saturated Solution 3:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diluted 2.5 uL to 10 mL MeCN</td>
<td>Diluted 2.5 uL to 10 mL MeCN</td>
<td>Diluted 2.5 uL to 10 mL MeCN</td>
</tr>
<tr>
<td>$A = 0.13052$</td>
<td>$A = 0.15207$</td>
<td>$A = 0.13813$</td>
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<tr>
<td>$C = 2.575 \text{ E-5 M}$</td>
<td>$C = 3.00 \text{ E-5 M}$</td>
<td>$C = 2.725 \text{ E-5 M}$</td>
</tr>
<tr>
<td>10mL(2.575 E-5 M) = 2.5uL (X M)</td>
<td>10mL(3.00 E-5 M) = 2.5uL (X M)</td>
<td>10mL(2.725 E-5 M) = 2.5 uL (X M)</td>
</tr>
<tr>
<td>X= 0.103 M</td>
<td>X= 0.120 M</td>
<td>X= 0.109 M</td>
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</tbody>
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Average Solubility = 111 mM
Figure S23. (a) absorbance spectra of $\text{8-V}_6\text{O}_7\text{(OEt)}_{12}^-$ at various concentrations in MeCN with 0.1 M [NBu$_4$][PF$_6$] (b) Beer’s Law plot of absorbance at 626 nm for $\text{8-V}_6\text{O}_7\text{(OEt)}_{12}^-$ in MeCN.

Molar Absorptivity at 325 nm: 5,971 M$^{-1}$cm$^{-1}$

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Diluted</td>
<td>2.5 uL to 10 mL MeCN</td>
<td>2.5 uL to 10 mL MeCN</td>
<td>2.5 uL to 10 mL MeCN</td>
</tr>
<tr>
<td>A</td>
<td>0.34333</td>
<td>0.33587</td>
<td>0.32691</td>
</tr>
<tr>
<td>C</td>
<td>5.750 E-5 M</td>
<td>5.625 E-5 M</td>
<td>5.475 E-5 M</td>
</tr>
<tr>
<td>10mL(5.750 E-5 M) = 2.5uL (X M)</td>
<td>10mL(5.625 E-5 M) = 2.5uL (X M)</td>
<td>10mL(5.475 E-5 M) = 2.5 uL (X M)</td>
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<tr>
<td>X</td>
<td>0.230 M</td>
<td>0.225 M</td>
<td>0.219 M</td>
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</table>

Average Solubility = 225 mM
Molar Absorptivity at 325 nm: 6,787 M$^{-1}$cm$^{-1}$

Saturated Solution 1: Diluted 10 uL to 10 mL MeCN
A = 0.29190
C = 4.301 E-5 M
10mL(4.301 E-5 M) = 10 uL (X M)
X= 0.043 M

Saturated Solution 2: Diluted 10 uL to 10 mL MeCN
A = 0.37559
C = 5.534 E-5 M
10mL(5.534 E-5 M) = 10 uL (X M)
X= 0.055 M

Saturated Solution 3: Diluted 10 uL to 10 mL MeCN
A = 0.32224
C = 4.748 E-5 M
10mL(4.748 E-5 M) = 10 uL (X M)
X= 0.047 M

Average Solubility = 48 mM

Figure S24. (a) absorbance spectra of $\text{6-V}_6\text{O}_7\text{(OEt)}_{12}$ at various concentrations in MeCN with 0.1 M [NBu$_4$][PF$_6$] (b) Beer’s Law plot of absorbance at 626 nm for $\text{6-V}_6\text{O}_7\text{(OEt)}_{12}$ in MeCN.
**Figure S25.** (a) absorbance spectra of $\text{9-V}_6\text{O}_7(\text{OEt})_{12}^+$ at various concentrations in MeCN with 0.1 M [NBu$_4$][PF$_6$] (b) Beer’s Law plot of absorbance at 626 nm for $\text{9-V}_6\text{O}_7(\text{OEt})_{12}^+$ in MeCN.

Molar Absorptivity at 325 nm: 7,767 M$^{-1}$cm$^{-1}$

Saturated Solution 1: Diluted 2.5 uL to 10 mL MeCN  
A = 0.38640  
C = 4.975 E-5 M  
$10\text{mL}(4.975 \text{ E-5 M}) = 2.5\text{uL (X M)}$  
X = 0.199 M

Saturated Solution 2: Diluted 2.5 uL to 10 mL MeCN  
A = 0.39619  
C = 5.101 E-5 M  
$10\text{mL}(5.101 \text{ E-5 M}) = 2.5\text{uL (X M)}$  
X = 0.204 M

Saturated Solution 3: Diluted 2.5 uL to 10 mL MeCN  
A = 0.41553  
C = 5.350 E-5 M  
$10\text{mL}(5.350 \text{ E-5 M}) = 2.5\text{uL (X M)}$  
X = 0.214 M

Average Solubility = 206 mM
**Figure S26.** (a) absorbance spectra of $10\text{-}V_6\text{O}_{7}(\text{OEt})_{12}^{2+}$ at various concentrations in MeCN with 0.1 M $[\text{NBu}_4][\text{PF}_6]$ (b) Beer’s Law plot of absorbance at 626 nm for $10\text{-}V_6\text{O}_{7}(\text{OEt})_{12}^{2+}$ in MeCN.

![Absorbance Spectra](image)

Molar Absorptivity at 325 nm: 9,803 M$^{-1}$cm$^{-1}$

<table>
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<td>Diluted 2.5 uL to 10 mL MeCN</td>
</tr>
<tr>
<td>$A = 0.31869$</td>
<td>$A = 0.34555$</td>
<td>$A =0.321048$</td>
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<tr>
<td>$C = 3.251 \text{ E-5 M}$</td>
<td>$C = 3.525 \text{ E-5 M}$</td>
<td>$C = 3.275 \text{ E-5 M}$</td>
</tr>
<tr>
<td>$10\text{mL}(3.251 \text{ E-5 M}) = 2.5\text{uL (X M)}$</td>
<td>$10\text{mL}(3.525 \text{ E-5 M}) = 2.5\text{uL (X M)}$</td>
<td>$10\text{mL}(3.275 \text{ E-5 M}) = 2.5 \text{ uL (X M)}$</td>
</tr>
<tr>
<td>$X= 0.130 \text{ M}$</td>
<td>$X= 0.141 \text{ M}$</td>
<td>$X= 0.131 \text{ M}$</td>
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Average Solubility = 134 mM
Figure S27. (top) UV-vis in acetonitrile and (bottom) infrared absorption spectra of all charge states of $6$-$V_6O_7(OEt)_{12}$.
Figure S28. (a) Cyclic voltammograms at 100 mV/s and (b) absorption spectra of a 1 mM solution of $7$-$V_6O_7(OEt)_{12}^{2-}$ with 0.1 M $\text{NBu}_4\text{[PF}_6]$ in acetonitrile over the course of a week.
Figure S29. (a) Cyclic voltammograms at 100 mV/s and (b) absorption spectra of a 1 mM solution of \(8\text{-V}_6\text{O}_2\text{(OEt)}_{12}^-\) with 0.1 M \([\text{NBu}_4][\text{PF}_6]\) in acetonitrile over the course of a week.
Figure S30. (a) Cyclic voltammograms at 100 mV/s and (b) absorption spectra of a 1 mM solution of 6-V₆O₇(OEt)₁₂ with 0.1 M [NBu₄][PF₆] in acetonitrile over the course of a week.
**Figure S31.** (a) Cyclic voltammograms at 100 mV/s and (b) absorption spectra of a 1 mM solution of $9\text{-V}_6\text{O}_7\text{(OEt)}_{12}^+$ with 0.1 M [NBu$_4$][PF$_6$] in acetonitrile over the course of a week.
Figure S32. (a) Cyclic voltammograms at 100 mV/s and (b) absorption spectra of a 1 mM solution of 6-V6O7(OEt)12$^{2+}$ with 0.1 M [NBu4][PF6] in acetonitrile over the course of a week.
Figure S33. (top) Bulk oxidation (+1.1 V) of 0.1 mM 6-V$_6$O$_{12}$(OEt)$_{12}$ in acetonitrile with 0.1 M [NBu$_4$][PF$_6$] supporting electrolyte and (bottom) CV of the solution before and after the oxidation.
References:


