### Article

Designer Two-Electron Storage Viologen Anolyte Materials for Neutral Aqueous Organic Redox Flow Batteries



Liu and co-workers reported a series of rationally designed two-electron storage viologen molecules as anolytes for high-voltage and high-power pH-neutral aqueous organic redox flow batteries. The synthetic and computational chemistry presented has opened a new avenue for designing energy-dense redox-active organic molecules for building neutral AORFBs with high power density and high energy density, and it promises economical, benign, and widespread uses of redox flow batteries in large-scale energy storage.



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### HIGHLIGHTS

Two-electron storage viologens were designed for energy-storage applications

Neutral aqueous organic redox flow batteries up to 1.38 V and 130 mW/cm<sup>2</sup>

An integrated approach of synthesis, electrochemistry, and computational modelling

Molecular engineering is a powerful strategy for developing redox-active molecules

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### Article

# Designer Two-Electron Storage Viologen Anolyte Materials for Neutral Aqueous Organic Redox Flow Batteries

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### **SUMMARY**

Aqueous organic redox flow batteries (AORFBs) are highly attractive for largescale energy storage because redox-active organic molecules are synthetically tunable, sustainable, and potentially low cost. Here, we show that rational molecular engineering yielded a series of two-electron storage viologen molecules as anolyte materials for AORFBs. In neutral NaCl solutions, these viologen anolytes have a theoretical capacity of up to 96.5 Ah/L in H<sub>2</sub>O and exhibit a reduction potential as low as -0.78 V versus normal hydrogen electrode. The neutral aqueous flow batteries with two two-electron storage viologen molecules delivered a cell voltage of up to 1.38 V and outstanding battery performance, including a power density of up to 130 mW/cm<sup>2</sup>, capacity retention of up to 99.99% per cycle, and energy efficiency of up to 65% at 60 mA/cm<sup>2</sup>. Density functional theory calculations revealed that the 1e<sup>-</sup> and 2e<sup>-</sup> reduced redox states of these molecules were stabilized by the high charge delocalization of their frontier SOMO or HOMO.

### INTRODUCTION

Steadily increasing utilization of renewable energy resources such as solar and wind power requires affordable and sustainable energy-storage technologies at grid scales up to MW/MWh.<sup>1-3</sup> Redox flow batteries (RFBs) represent one of the most promising battery technologies to overcome the intermittence of renewable energy and supply reliable renewable electricity to grids.<sup>2,3</sup> Simultaneously, implementation of renewable electricity can significantly address the dependence of diminishing fossil fuels and their adverse environmental impacts. Operating on the general principle of rechargeable batteries, RFBs use redox-active materials dissolved in liquid supporting electrolytes as anode and cathode electrolytes (called anolyte and catholyte, respectively).<sup>2-4</sup> During the charge-discharge process, the redox-active anolyte and catholyte stored in two separated reservoirs are pumped through the electrode surface to conduct electrochemical reactions.<sup>2-4</sup> The distinctive cell architecture of RFBs empowers a number of attractive technical strengths for large-scale energy storage in comparison with traditional static cells, including decoupled energy and power, high current and high power performance, and safety advantages.<sup>2-4</sup>

However, despite these merits, traditional inorganic RFBs such as vanadium RFBs and Zn-Br<sub>2</sub> RFBs endure a number of material challenges for widespread implementation, including expensive active materials (vanadium RFBs), electrolyte crossover (both RFBs), and corrosive and/or hazardous electrolytes (both RFBs).<sup>3–5</sup> Thus, there is an indispensable need to develop new RFB chemistry to address these challenges

### The Bigger Picture

Renewable energy (e.g., solar and wind) can make a significant contribution to meeting the increasing global energy demands. However, its successful penetration into the existing electrical grids requires effective energy-storage solutions to overcome its intermittence. Redox flow batteries (RFBs) are a suitable option for large-scale energy-storage applications (up to MW/MWh). There is an urgent call to develop low-cost and benign RFB technologies to meet the burgeoning energy-storage demands. A new generation of aqueous organic RFBs utilizing sustainable and tunable redoxactive organic molecules has emerged as a game changer for electrochemical energy storage. In the present study, we report a class of rationally designed highly reductive and high-charge capacity redox-active viologen molecules as a class of twoelectron storage anolyte materials that promise aqueous organic RFBs with high voltage, high power density, and high energy density.



and achieve sustainable and "green" electrochemical energy storage.<sup>6,7</sup> Given that resource-abundant redox-active organic molecules have been advocated to replace inorganic materials in traditional RFBs, recently, aqueous organic RFBs (AORFBs) and nonaqueous organic RFBs (NAORFBs) have received increasing attention as viable alternatives.<sup>8–28</sup>

Besides the general technical merits of RFBs discussed above, AORFBs have several outstanding advantages for large-scale energy storage, five of which are outlined here.<sup>15</sup> (1) Using organic redox-active molecules consisting of earth-abundant elements is a sustainable practice. (2) Redox-active molecules are also synthetically tuneable to gain high oxidation or low reduction redox potentials and can have high solubility, thus offering high energy density RFBs, as well as provide optimal membrane compatibility. (3) Utilization of non-flammable aqueous electrolytes offers safety benefits. (4) Aqueous electrolytes consisting of water and simple inorganic supporting electrolytes, such as NaCl and KOH, are inexpensive. (5) High-conductivity aqueous electrolytes (>100 mS/cm) and well-developed selective ion-conductive membranes for aqueous electrolytes allow high current and high power operation while achieving high energy efficiency. Rapid progress has been made in the emerging AORFB technology, including high-power acid/alkaline AORBFs<sup>8,9,12,29</sup> and high-voltage and low-cost neutral AORFBs.<sup>10,11,14–16</sup> Thus far, pH-neutral AORFBs have demonstrated the most stable flow battery performance and stand for the state of the art for organic RFBs.<sup>14-16,27</sup> For example, our group<sup>15,16</sup> and Aziz and colleagues<sup>15,16</sup> have reported rather stable viologen and ferrocene AORFBs with capacity retention of up to 99.99% per cycle for up to 700 cycles at 60 mA/cm<sup>2</sup> by using at least 0.5 M active materials.<sup>15,16</sup> In terms of the battery performance status of AORFBs, it is realistic to develop an AORFB system of 1-2 M active materials at a cost of \$5/kg, 0.8 V cell voltage, and area-specific resistance of  $0.5 \,\Omega$  cm<sup>2</sup>, meeting the cost target of RFBs for large-scale energy storage, in the range from \$100/kWh to \$150/kWh, that is proposed by the United States Department of Energy.<sup>30,31</sup>

On the other hand, NAORFBs are claimed to have higher cell voltages and higher energy densities by avoiding the water-splitting voltage window seen in aqueous electrolytes.<sup>6,31</sup> However, compared with AORFBs, NAORFBs encounter several major technical challenges for practical applications, four of which are outlined here.<sup>10</sup> (1) The use of flammable organic solvents not only is a safety concern but also adds additional capital costs.<sup>30,31</sup> (2) Because of the lack of selective ionconductive exchange membranes in organic solvents, NAORFBs commonly run into a severe crossover problem of redox-active molecules and the resulting capacity decay. To minimize the crossover, a mixture of anolyte molecules and catholyte molecules is used as both catholyte and anolyte in flow battery studies.<sup>32,33</sup> However, the strategy doubles the use of redox-active molecules, making NAORFBs more expensive to implement. It is contended that developing selective ion-conductive exchange membranes for organic electrolytes is a major challenge for practical applications of NAORFBs. (3) Largely because of the low conductivity of organic electrolytes (ca. 10 mS/cm versus >100 mS/cm for aqueous electrolytes), NAORFBs are typically operated at low current densities (<35 mA/cm<sup>2</sup>) to achieve reasonable energy efficiency, and the power density performance of NAORFBs is still unclear.<sup>6,31</sup> (4) In addition, in organic solvents, organic radicals are easily subjected to radical side reactions that lead to capacity decay even in the state-of-the-art NAORFBs.<sup>32,33</sup> In terms of battery performance, NAORFBs are still at the stage of proof of concept. For example, the state-of-the-art NAORFBs reported by Wei et al.<sup>32,33</sup> demonstrated only limited cycling tests ( $\leq$ 50 cycles at 10–35 mA/cm<sup>2</sup> with 0.5 M active

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materials) with capacity retention less than 99.98% per cycle. It is anticipated that, in the near future, it will remain very challenging to develop an NAORFB system of 4–5 M active materials at a cost of \$5/kg, 3.0 V cell voltage, and area specific resistance of 5  $\Omega$  cm<sup>2</sup>, to meet the cost target of RFBs for large-scale energy storage.<sup>30,31</sup> From the above comparison, it can be reasonably argued that AORFBs are more promising for practical applications in the near future.

In order to achieve high-performance AORFBs, limited but ingenious synthetic work has been done to tune the redox potential, solubility, and stability of alloxazine,<sup>12</sup> TEMPO,<sup>14</sup> and ferrocene<sup>15</sup> molecules. However, only very few organic molecular electrolytes are capable of storing two electrons in AORFBs.<sup>12,34,35</sup> To advance the art of molecular engineering in redox flow battery materials, here we report a class of rationally designed highly reductive and high-charge-capacity redox-active viologen molecules as two-electron storage analyte materials. These two-electron storage viologen molecules provide charge capacities up to 96.5 Ah/L in H<sub>2</sub>O (or 75.0/L in 2.0 M NaCl) and redox potentials as low as -0.78 V versus a normal hydrogen electrode (NHE), among the highest values of the reduction potentials and charge capacity that have been experimentally determined in aqueous electrolytes. AORFB applications with two two-electron storage viologen anolytes in neutral and non-corrosive NaCl delivered up to 1.38 V cell voltage, an impressive power density of up to 130 mW/cm<sup>2</sup>, energy efficiency of up to 65%, and capacity retention of 99.99% per cycle at 60 mA/cm<sup>2</sup>. We also applied a density functional theory (DFT) calculation to gain in-depth information on the chemical and electronic structures of the three redox states of these viologen molecules.

### **RESULTS AND DISCUSSION**

## Design, Synthesis, and Electrochemical Properties of Two-Electron Storage Viologen Molecules

We previously reported that methyl viologen (MV) via its stable  $MV^{2+/+}$  redox couple functioned as a high-performance analyte material in  $MV/TEMPO^{10}$  and MV/ferro $cene^{15,27}$  AORFBs. MV showed impressive solubility in H<sub>2</sub>O (ca. 2.5 M in H<sub>2</sub>O, ca. 2.0 M in 2.0 M NaCl solution), redox stability, and a highly negative redox potential at -0.45 V versus NHE as its first redox potential. However, its second redox couple,  $MV^{+/0}$ , could not be utilized because of insolubility of the charge-neutral  $MV^{0}$  state in aqueous solution.  $MV^{0/r}$ s insolubility manifests as deposition and stripping behaviors in the cyclic voltammogram of the second redox couple at -0.76 V versus NHE (Figure 1,

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Scheme 1. Synthesis of Two-Electron Storage Viologen Molecules

black dash trace). The stripping behavior of the MV<sup>+/0</sup> redox couple is typical for viologen molecules.<sup>36</sup> We envisaged that if the second reduction is reversible and utilized, viologen molecules could simultaneously achieve two-electron storage and a more negative averaged reduction potential. Consequently, both improvements can contribute to boost the energy density of AORFBs. We further rationalized that the insolubility of MV<sup>0</sup> in the aqueous NaCl electrolyte is ascribed to its charge neutrality and thus a decreased molecular polarity/hydrophilicity. To overcome the solubility issue of the MV<sup>0</sup> oxidation state, our strategy is to increase the hydrophilicity of the MV<sup>0</sup> state by using a more hydrophilic functional group to replace the methyl group on the N atoms. In our previous work, we have demonstrated that the ammonium functionality can effectively improve the water solubility of hydrophobic ferrocene.<sup>15</sup> Additionally, a recent computational work also suggests that a hydrophilic sulfonate and phosphate group can improve the solubility of computationally designed quinone molecules in water for RFB applications.<sup>37</sup> To this end, we first synthesized 1-methyl-1'-[3-(trimethylammonio)propyl]-4,4'-bipyridinium trichloride, [(Me)(NPr)V]Cl<sub>3</sub>, a viologen molecule exhibiting a hydrophilic ammonium functional group, 3-(trimethylammonio)propyl (abbreviated as NPr), on one pendant arm, as displayed in Scheme 1A. The synthesis of [(Me)(NPr)V]Cl<sub>3</sub> was demonstrated at a 50 g scale with a moderate isolated yield of 78%. The structure and purity of [(Me)(NPr)V]Cl<sub>3</sub> was characterized by <sup>1</sup>H NMR and elemental analysis (Figure S2).

As expected, the highly charged ionic [(Me)(NPr)V]Cl<sub>3</sub> exhibited high solubility in H<sub>2</sub>O (1.8 M or 1.4 M in 2.0 M NaCl), and most importantly, cyclic voltammetry studies showed that both redox couples [(Me)(NPr)V]<sup>3+/2+</sup> and [(Me)(NPr)V]<sup>2+/1+</sup> were fully reversible, confirming the solubility of the two-electron reduced [(Me)(NPr)V]<sup>+</sup> state (Figure 1, red trace). The two reductions of [(Me)(NPr)V]Cl<sub>3</sub> were observed at -0.39 V and -0.78 V versus NHE. [(Me)(NPr)V]Cl<sub>3</sub> has a relatively lower solubility in aqueous solution than that of MV (2.5 M in H<sub>2</sub>O or 2.0 M in 2.0 NaCl), but [(Me)(NPr)V]Cl<sub>3</sub>'s ability to store two electrons per molecule, equivalent to 96.5 Ah/L charge capacity in H<sub>2</sub>O (75.0 Ah/L in 2.0 M NaCl), places it among the most energy-dense organic anolytes currently available.<sup>8–15</sup> It should be noted that [(Me)(NPr)V]Cl<sub>3</sub> has a gravimetric capacity of 141.5 Ah/kg. In addition, its lower effective redox potential of -0.59 V (the average of -0.39 and -0.78 V) than that of MV (-0.45 V) can further increase the energy density of AORFBs when paired with the same catholyte.

### Table 1. A Summary of the Physical and Chemical Properties of $[(Me)(NPr)V]Cl_3,\ [(NPr)_2V]Br_4, and\ [(NPr)(SPr)V]Br_2$

Compound	[C] in H <sub>2</sub> O (mol/L)	[ <i>C</i> ] in 2.0 M NaCl (mol/L)	E <sub>1/2</sub> (V versus NHE)	$D \times 10^{-5}$ (cm <sup>2</sup> /s)	k <sup>0</sup> (cm/s)
[(Me)(NPr)V]Cl <sub>3</sub>	1.8	1.4	-0.39	0.54	>0.364
			-0.78	0.53	>0.360
[(NPr) <sub>2</sub> V]Br <sub>4</sub>	1.6	1.3	-0.35	0.39	>0.309
			-0.72	0.38	>0.305
[(NPr)(SPr)V]Br <sub>2</sub>	1.6	1.3	-0.37	0.50	>0.350
			-0.74	0.50	>0.350

Abbreviations are as follows: [C], solubility in water or 2.0 M NaCl;  $E_{1/2}$ , redox potential; D, diffusion coefficient; and  $k^0$ , electron-transfer rate constant.

Encouraged by the results of [(Me)(NPr)V]Cl<sub>3</sub>, we expanded the concept of twoelectron storage viologens and prepared 1,1'-bis[3-(trimethylammonio)propyl]-4,4'-bipyridinium tetrabromide, [(NPr)<sub>2</sub>V]Br<sub>4</sub>, and 1-[3-(trimethylammonio)propyl]-1'-(3-sulfonatopropyl)-4,4'-bipyridinium dibromide, [(NPr)(SPr)V]Br2, in isolated yields of 68% and 86%, respectively (Schemes 1B and 1C). The first electron reduction of  $[(NPr)_2V]Br_4$  was previously reported but its synthesis is not available.<sup>36</sup> In addition, the second reduction of [(NPr)<sub>2</sub>V]Br<sub>4</sub> remains unknown prior to this work. We noticed that an analogous compound, 1,1'-bis[3-(trimethylammonio)propyl]-4,4'-bipyridinium tetrachloride (abbreviated as BTMAP-Vi) was prepared by a more complicated synthesis with a lower yield of 44%.<sup>16</sup> A comparison of the synthesis of [(NPr)<sub>2</sub>V]Br<sub>4</sub> and BTMAP-Vi is highlighted in Scheme S1. Cyclic voltammetry studies confirmed that these two compounds demonstrated two successive fully reversible redox waves (Figure S7). [(NPr)<sub>2</sub>V]Br<sub>4</sub> exhibited reductions at -0.35 and -0.72 V versus NHE with a solubility of 1.6 M in H<sub>2</sub>O (or 1.3 M in 2.0 M NaCl), and charge capacity of 85.8 Ah/L (or 69.7 Ah/L in 2.0 M NaCl) (Figure S7B and Table 1). [(NPr)(SPr)V]Br<sub>2</sub> exhibited two reversible reduction events at -0.37 and -0.74 V versus NHE (Figure S7C and Table 1). [(NPr)(SPr)V]Br2 also has a solubility of 1.6 M in H<sub>2</sub>O (or 1.3 M in 2.0 M NaCl) and thus can provide 85.8 Ah/L charge capacity (or 69.7 Ah/L in 2.0 M NaCl). [(NPr)<sub>2</sub>V]Br<sub>4</sub> and [(NPr)(SPr)V]Br<sub>2</sub> have a gravimetric capacity of 107.1 and 99.4 Ah/kg, respectively.

To better qualify these compounds as an anolyte candidate in an AORFB, we investigated the diffusion coefficients of [(Me)(NPr)V]Cl<sub>3</sub>, [(NPr)<sub>2</sub>V]Br<sub>4</sub> and [(NPr)(SPr)V]Br<sub>2</sub> by using linear sweep voltammetry (LSV) with a glassy carbon rotating-disk electrode. LSV plots and derived Levich plots for [(Me)(NPr)V]Cl<sub>3</sub> are shown in Figure 2. We constructed two linear Levich plots (Figure 2B) for the two reductions of [(Me)(NPr)V]Cl<sub>3</sub> by using limiting currents (Figure 2A) and the square root of rotation speeds. We transformed the corresponding slopes from the linear relationships by using the Levich equation (Equation 1; all equations are given in the Experimental Procedures) to calculate the diffusion coefficients for [(Me)(NPr)V]Cl<sub>3</sub>: 5.40  $\times$  10<sup>-6</sup> and 5.29  $\times$  10<sup>-6</sup> cm<sup>2</sup>/s for its first and second electron reductions, respectively. [(Me)(NPr)V]Cl<sub>3</sub> shows no significant change in diffusion coefficients between the first and second reduction, suggesting a comparable molecular size of [(Me)(NPr)V]<sup>3+</sup> and [(Me)(NPr)V]<sup>2+</sup>. Furthermore, we estimated the rate constants for the electron transfers of (Me)(NPr)V by using Nicholson's method, <sup>38</sup> >0.38 cm/s for both reductions (see Supplemental Information for details), consistent with the observed ideal Levich behaviors. Diffusion constants and electron-transfer rate constants for [(NPr)<sub>2</sub>V]Br<sub>4</sub> and [(NPr)(SPr)V]Br<sub>2</sub> (see Figures S11 and S12) were determined by the same approaches and are





Figure 2. RDE Data and Analysis for [(Me)(NPr)V]Cl<sub>3</sub> (A) LSV scans with rotating working electrode. (B) Levich analysis for each reduction.

summarized in Table 1. As shown in Table 1, the observed differences in the physical and chemical properties of these compounds are attributed to their structural differences. All three compounds exhibit faster diffusion and have larger rate constants than most inorganic compounds and are on par with organic compounds applied in ARFBs.<sup>6,8–13,39</sup> Regarding the physical and chemical properties of these two-electron storage molecules, they are promising anolyte candidates for AORFBs using a Cl<sup>-</sup> exchange mechanism.

## Flow Battery Studies of Two-Electron Storage Molecules [(Me)(NPr)V]Cl<sub>3</sub>, [(NPr)<sub>2</sub>V]Br<sub>4</sub>, and [(NPr)<sub>2</sub>V]Cl<sub>4</sub>

To demonstrate the proof of concept of the two-electron storage capability, we examined [(Me)(NPr)V]Cl<sub>3</sub> in redox flow battery tests by pairing with an established catholyte recently reported by us, (ferrocenylmethyl)trimethylammonium chloride, FcNCl.<sup>15</sup> In Figure 3B, cyclic voltammetry data of [(Me)(NPr)V]Cl<sub>3</sub> and FcNCl are shown together to determine the cell voltage: -0.39 V and -0.78 V versus NHE for [(Me)(NPr)V]Cl<sub>3</sub> and 0.61 V versus NHE for FcNCl. The three redox potentials observed for [(Me)(NPr)V]Cl<sub>3</sub> and FcNCl are suitably distanced from the onset potentials for the hydrogen and oxygen evolution reactions at neutral pH (Figure 3B). These onset potentials delineate the traditional voltage extrema for designing neutral aqueous RFBs. Aqueous battery systems must strike a balance between maximizing voltage and avoiding these energy-wasting side reactions. When utilizing only the first redox couple of [(Me)(NPr)V]Cl<sub>3</sub> paired with FcNCl, the battery would have a theoretical energy density of 33.3 W hr/L at a 1.00 V cell voltage (see Experimental Procedures for the calculation of energy density). Utilizing only the second higher-voltage redox couple of [(Me)(NPr)V]Cl<sub>3</sub>, the battery would have a theoretical energy density of 46.2 Wh/L at 1.38 V. Operating the battery utilizing both redox couples would have a theoretical energy density of 79.5 Wh/L at an average cell voltage of 1.19 V, which represents the highest theoretical energy density known for AORFBs.

A flow cell was constructed using 0.25 M [(Me)(NPr)V]Cl<sub>3</sub> and 0.5 M FcNCl in 2.0 M NaCl supporting electrolyte, as shown in Figure 3A. When [(Me)(NPr)V]Cl<sub>3</sub> (and also  $[(NPr)_2V]Br_4$ ) was tested at 0.25 M, it had the same charge capacity as 0.5 M MV used in our recent study of the MV/FcNCl AORB (13.4 Ah/L, 7.1 Wh/L).<sup>15</sup> Taking advantage of both redox couples of [(Me)(NPr)V]Cl<sub>3</sub>, the cell was galvanostatically charged and discharged between 1.8 and 0.1 V. In this configuration, the cell had a capacity of 13.4 Ah/L and an energy density of 8.04 Wh/L. The rate performance of the battery was tested by operating at increasing current densities from





40 mA/cm<sup>2</sup> to 100 mA/cm<sup>2</sup> at increments of 20 mA/cm<sup>2</sup> (Figures 4A–4C). Because of the two distinctive redox processes of [(Me)(NPr)V]Cl<sub>3</sub>, each cycle consisted of two charge plateaus and two discharge plateaus (Figure 4B). For each current density, capacity remained nearly constant (Figure 4B). The observed capacity of the cell decreased with increasing current density as a result of increased ohmic loss within the cell. Compared with 40 mA/cm<sup>2</sup>, capacity retention was 96% at 60 mA/cm<sup>2</sup>, 90% at 80 mA/cm<sup>2</sup>, and 74% at 100 mA/cm<sup>2</sup> (Table S1). Similarly, the energy efficiency and the voltage efficiency decreased linearly with increasing current density from 75% at 40 mA/cm<sup>2</sup> to 45% at 100 mA/cm<sup>2</sup> (Figure 4C and Table S1). The Coulombic efficiency remained above 99% for all tests.

This [(Me)(NPr)V]Cl<sub>3</sub>/FcNCl system was further studied by operating the battery at 60 mA/cm<sup>2</sup> for extended 50 cycles (Figure 4D). The Coulombic efficiency remained above 99% throughout testing, and the energy efficiency stayed around 63%. The battery showed 99.82% capacity retention per cycle. The two charge plateaus occur near 1.2 and 1.6 V, whereas the two discharge plateaus occur near 1.2 and 0.7 V (Figure 4D, inset). At 50% state of charge, the cell managed 63 mW/cm<sup>2</sup> of peak power output (Figure 4E, blue trace). At 100% state of charge, the higher cell voltage achieved from [(Me)(NPr)V]Cl<sub>3</sub>'s second electron more than doubled the cell's power output up to 130 mW/cm<sup>2</sup> (Figure 4E, red trace), which represents the highest power density reported for neutral AORFBs.<sup>10,11,14–16</sup>

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Figure 4. Operational Data of the [(Me)(NPr)V]Cl<sub>3</sub>/FcNCl and [(NPr)<sub>2</sub>V]Br<sub>4</sub>/FcNCl AORFBs (0.25 and 0.50 M)

(A) Charge and discharge capacities of the [(Me)(NPr)V]Cl<sub>3</sub>/FcNCI AORFB operated at increasing current densities.

(B) Charge and discharge curves collected at current densities of 40 mA/cm<sup>2</sup> (red trace), 60 mA/cm<sup>2</sup> (yellow trace), 80 mA/cm<sup>2</sup> (green trace), and 100 mA/cm<sup>2</sup> (blue trace) for the [(Me)(NPr)V]Cl<sub>3</sub>/FcNCI AORFB.

(C) Plots of average Coulombic efficiency (CE), energy efficiency (EE), and voltage efficiency (VE) at varying operational current densities for the [(Me)(NPr)V]Cl<sub>3</sub>/FcNCl AORFB.

(D) Extended 50-cycle data of the [(Me)(NPr)V]Cl<sub>3</sub>/FcNCl AORFB show charge capacity, discharge capacity, and Coulombic efficiency versus cycle number at 60 mA/cm<sup>2</sup>. Inset: representative charge and discharge curve from the experiment.

(E) Polarization and power density data collected at 50% and 100% state of charge of the [(Me)(NPr)V]Cl<sub>3</sub>/FcNCl AORFB.

(F) Extended 100-cycle data of the [(NPr)<sub>2</sub>V]Br<sub>4</sub>/FcNCI AORFB show charge capacity, discharge capacity, and Coulombic efficiency versus cycle number at 60 mA/cm<sup>2</sup>.

(G) Polarization and power density data collected at 50% and 100% state of charge for the [(NPr)<sub>2</sub>V]Br<sub>4</sub>/FcNCI AORFB.

To understand how each redox process affects the battery performance, the [(Me)(NPr) V]Cl<sub>3</sub>/FcNCl cell was operated with restricted charge and discharge cutoff voltages (Figure S8 and Table S2). By limiting the voltage range of 0.1–1.35 V, the cell was tested using the lower-voltage redox couple of [(Me)(NPr)V]Cl<sub>3</sub> from 40 to 100 mA/cm<sup>2</sup>. At four current densities, this lower-voltage cell showed lower energy efficiency compared with the full two-electron system. For instance, just 56% energy efficiency was observed at 60 mA/cm<sup>2</sup>. With the cycling voltage between 0.85 V and 1.8 V, the cell was limited to use only [(Me)(NPr)V]Cl<sub>3</sub>'s higher-voltage redox couple. This configuration showed

higher energy efficiency, nearly 70% at a current density of 60 mA/cm<sup>2</sup>. The energy efficiency of the two-electron process is right about the average of the energy efficiency of two individual one-electron processes. These results indicated that the first electron process is a limiting step for the energy efficiency of the battery. It is believed that the viologen analyte after one-electron reduction becomes more conductive, thereby making the flow battery more energy efficient.

To explore the substituent effect of the 3-(trimethylammonio)propyl group on battery performance,  $[(NPr)_2V]Br_4$  was also studied with FcNCl in a flow battery under similar conditions. The battery would have a theoretical energy density of 28.5 Wh/L at a 0.95 V cell voltage for the first electron utilization of  $[(NPr)_2V]Br_4$  and have an energy density of 39.6 Wh/L at 1.32 V by using the second electron. Operating the battery utilizing both electrons would have a theoretical energy density of 68.1 Wh/L at an average cell voltage of 1.14 V. The cell voltages and theoretical energy densities of the  $[(NPr)_2V]Br_4/FcNCIAORFB$  using the first, second, and both electrons are slightly smaller than those of the [(Me)(NPr)V]Cl<sub>3</sub>/FcNCl AORFB. The [(NPr)<sub>2</sub>V]Br<sub>4</sub>/FcNCl AORFB using 0.25 M [(NPr)<sub>2</sub>V]Br<sub>4</sub> and 0.5 M FcNCl (13.4 Ah/L and 7.64 Wh/L) was tested from 40 to 100 mA/cm<sup>2</sup> (Figure S9) and also demonstrated two charge plateaus and two discharge plateaus (Figures S9B and 4D). As shown in Table S1 and Figure S9C, at each current density, the battery delivered >99% Coulombic efficiency but relatively lower capacity utilization, energy efficiency, and voltage efficiency than the [(Me)(NPr)V]Cl<sub>3</sub>/FcNCl AORFB. For instance, at 60 mA/cm<sup>2</sup>, the energy efficiency of the  $[(NPr)_2V]Br_4/FcNCI$  AORFB is 59% compared with 63% for the [(Me)(NPr)V]Cl<sub>3</sub>/FcNCl AORFB. It was found that 0.25 M [(NPr)<sub>2</sub>V]Br<sub>4</sub> (150.1 mS/cm) is less conductive than 0.25 M (Me)(NPr)V (159.8 mS/cm), making the [(NPr)<sub>2</sub>V]Br<sub>4</sub>/FcNCl AORFB less efficient than the [(Me)(NPr)V]Cl<sub>3</sub>/FcNCl AORFB. However, the [(NPr)<sub>2</sub>V]Br<sub>4</sub>/FcNCl AORFB delivered improved cycling stability. Specifically, for 100 extended cycles at 60 mA/cm<sup>2</sup>, the battery showed 99.99% capacity retention per cycle (Figure 4F). The [(NPr)<sub>2</sub>V]Br<sub>4</sub>/FcNCl AORFB exhibited a peak power density of 92 mW/cm<sup>2</sup> at 100% state of charge (Figure 4G). Similar to the [(Me)(NPr)V]Cl<sub>3</sub>/FcNCl AORFB, the [(NPr)<sub>2</sub>V]Br<sub>4</sub>/FcNCl AORFB exhibited a higher energy efficiency for its second electron (69% at 60 mA/cm<sup>2</sup>) than for its first electron (56% at 60 mA/cm<sup>2</sup>) (Figures S9F and S9I and Table S3).

The data presented above clearly indicate that the structural modification of the twoelectron storage viologen molecules affects their physical and chemical properties and battery performance (Table 1 and Table S1). Regarding the improved cycling stability of the [(NPr)<sub>2</sub>V]Br<sub>4</sub>/FcNCl AORFB, it is believed that two (trimethylammonio)propyl groups of [(NPr)<sub>2</sub>V]Br<sub>4</sub> can provide a better stabilization effect for its reduced states than just one for [(Me)(NPr)V]Cl<sub>3</sub> in the case of the bimolecular degradation.<sup>36</sup> The demonstrated [(NPr)<sub>2</sub>V]Br<sub>4</sub>/FcNCl AORFB (7.76 Wh/L) delivered cycling stability comparable with that of the previous MV/FcNCl AORFB (7.1 Wh/L) but significantly improved power density of 93 mW/cm<sup>2</sup> versus 67 mW/cm<sup>2</sup> for the MV/FcNCI AORFB (see Figure S15), which benefits from the higher operational cell voltage of [(NPr)<sub>2</sub>V] Br₄/FcNCI AORFB (1.32 V) compared with that of the MV/FcNCI AORFB (1.06 V). In addition, the effect of the bromide counter ion was tested by preparing  $[(NPr)_2V]Cl_4$ via anion exchange. A flow cell was assembled with 0.25 M [(NPr)<sub>2</sub>V]Cl<sub>4</sub> and 0.5 M FcNCl and tested identically to the [(NPr)<sub>2</sub>V]Br<sub>4</sub> system (Figure S10). As shown in Table S4, the choice of chloride or bromide anion had little effect on energy efficiency and capacity utilization. It is expected that structural modification of the hydrophilic substituent and battery engineering<sup>27</sup> will further improve the battery performance of the two-electron storage viologen molecules and lead to new battery chemistry, which warrants further studies of these two-electron storage viologen molecules.

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#### Figure 5. Operational Data of the [(NPr)<sub>2</sub>V]Cl<sub>4</sub>/N<sup>Me</sup>-TEMPO AORFB (0.05 and 0.1 M)

(A) Cyclic voltammograms of 4.0 mM [(NPr)<sub>2</sub>V]Cl<sub>4</sub> (-0.35 and -0.72 V) and 4 mM N<sup>Me</sup>-TEMPO (1.0 V) in 0.5 M NaCl aqueous electrolyte (solid curves). The dashed curve is a cyclic voltammogram of only the 0.5 M NaCl electrolyte, and labels are given for the onset potentials for the hydrogen evolution reaction (-1.00 V) and oxygen evolution reaction (1.50 V).

(B) Battery reactions of the  $[(NPr)_2V]Cl_4/N^{Me}$ -TEMPO AORFB.

(C) Extended 50-cycle data of the  $[(NPr)_2V]CI_4/N^{Me}$ -TEMPO AORFB show discharge capacity and Coulombic efficiency versus cycle number at 60 mA/cm<sup>2</sup>. Inset: representative charge and discharge curves from the experiment.

The two-electron storage viologen molecules with their highly negative redox potentials, when paired with a TEMPO catholyte, <sup>10,14</sup> can deliver a cell voltage greater than 1.5 V. To demonstrate the proof of concept of the high-voltage total-organic TEMPO and viologen RFBs, 4-trimethylammoinium-TEMPO (abbreviated as N<sup>Me</sup>-TEMPO; see Scheme S2 and Figure S6),<sup>10,14</sup> which exhibits reversible oxidation at 1.0V versus NHE (Figure 5A), was selected as catholyte. To avoid the oxidation overlap of  $N^{Me}\mbox{-}TEMPO$  and  $Br^-\mbox{(}1.05\,V$ versus NHE), [(NPr)<sub>2</sub>V]Cl<sub>4</sub> instead of [(NPr)<sub>2</sub>V]Br<sub>4</sub> was used as anolyte. The [(NPr)<sub>2</sub>V]Cl<sub>4</sub>/ N<sup>Me</sup>-TEMPO AORFB features an ultrahigh cell voltage, 1.35 V for the first reduction of [(NPr)<sub>2</sub>V]Cl<sub>4</sub> and 1.72 V for the second reduction of [(NPr)<sub>2</sub>V]Cl<sub>4</sub>. 1.72 V is the highest cell voltage known for AORFBs to date. The battery reactions of the [(NPr)<sub>2</sub>V]Cl<sub>4</sub>/N<sup>Me</sup>-TEMPO AORFB are given in Figure 5B. We conducted a preliminary study of the flow battery using 0.05 M [(NPr)<sub>2</sub>V]Cl<sub>4</sub> in 2.0 M NaCl and 0.1 M N<sup>Me</sup>-TEMPO in 2.0 M NaCl at 60 mA/cm<sup>2</sup>. The flow battery delivered 60% energy efficiency, nearly 100% Coulombic efficiency, and 99.96% capacity efficiency per cycle (Figure 5C). Compared with the capacity retention of the 0.5 M [(NPr)<sub>2</sub>V]Cl<sub>4</sub>/FcNCl AORFB (99.99% per cycle), it can be inferred that N<sup>Me</sup>-TEMPO as a catholyte is not stable as FcNCI. The preliminary results indicate that more studies are needed to improve the electrochemical performance of the TEMPO catholyte.

## DFT Modeling of Two-Electron Storage Molecules $[(Me)(NPr)V]Cl_3$ and $[(NPr)_2V]Br_4$

It is fundamentally important to understand structural evolution during the redox process for these charge storage molecules to gain an in-depth understanding of





Figure 6. DFT-Optimized Structure (Top and Side Views), Frontier HOMO/SOMO and LUMO Orbitals, and Assigned Primary Resonance Structure of [(Me)(NPr)V]<sup>3+</sup> (Left), [(Me)(NPr)V]<sup>2+</sup>(Middle), and [(Me)(NPr)V]<sup>+</sup> (Right)

Selected bonding distances (Å) for **[(Me)(NPr)V]**<sup>3+</sup>: N1–C1, 1.347; N1–C5, 1.347; C1–C2, 1.380; C2–C3, 1.398; C3–C4, 1.398; C4–C5, 1.380; C3–C8, 1.483; N2–C6, 1.347; N2–C10, 1.346; C6–C7, 1.380; C7–C8, 1.397; C8–C9, 1.398; C9–C10, 1.381. Selected bonding distances for **[(Me)(NPr)V]**<sup>2+</sup>: N1–C1, 1.366; N1–C5, 1.366; C1–C2, 1.365; C2–C3, 1.432; C3–C4, 1.432; C4–C5, 1.364; C3–C8, 1.426; N2–C6, 1.363; N2–C10, 1.365; C6–C7, 1.366; C7–C8, 1.430; C8–C9, 1.431; C9–C10, 1.364. Selected bonding distances for **[(Me)(NPr)V]**<sup>+</sup>: N1–C1, 1.393; N1–C5, 1.393; C1–C2, 1.350; C2–C3, 1.465; C3–C4, 1.465; C3–C4, 1.465; C3–C4, 1.455; C4–C5, 1.350; C3–C8, 1.375; N2–C6, 1.385; N2–C10, 1.385; C6–C7, 1.352; C7–C8, 1.464; C8–C9, 1.464; C9–C10, 1.352.

their chemical properties. To this end, we conducted DFT calculations (using M06-2x functional, 6-31+G(d) basis sets and the SMD solvation model) to define the chemical and electronic structures of  $[(Me)(NPr)V]CI_3$ . Shown in Figure 6 are the optimized ground states (top view and side views), frontier orbitals, and assigned primary resonance structures of three redox states,  $[(Me)(NPr)V]^{3+}$  (Figure 6, left),  $[(Me)(NPr)V]^{2+}$  (Figure 6, middle), and  $[(Me)(NPr)V]^{+}$  (Figure 6, right).  $[(Me)(NPr)V]^{3+}$  has two pyridinium rings that have almost identical bond distances (Figure 6, caption), indicating that *N*-(trimethylammonio)propyl and *N*-methyl groups have a similar effect on the structure of the pyridinium ring. The C3–C8 bond between the two pyridinium rings is 1.483 Å, assigned as a C–C single

bond. It is also noted that two pyridinium rings of [(Me)(NPr)V]<sup>3+</sup> have a dihedral angle of 37.27° (<C4–C3–C8–C9). Both HOMO (highest occupied molecular orbital) and LUMO (lowest occupied molecular orbital) of [(Me)(NPr)V]<sup>3+</sup> are symmetrically spread throughout the two pyridinium rings. The one-electron reduced species, [(Me)(NPr)V]<sup>2+</sup> (Figure 6, middle), exhibits a C3–C8 bond between two pyridine or pyridinium rings of 1.426 Å, ca. 0.05 Å shorter than that of [(Me)(NPr)V]<sup>3+</sup>. By inspecting the SOMO (singly occupied molecular orbital) of [(Me)(NPr)V]<sup>2+</sup> (Figure 6, middle), the shorter C3-C8 bond is attributed to the Pi-bonding interaction between C3 and C8 atoms. In addition, it can be seen that the unpaired electron is highly delocalized within two pyridine or pyridinium rings. Consistent with the two-ring delocalization and the Pi-bonding interaction, two pyridine or pyridinium rings are coplanar with a very small dihedral angle of 0.96°, a striking structural change from [(Me)(NPr)V]<sup>3+</sup>. Two major resonance structures of [(Me)(NPr)V]<sup>2+</sup> are shown in Figure 6 (the top row in the middle). Because of the increased Pi interaction between C3 and C8 atoms, the two-electron reduced species, [(Me)(NPr)V]<sup>+</sup>, has an even shorter C-C bond, 1.38 Å, between two rings, which is assigned as a C=C double bond in its resonance structure (Figure 6, right). Its HOMO also confirmed high charge delocalization within its two co-planar rings and an even smaller dihedral angle of 0.74°. Importantly, according to the molecular orbital theory, the charge delocalization is essential to stabilize the energetic [(Me)(NPr)V]<sup>2+</sup> and [(Me)(NPr)V]<sup>+</sup> states, and echoes the observed electrochemical reversibility and stable battery performance of the  $[(Me)(NPr)V]^{3+/2+}$  and  $[(Me)(NPr)V]^{2+/+}$  redox couples. Consistently, similar chemical and electronic structure features were observed in the three redox states of [(NPr)<sub>2</sub>V]Br<sub>4</sub> (Figure S16).

In summary, functionalization of 4,4'-bipyridine with hydrophilic substituents offers opportunities to develop two-electron storage viologen compounds with low reduction potentials and high charge capacity for AORFBs that are among the most energy-dense organic anolyte materials having been reported. Synthesis of these viologen compounds is convenient from the bis-alkylation of 4,4'-bypyridine with commercially available alkylation reagents. Paired with a selected watersoluble ferrocene catholyte, both [(Me)(NPr)V]Cl<sub>3</sub> and [(NPr)<sub>2</sub>V]Br<sub>4</sub> demonstrated viable AORFB performance. It is also promising to apply these two-electron storage molecules to develop ultrahigh-voltage TEMPO and viologen AORFBs (>1.7 V). At the fundamental level, DFT calculations offered insightful information on the chemical and electronic structures of three redox states of these two-electron storage molecules. The synthetic and computational chemistry presented has opened a new avenue of viologen derivatization for building neutral AORFBs with high voltage, high power density, and high energy density, which promises economical and widespread uses of RFBs in large-scale energy storage. The presented research highlights the art of molecular engineering as a powerful tool for developing energy-dense redox-active electrolyte materials for RFBs.

### **EXPERIMENTAL PROCEDURES**

#### **Chemicals and Instrumentation**

All chemicals were purchased from either TCI Chemicals or Sigma-Aldrich, stored in an argon glovebox, and used as received. FcNCI was prepared as before.<sup>15</sup> All experiments were conducted under a N<sub>2</sub> or Ar atmosphere. Elemental analysis was performed by Atlantic Microlab. <sup>1</sup>H NMR data were collected with either a Bruker 500 MHz or Joel 300 MHz spectrometer. Battery performance data were collected with a Land battery testing system. Electrochemical measurements were conducted using a Gamry 5000E potentiostat.

#### Synthesis of 4-Pyridine-1'-methyl-4'-pyrdinium lodide, (MeBpy)I

In a 1 L N<sub>2</sub> purged Schlenk flask, 4,4'-bipyridine (30 g, 192 mmol) was combined with methyl iodide (26.8 g, 188.7 mmol) in 480 mL of acetone and stirred at room temperature for 24 hr. The resulting yellow precipitate was filtered and stored in a dry desiccator.

Yield: 88%; <sup>1</sup>H NMR (500 MHz,  $D_2O$ ):  $\delta$  (ppm) 8.82 (d,  $J_{H-H} = 6.4$  Hz, 2H), 8.70 (d,  $J_{H-H} = 4.9$  Hz, 2H), 8.31 (d,  $J_{H-H} = 6.3$  Hz, 2H), 7.83 (d,  $J_{H-H} = 4.9$  Hz, 2H), 4.36 (s, 3H); elemental analysis for  $C_{11}H_{11}IN_2$ : calculated C 44.32, H 3.72, N 9.40; found C 44.07, H 3.61, N 9.34.

### Synthesis of 1-Methyl-1'-[3-(trimethylammonio)propyl]-4,4'-bipyridinium Trichloride, [(Me)(NPr)V]Cl\_3

In a 1 L N<sub>2</sub> purged Schlenk flask, (MeBpy)I (50 g, 168 mmol) was combined with (3-bromopropyl)trimethylammonium bromide (48.2 g, 184 mmol) in 600 mL of DMF and heated to 95°C for 24 hr. The resulting orange precipitate was filtered and washed with 200 mL of diethyl ether before being dried at 60°C in a vacuum oven. The mixed bromide and iodide counter ions were exchanged for chloride by column anion exchange.

Yield: 88% (overall yield for [(Me)(NPr)V]Cl<sub>3</sub> was 78%); <sup>1</sup>H NMR (500 MHz, D<sub>2</sub>O):  $\delta$  (ppm) 9.11 (d, J<sub>H-H</sub> = 6.6 Hz, 2H), 8.99 (d, J<sub>H-H</sub> = 6.5 Hz, 2H), 8.53 (d, J<sub>H-H</sub> = 6.5 Hz, 2H), 8.46 (d, J<sub>H-H</sub> = 6.4 Hz, 2H), 4.78 (t, J<sub>H-H</sub> = 7.8 Hz, 2H), 4.43 (s, 3H), 3.54–3.48 (m, 2H), 3.12 (s, 9H), 2.61 (m, 2H); elemental analysis for C<sub>17</sub>H<sub>26</sub>Cl<sub>3</sub>N<sub>3</sub>·2H<sub>2</sub>O: calculated C 49.22, H 7.29, N 10.13; found C 49.49, H 7.24, N 9.95.

## Synthesis of 1,1'-Bis[3-(trimethylamonium)propyl]-4,4'-bipyridinium Tetrabromide, [(NPr)<sub>2</sub>V]Br<sub>4</sub>

According to the 1981 review article,<sup>36</sup> the target compound, the  $[(NPr)_2V]^{4+}$  halide, was studied for herbicidal activity by ICI's Jealott's Hill Laboratories (Plant Protection), and no information was disclosed publically. The review only quoted the data for its first reduction with the permission of the company. Here, we report a simple and high-yield synthesis of  $[(NPr)_2V]Br_4$ . In a 250 mL N<sub>2</sub> purged Schlenk flask, 4,4'-bipyridine (2.0 g, 12.8 mmol) was combined with (3-bromopropyl)trimethylammonium bromide (10 g, 38.3 mmol) in 15 mL of DMSO and stirred at 100°C for 3 hr. The resulting light-yellow precipitate was filtered and washed with 10 mL of cold DMSO and 3 × 20 mL acetonitrile and then dried under vacuum.

Yield: 68%; <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O):  $\delta$  9.12 (d, J<sub>H-H</sub> = 7.0 Hz, 4H), 8.54 (d, J<sub>H-H</sub> = 6.9 Hz, 4H), 4.87 (t, J<sub>H-H</sub> = 7.7 Hz, 4H), 3.57–3.45 (m, 4H), 3.11 (s, 18H), 2.67–2.54 (m, 4H); elemental analysis for C<sub>22</sub>H<sub>38</sub>Br<sub>4</sub>N<sub>4</sub>·H<sub>2</sub>O: calculated C 37.95, H 5.79, N 8.05; found C 37.21, H 5.93, N 7.72.

## Synthesis of 1,1'-Bis[3-(trimethylamonium)propyl]-4,4'-bipyridinium Tetrachloride, [(NPr)\_2V]Cl\_4

The bromide ions of  $[(NPr)_2V]Br_4$  were exchanged for chloride by an anion-exchange column with an Amberlite IRA-900 chloride-form anion-exchange resin to give  $[(NPr)_2V]Cl_4$ .

Yield: 100%;  $[(NPr)_2V]Cl_4$  displayed identical <sup>1</sup>H NMR resonances as  $[(NPr)_2V]Br_4$ ; elemental analysis for C<sub>22</sub>H<sub>38</sub>Cl<sub>4</sub>N<sub>4</sub>·2H<sub>2</sub>O: calculated C 49.26, H 7.89, N 10.45; found C 49.49, H 7.77, N 10.10.

### Synthesis of 4'-Pyridine-1-[3-sulfonatopropyl]-4-pyrdinium (SPy)

In a 250 mL N<sub>2</sub> purged Schlenk flask, 4,4'-bipyridine (2.5 g, 16 mmol) was combined with propane sultone (1.96 g, 16 mmol) in 25 mL of acetonitrile and refluxed at 80°C for 24 hr. The resulting white precipitate was filtered and dried under vacuum.

Yield: 90%; <sup>1</sup>H NMR (300 MHz,  $D_2O$ ):  $\delta$  (ppm) 8.88 (d,  $J_{H-H} = 5.2$  Hz, 2H), 8.65 (d,  $J_{H-H} = 4.5$  Hz, 2H), 8.30 (d,  $J_{H-H} = 5.1$  Hz, 2H), 7.79 (d,  $J_{H-H} = 4.6$  Hz, 2H), 4.72 (t,  $J_{H-H} = 8.8$  Hz, 2H), 2.90 (t,  $J_{H-H} = 6.2$  Hz, 2H), 2.44–2.33 (m, 2H); elemental analysis for  $C_{13}H_{14}N_2O_3S$ : calculated C 56.1, H 5.07, N 10.07; found C 55.49, H 5.16, N 9.84.

### Synthesis of 1-[3-(Trimethylammonio)propyl]-1'-(3-sulfonatopropyl)-4,4'bipyridinium Dibromide, [(NPr)(SPr)V]Br<sub>2</sub>

In a 250 mL N<sub>2</sub> purged Schlenk flask, SPy (1.2 g, 4.3 mmol) was combined with (3-bromopropyl)trimethylammonium bromide (1.1g, 4.3 mmol) in 50 mL of CH<sub>3</sub>CN and refluxed at 80°C for 7 days. The resulting yellow precipitate was filtered and washed with 10 mL of MeOH.

Yield: 95%; <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O):  $\delta$  (ppm) 9.12–9.01 (m, 4H), 8.48 (t,  $J_{H-H}$  = 7.1 Hz, 4H), 4.83–4.70 (m, 4H), 3.52–3.41 (m, 2H), 3.08 (s, 9H), 2.92 (t,  $J_{H-H}$  = 7.1 Hz, 2H), 2.65–2.49 (m, 2H), 2.49–2.34 (m, 2H); elemental analysis of C<sub>19</sub>H<sub>29</sub>Br<sub>2</sub>N<sub>3</sub>O<sub>3</sub>S·H<sub>2</sub>O: calculated C 40.95, H 5.61, N 7.54; found C 40.58, H 5.41, N 7.25.

## Synthesis of *N*,*N*,*N*,2,2,6,6-Heptamethylpiperidinyloxy-4-ammonium Chloride (N<sup>Me</sup>-TEMPO)

2,2,6,6-Tetramethyloxy-4-aminopiperidine (1.71 g, 10 mmol) and methyl iodide (8.52 g, 60 mmol) were dissolved in 20 mL of acetone. The solution was stirred at room temperature overnight. The generated orange precipitate was filtered and washed with 5.0 mL of acetone three times. After drying, the orange powder was dissolved in 10.0 mL of deionized water and flushed through an anion exchange column with an Amberlite IRA-900 chloride form anion exchange resin. Cyclic voltammetry was applied to validate the replacement of iodide. After removing water under a vacuum, the product was obtained as orange powder.

Yield: 36%; <sup>1</sup>H NMR (500 MHz, D<sub>2</sub>O with one drop of phenylhydrazine):  $\delta$  (ppm) 3.53 (t,  $J_{H-H}$  = 12.6 Hz, 1H), 2.89 (s, 9H), 2.01 (d,  $J_{H-H}$  = 11.9 Hz, 2H), 1.59 (t,  $J_{H-H}$  = 12.2 Hz, 2H), 1.15 (s, 6H), 1.09 (s, 6H); elemental analysis of C<sub>12</sub>H<sub>20</sub>N<sub>2</sub>OCI: calculated C 55.72, H 10.42, N 11.22; found C 55.63, H 10.51, N 11.14.

#### **Cyclic Voltammetry Studies**

All experiments were conducted in an N<sub>2</sub> purged, 0.5 M NaCl aqueous solution and performed with a Gamry 5000E potentiostat. A 1 mm polyetheretherketone-encased glassy carbon disk was used as the working electrode. The working electrode was polished with 0.05  $\mu$ m Al<sub>2</sub>O<sub>3</sub> powder and rinsed with deionized H<sub>2</sub>O. A glassy carbon rod was used as the counter electrode. A silver wire coated with AgCl and suspended in 3.0 M KCl electrolyte was used as the reference electrode.

#### **Electrochemical RDE Studies**

LSV experiments were conducted with a Gamry 5000E potentiostat with a threeelectrode system. A 5-mm-diameter rotating glassy carbon disk encased in Teflon served as the working electrode. A glassy carbon rod was used as the counter electrode. An Ag/AgCl electrode served as the reference electrode. The working electrode was cleaned by the same method as in the cyclic voltammetry experiments.

During the experiments, the working electrode rotated from 300 rpm to 2,400 rpm at increments of 300 rpm. Three scans at each rotation rate were collected to ensure accuracy. For  $[(Me)(NPr)V]Cl_3$ , LSV scans were conducted at a rate of 5 mV/s from 0.1 to -1.2 V versus NHE. The limiting currents (mass transport-limited current intensity) at each rotation rate were recorded at -0.58 and -0.95 V versus NHE. To calculate the limiting current for the second reduction, the current from the first reduction must be subtracted. The Levich plots of limiting current versus the square root of the rotation rate showed linear relationships for both reductions. The slopes of these fitted lines are defined by the Levich equation,

Levich plot slope = 
$$0.620nFAC_0D^{2/3}\nu^{-1/6}$$
, (Equation 1)

where n = 1 for a single electron process, Faraday's constant F = 96,485 C/mol, electrode area A = 0.1963 cm<sup>2</sup>, [(Me)(NPr)V]Cl<sub>3</sub> concentration  $C_0 = 1 \times 10^{-6}$  mol/cm<sup>3</sup>, D represents the diffusion coefficient, and the kinematic viscosity of 0.5 M NaCl aqueous solution  $\nu = 0.009$  cm<sup>2</sup>/s.

For  $[(NPr)_2V]Br_4$  and  $[(NPr)(SPr)V]Br_2$ , LSV scans were collected and analyzed by the same techniques described for  $[(Me) (NPr)V]Cl_3$ .

#### Nicholson's Method for Estimating Electron-Transfer Rate Constants

According to the well-known Nicholson's method,<sup>38</sup> the peak( $E_{pc}$ ) – peak ( $E_{pa}$ ) separation,  $\Delta E_p$ , was used to obtain the kinetic parameter,  $\Psi$ , and then Equation 2 was applied to calculate  $k^0$ . Both reductions of [(Me)(NPr)V]Cl<sub>3</sub> displayed a nearly constant  $\Delta E_p$  around 58 mV from 20 to 500 mV/s, confirming fast and reversible Nernst reduction processes (Figure S13). For Nicholson's method,  $\Delta E_p$  has a limit value of 61 mV, corresponding to  $\Psi$  as 20. Thus, a lower limit of  $k^0$  for the two reductions of [(Me)(NPr)V]Cl<sub>3</sub> were estimated with  $\Psi = 20$ , scan rate at 500 mV/s, and corresponding diffusion constants.  $k^0$  of the first reduction was greater than 0.364 cm/s, and  $k^0$  of the second reduction was greater than 0.360 cm/s. Both reductions of [(NPr)<sub>2</sub>V]Br<sub>4</sub> displayed a nearly constant  $\Delta E_p$  around 58 mV from 20 to 500 mV/s.  $k^0$  of the first reduction was greater than 0.309 cm/s, and  $k^0$  of the second reduction was greater than 0.309 cm/s, and  $k^0$  of the first reduction was greater than 0.309 cm/s.  $k^0$  of the first reduction was greater than 0.305 cm/s. Both reductions was greater than 0.350 cm/s.  $k^0$  of the first reduction was greater than 0.350 cm/s.  $k^0$  of the first reduction was greater than 0.350 cm/s.  $k^0$  of the first reduction was greater than 0.350 cm/s.  $k^0$  of the first reduction was greater than 0.350 cm/s.  $k^0$  of the first reduction was greater than 0.350 cm/s.  $k^0$  of the first reduction was greater than 0.350 cm/s.  $k^0$  of the first reduction was greater than 0.350 cm/s.

 $k^{0} = \Psi[\pi DnvF/RT]^{1/2},$ 

(Equation 2)

where F, D, and n are defined in Equation 1, and v represents the scan rate.

### **Flow Cell Tests**

The flow cell was constructed from two graphite chambers, each housing a graphite felt electrode (SGL Carbon Group, Germany). Sandwiched between the chambers was a sheet of anion exchange membrane (AME 115, 120  $\mu$ m thickness, pore size <10 Å; Selemion, Japan). The cell had an active area of 10 cm<sup>2</sup> that was determined by the membrane size. On the exterior of each graphite chamber was a copper current collector. A Masterflex L/S peristaltic pump (Cole-Parmer, USA) circulated the electrolyte solutions through the cell and reservoirs at 60 mL/min. Each reservoir contained 12 mL of 2.0 M NaCl aqueous solution. The anode reservoir contained 0.25 M [(Me)(NPr)V]Cl<sub>3</sub>, and the cathode reservoir contained 0.5 M FcNCl. The reservoirs were purged with N<sub>2</sub> to displace any O<sub>2</sub> in the system, then sealed. The flow cell was galvanostatically charged and discharged at 25°C on

a battery tester (Land Instruments). When utilizing both redox events from  $[(Me)(NPr)V]Cl_3$ , the cell operated between 1.8 and 0.1 V. When isolating only the first redox couple from  $[(Me)(NPr)V]Cl_3$ , the cell was operated between 1.35 and 0.1 V. To isolate only the second redox couple of  $[(Me)(NPr)V]Cl_3$ , the battery was first charged from 0 to 1.8 V and then cycled between 1.8 and 0.85 V. The flow cell operated at current densities from 40 to 100 mA/cm<sup>2</sup>. The extended cycling experiment was conducted at 60 mA/cm<sup>2</sup>. The  $[(NPr)_2V]Br_4/FcNCl$  and  $[(NPr)_2V]Cl_4$  in the anode solution, and all other assembly and testing characteristics were identical to those of the  $[(Me)(NPr)V]Cl_3/FcNCl$  system.

#### **Calculation of Theoretical Energy Density**

The theoretical energy density of the [(Me)(NPr)V]Cl<sub>3</sub>V/FcNCl AORFB was calculated with Equation 3, where *n* is the number of electrons involved in the cell reaction, *C* is the concentration of active materials, *F* is Faraday's constant of 26.8 Ah/mol, *V* is the cell voltage, and  $\mu_v$  is the factor that represents the overall volumes of anolyte and catholyte:

energy density (Wh/L) = 
$$nCFV/\mu_v$$
 (Equation 3)

 $\mu_v$  = 1 + (max solubility; less soluble electrolyte)/(max solubility; more soluble electrolyte)

For the [(Me)(NPr)V]Cl<sub>3</sub>/FcNCl AORFB,  $\mu_v = 1 + [(Me) (NPr)V]/[FcNCl] = 1 + 1.8/4.0 = 1.45. So, utilizing only the first redox couple of [(Me)(NPr)V]Cl<sub>3</sub>, the energy density = (1 × 1.8 × 26.8 × 1.00)/1.45 = 33.3 Wh/L. Utilizing only the second redox couple of [(Me)(NPr)V]Cl<sub>3</sub>, the energy density = (1 × 1.8 × 26.8 × 1.38)/1.45 = 46.2 Wh/L. To calculate the energy density of the two-electron AORFB, we averaged the operational voltages for the two electron transfers and then calculated the energy density as a two-electron system: energy density = (2 × 1.8 × 26.8 × 1.195)/ 1.45 = 79.5 Wh/L. The sum of the two energy densities for the individual redox is equal to the energy density of the full two-electron system. A similar analysis for the [(NPr)<sub>2</sub>V]Br<sub>4</sub>/FcNCl AORFB gives energy densities of 28.5 Wh/L with the first redox couple, 39.6 Wh/L with the second redox couple, and 68.1 Wh/L with both redox couples of [(NPr)<sub>2</sub>V]Br<sub>4</sub>.$ 

#### **Computational Methods**

Calculations for the structures of viologen compounds were performed with the Gaussian 09 package. All compounds were modeled as isolated molecules at 298 K. For all candidates, the ground-state structure was optimized for the initial oxidation state, one-electron reduced oxidation state, and two-electron reduced oxidation state. Basis sets consisted of 6-31+G(d), and the electron correlation method was calculated with M06-2x: Minnesota '06 2x global hybrid functional with 54% Hartree-Fock exchange. All geometries were optimized in water as the implicit solvent. To model the implicit solvent, the universal solvation model SMD was used, which is based on the quantum mechanical charge density of a solute molecule interacting with a continuum description of the solvent. Energy minimum of each optimized structure was confirmed by frequency calculations.

### SUPPLEMENTAL INFORMATION

Supplemental Information includes 22 figures, 4 tables, and 2 schemes and can be found with this article online at https://doi.org/10.1016/j.chempr.2017.11.001.

### **AUTHOR CONTRIBUTIONS**

T.L.L. designed the project. C.D. and B.H. synthesized the compounds. C.D. and B.H. collected the experimental data and made equal contributions. J.M. performed the computational work. C.D., B.H., J.M., and T.L.L. analyzed experimental and computational data. J.L., X.L., and Y.S. helped with the synthesis of (Me)(NPr)V and (NPr)<sub>2</sub>V. T.L.L., C.D., B.H., and J.L. wrote the paper, and all authors contributed to revising the paper.

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