Electronic Supporting Information (ESI)

# An Organofunctionalized Polyoxovanadium Cluster as a Molecular Model of Interfacial Pseudocapacitance

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# Experimental

General Considerations. Where specified, air- and moisture-sensitive 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 glove box. Anhydrous methanol was purchased from Sigma-Aldrich and stored over activated 4 Å molecular sieves (Fisher Scientific). Acetonitrile (Fisher for electrochemical Chemical) used experiments was deoxygenated and dried on a Glass Contour System (Pure Process Technology, LLC) and stored over activated 4 Å molecular sieves (Fisher Scientific). All other solvents (acetone and diethyl ether) were used as received outside the glove box without drying or degassing. {"Bu<sub>4</sub>N}OTf and  ${}^{n}Bu_{4}N$  PF<sub>6</sub> were purchased from Sigma-Aldrich, recrystallized three times from hot ethanol, and stored under dynamic vacuum for at least one day prior to use. LiOTf, NaOTf, and KOTf were purchased from Sigma Aldrich and used as received. Complexes  $[V_6O_7(OCH_3)_{12}]$ , {<sup>n</sup>Bu<sub>4</sub>N}[V<sub>6</sub>O<sub>7</sub>(OCH<sub>3</sub>)<sub>12</sub>], and {<sup>n</sup>Bu<sub>4</sub>N}<sub>2</sub>[V<sub>6</sub>O<sub>7</sub>(OCH<sub>3</sub>)<sub>12</sub>] were synthesized according to literature procedures.<sup>[1]</sup>

<sup>1</sup>H NMR spectra were recorded at 400 MHz on a Bruker DPX-400 spectrometer at 9.4 Tesla while locked on to deuterated solvent. Deuterated  $C_3H_6O$  and  $CH_3CN$  were purchased from Cambridge lsotope Laboratories and used as received from the manufacturer. Elemental analysis was performed by Midwest Microlabs (Indianapolis, Indiana). X-ray quality single crystals were mounted on a thin Nylon loop and positioned on a XtaLab Synergy-S Dualflex diffractometer equipped with a HyPix-6000He HPC area detector for data collection at 100.0(5) K. Structure solutions were obtained using SHELXT-2014/5<sup>[2]</sup> and refined using SHELXL-2014/7<sup>[3]</sup>.

Electrochemical Analysis (Cyclic & Square Wave Voltammetry). For all cyclic voltammetry (CV) experiments, concentrations of active species (vanadium cluster) and all supporting electrolytes ({<sup>n</sup>Bu<sub>4</sub>N}OTf, LiOTf, NaOTf, and KOTf), and titrant solutions used were 1 mM, 100 mM, and 10mM respectively. CV measurements were carried out using а Bio-Logic SP 150 potentiostat/galvanostat and the EC-Lab software suite. Glassy carbon discs (3 mm, CH Instruments, USA) were used as working electrodes. Working electrodes were polished using a micro cloth pad and 0.05 µM alumina powder. Potentials recorded during CV were measured relative to a nonaqueous Ag/Ag+ reference electrode with 10 mM AgNO<sub>3</sub> and 100 mM {<sup>n</sup>Bu<sub>4</sub>N}{PF<sub>6</sub>} in acetonitrile (Bio-Logic). A platinum wire served as the counter electrode. All experiments were carried out at room temperature inside a nitrogen-filled glove box (MBraun, USA). All CV measurements were iR compensated at 85% with impedance taken at 100 kHz using the ZIR tool included with the EC-Lab software. CV experiments were conducted at 100 mV/s. All concentrations, hardware, software, electrodes, reference, and atmospheric parameters for square wave voltammetry experiments were the same as for cyclic voltammetry. Square wave experiments were conducted at 50 mV/s (pulse height: 25 mV, pulse width: 100 ms, step height: 10 mV).

**Preparation of**  $\{Li\}_2[V_6O_7(OCH_3)_{12}]$ . A 20 mL scintillation vial was charged with {<sup>n</sup>Bu<sub>4</sub>N}<sub>2</sub>[V<sub>6</sub>O<sub>7</sub>(OCH<sub>3</sub>)<sub>12</sub>] (0.074 g, 0.058 mmol) and 5 mL of acetonitrile. To this solution was added three equivalents of LiOTf (0.027 g, 0.174 mmol), weighed by difference. The blue solution was stirred for 20 minutes, during which a blue powder precipitated from the reaction mixture. The reaction was filtered over a glass fritted funnel and the blue powder was washed, three times with acetonitrile (2 mL) and three times with diethyl ether (4 mL). The solid was dried under reduced pressure for 1 hour, resulting in isolation of the product as a light blue powder (0.0402 g, 0.050 mmol, 86 %). Crystals suitable for X-ray analysis were grown from slow diffusion of diethyl ether into a concentrated solution of the product dissolved in acetone. After four days, teal blue needles suitable for crystallographic analysis were obtained. <sup>1</sup>H NMR (400 mHz, (CD<sub>3</sub>)CO):  $\delta$  = 21.83 ppm (fwhh = 640 Hz). Elemental Analysis for C<sub>12</sub>H<sub>36</sub>O<sub>19</sub>V<sub>6</sub>Li<sub>2</sub> (MW = 803.93 g/mol) Calcd (%): C, 17.93; H, 4.51; Found (%): C, 17.88; H, 4.63.



**Figure S1.** Electrochemical data to test the reversibility of the most reducing redox couple (R2) for complex **1-V**<sub>6</sub>**O**<sub>7</sub>. (a) Cyclic voltammogram of complex **1-V**<sub>6</sub>**O**<sub>7</sub> (1 mM) taken at scan rates ranging from 5 to 2000 mV s<sup>-1</sup> in MeCN with 0.1M LiOTf as the supporting electrolyte; (b) plot of the current density (j<sub>p</sub>) versus the square root of the scan rate (n<sup>1/2</sup>) for complex **1-V**<sub>6</sub>**O**<sub>7</sub> (c) plot of peak separation (V) vs. scan rate (mV/s) for complex **1-V**<sub>6</sub>**O**<sub>7</sub>.

KOTf						
	R1			R2		
	E (V) vs Ag/Ag+		E (V) vs Ag/Ag+			
Equiv	CV	SWV	Equiv	CV	SWV	
0	-0.1989	-0.1906	0	-0.701	-0.699	
0.2	-0.1989	-0.1905	0.2	-0.6944	-0.6915	
0.5	-0.1988	-0.1906	0.5	-0.6884	-0.6816	
1	-0.198	-0.1905	1	-0.6804	-0.6715	
2	-0.1965	-0.1905	2	-0.6745	-0.665	

**Table S1.** Substoichiometric electrochemical titration of alkali salts into  $V_6O_7(OCH_3)_{12}$  analyzed<br/>by CV and SWV.

NaOTf					
R1				R2	
E (V) vs Ag/Ag+			E (V) vs /	Ag/Ag+	
Equiv	CV	SWV	Equiv	CV	SWV
0	-0.1945	-0.2006	0	-0.6923	-0.7018
0.2	-0.1928	-0.197	0.2	-0.6708	-0.6717
0.5	-0.19	-0.1905	0.5	-0.6492	-0.6316
1	-0.1895	-0.1905	1	-0.6261	-0.6116
2	-0.1879	-0.1906	2	-0.6065	-0.6015

LiOTf								
	R	1		R1	.5		R2	2
	E (V) vs	Ag/Ag+		E (V) vs	Ag/Ag+		E (V) vs	Ag/Ag+
Equiv	CV	SWV	Equiv	CV	SWV	Equiv	CV	SWV
0	-0.1973	-0.2008	0	-	-	0	-0.6977	-0.7018
0.2	-0.191	-0.1907	0.2	-	-0.5014	0.2	-0.693	-0.698
0.5	-0.1919	-0.1907	0.5	-0.4887	-0.4814	0.5	-0.6657	-
1	-0.1879	-0.186	1	-0.4748	-0.4513	1	-	-
2	-0.1813	-0.1807	2	-0.4539	-0.4413	2	-	-

SWV Integrated Area Ratio (R2/R1)				
Equiv	LiOTf	NaOTf		
0	0.953	0.969		
0.2	0.998	0.976		
0.5	0.894	0.934		
1	0.906	0.957		
2	0.893	0.958		

 Table S2. Integrated SWV data for Figure 3.



Figure S2a. <sup>1</sup>H NMR spectrum of complex {<sup>n</sup>Bu<sub>4</sub>N}[V<sub>6</sub>O<sub>7</sub>(OCH<sub>3</sub>)<sub>12</sub>] collected in CD<sub>3</sub>CN (21 °C)



**Figure S2b.** <sup>1</sup>H NMR spectrum of cation exchange reaction of {**"Bu**<sub>4</sub>**N**}[**V**<sub>6</sub>**O**<sub>7</sub>(**OCH**<sub>3</sub>)<sub>12</sub>] with LiOTf collected in CD<sub>3</sub>CN (21 °C)



Figure S3a. <sup>1</sup>H NMR spectrum of complex {"Bu<sub>4</sub>N}<sub>2</sub>[V<sub>6</sub>O<sub>7</sub>(OCH<sub>3</sub>)<sub>12</sub>] collected in CD<sub>3</sub>CN (21 °C)



Figure S3b. <sup>1</sup>H NMR spectrum of complex {Li}<sub>2</sub>[V<sub>6</sub>O<sub>7</sub>(OCH<sub>3</sub>)<sub>12</sub>] collected in (CD<sub>3</sub>)<sub>2</sub>CO (21 °C)

Empirical formula	C <sub>16</sub> H <sub>50</sub> O <sub>22</sub> V <sub>6</sub> Li <sub>2</sub> (CCDC = 1955968)			
Formula weight	914.08			
Temperature	100.0(10) K			
Wavelength	1.54184 Å			
Crystal system	Monoclinic			
Space group	P21/c			
Unit cell dimensions	a = 17.4358(2) Å b = 10.35010(10) Å c = 20.6189(2) Å	α = 90° β = 105.5010(10)° γ = 90°		
Volume	3585.59(7) Å <sup>3</sup>			
Z	4			
Reflections collected	36183			
Independent reflections	7544			
Goodness-of-fit on F2	1.069			
Final R indices [I>2sigma(I)]	R1 = 0.0309, wR2 = 0.0757			

Table S3. Crystallographic parameters for complex {Li}<sub>2</sub>[V<sub>6</sub>O<sub>7</sub>(OCH<sub>3</sub>)<sub>12</sub>].

### References.

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