Supporting Information

Thienoviologen Anolytes for Aqueous Organic Redox Flow Batteries with Simultaneously Enhanced Capacity Utilization and Capacity Retention

Xu Liu⁺,^[a] Xuri Zhang⁺,^[a] Guoping Li,^[a] Sikun Zhang,^[a] Bingjie Zhang,^[a] Wenqiang Ma,^[a] Zengrong Wang,^[a] Yueyan Zhang,^[a] and Gang He^{*[a]}

Abstract: A series of thienoviologen derivatives (**[(NPr)**₂**TV]CI**₄, **[(OHPr)**₂**TV]CI**₂) with narrow bandgap high solubility and two-electron transfer properties as anolyte for high performance aqueous organic redox flow batteries (AORFBs) is reported. Compared with **[(OHPr)**₂**TV]CI**₂ and other viologen anolytes, **[(NPr)**₂**TV]CI**₄ showed higher diffusion coefficient (*D*, $3.36 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) and the electron transfer constant (*k*₀, 0.31 cm s⁻¹). Paired with (ferrocenylmethyl)-trimethylammonium chloride (**FcNCI**) as catholyte, the specific capacity of **[(NPr)**₂**TV]CI**₄/**FcNCI** AORFB reached 4.62 Ah L⁻¹, and the capacity utilization was up to 86.1%. Moreover, the system also maintained high stability in 300 cycles and delivered 87.9% capacity retention and 99.96% capacity retention per cycle. The simultaneously enhanced capacity retention and capacity utilization of **[(NPr)**₂**TV]CI**₄-based AORFBs were attributed to the high *D* and *k*₀, resulting from the smaller molecular volume (583.38 Å³) and appropriate dihedral angle (~18.37°) between the pyridines.

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Experimental procedures

1. Chemicals and Manipulations

All reactions were performed using standard Schlenk and glovebox (Vigor) techniques under argon atmosphere. All chemicals were purchased from Energy Chemical Inc, stored in an Argon glovebox. Toluene was distilled from sodium/benzophenone prior to use, and other chemicals were used as commercially available without further purification. Deionized water was purged overnight using Ar before use. NMR spectra spectrum were collected using a Bruker 400 MHz NMR spectrometer. UV-Vis measurements were performed using a DH-2000-BAL Scan spectrophotometer. The cyclic voltammetry (CV) in solution was measured using CHI660E B157216. The Linear sweep voltammetry (LSV) was measured on a rotating disk electrode (RDE) device (Pine Instruments Co., USA, 0.1963 cm²). Electrochemical Impedance analysis (EIS) was performed using an Autolab electrochemical workstation (AUT86797-302N, Metrohm instruments, Switzerland). High-resolution mass spectra (HRMS) were collected on a Bruker maxis UHR-TOF mass spectrometer in an ESI positive mode. All battery tests were conducted under an Ar atmosphere. The flow battery was galvanostatically charged/discharged at RT on a battery tester (NEWARE instrument, CT-4008T-5V12A-S1-F). The membrane was AMV anion-exchange membrane with film thickness (130 µm), tensile strength (0.16 MPa), and transfer number (>0.96 for Cl⁻ and Na⁺). X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Fisher ESCALAB Xi+. The scanning electron microscope (SEM) was using Quanta 250 FEG (X-Max 20, Q150R S) for testing. EPR was measured using a Bruker EMX PLUS6/1 instrument at room temperature in dry degassed methanol. All photographs were taken using a Nikon D5100 digital camera.

To simulate the experimental UV-Vis in water, the Polarizable Continuum Model (PCM) as a self-consistent reaction field (SCRF) was used for the calculation of equilibrium geometries, vibrational frequencies and excited state calculations. The geometries for the ground state of these compounds were optimized at the B3LYP hybrid functional and 6-311+G(d) basis set for all atoms.¹ The calculated maximum absorption wavelength (λ TD-DFT), oscillator strength (f), molecular orbitals (MOs) involved in the main transitions were reported in this work. It should be pointed out that the structures of all stationary points were fully optimized, and frequency calculations were performed at the same level. The frequency calculations confirmed the nature of all revealed equilibrium geometries: there were no imaginary frequencies. The simulated UV–Vis spectra for optimized molecules were performed at the time dependent density functional theory (TD-DFT/B3LYP) at the ground-state equilibrium geometries in water solution, in association with the 6-311+G(d) basis set. All of the above computational calculations reported in this work were performed using the Gaussian 09 code.^{2, 3} The dihedral angle for optimized molecules was measured by Mercury 3.6. The volume was estimated using Marching Tetrahedron (MT) mothed, based on the vdW surface defined by p=0.001 au isosurface, using the Multiwfn code.⁴

2. Synthetic procedures

The synthesis of thienoviologen derivatives



Synthesis of 2,5-di(pyridin-4-yl)thiophene – TDP.

The synthesis of **TDP** was consistent with those previously reported in the literature.⁵ To a mixture of 2,5-2,5-dibromothiophene (2.00 g, 8.27 mmol), 4-Pyridineboronic acid pinacol ester (4.24 g, 20.66 mmol), Pd(PPh₃)₄ (0.52 g, 0.42 mmol), 10 drops of Methyltrioctyl ammonium chloride, 80 mL K₂CO₃ (2 M) and 120 mL toluene were added. The solution was sealed in a pressure vial with a Teflon bushing and heated at 120 °C for 3 days. Upon completion, the reaction mixture was cooled to room temperature. The organic phase was concentrated under vacuum and the residue dissolved in CHCl₃ and washed three times with H₂O. And then concentrated HCl was added to the organic phase, resulting in precipitation of the product from the solution. The precipitate dissolved in H₂O. Finally, aqueous NaOH was added slowly dropwise to the H₂O layer until the pH was ca. 8~9, resulting in the precipitation of pure **2,5-di(pyridine-4-yl)thiophene.** A yellow solid. Yield: 1.42 g (72%). ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.61 (dd, J = 4.6, 1.6 Hz, 2H), 7.92 (s, 1H), 7.70 (dd, J = 4.6, 1.6 Hz, 2H). ¹³C NMR (101 MHz, DMSO) δ 150.99, 142.18, 140.31, 128.55, 119.94.

Synthesis of 4,4'-(thiophene-2,5-diyl)bis(1-(3-(trimethylammonio)propyl)pyridin-1-ium) tetrachloride – 1.

In a 250 mL Ar purged Schlenk flask, **TDP** (2 g, 8.4 mmol) was combined with (3-bromopropyl)trimethylammonium bromide (5.5 g, 21 mmol) in 60 mL DMF, and stirred at 100 °C for 3 days. The resulting suspension was cooled, collected by vacuum filtration, washed with 3 x 10 mL cold DMF, 3 x 10 mL MeCN and 3 x 10 mL ether, and then dried in vacuum to give **[(NPr)₂TV]Br₄**. The product was exchanged for chloride by column anion exchange with Amberlite® IRA-900 chloride form anion exchange resin to give **1**. A orange solid. Yield: 3.91 g (80%). ¹H NMR (400 MHz, D₂O) δ 8.81 (d, J = 6.3 Hz, 1H), 8.32 (d, J = 6.2 Hz, 1H), 8.11 (d, J = 0.7 Hz, 1H), 4.64 (t, J = 7.6 Hz, 1H), 3.49 (dd, J = 10.3, 6.6 Hz, 1H), 2.67 – 2.42 (m, 1H). ¹³C NMR (101 MHz, D₂O) δ 148.53, 144.52, 142.82, 133.19, 123.87, 62.44, 57.24, 53.17, 24.50. HRMS (ESI) m/z: [M-4CI]⁴⁺ calcd for C₂₆H₄₀N₄S 110.0737; found 110.0735.

Synthesis of 4,4'-(thiophene-2,5-diyl)bis(1-(3-hydroxypropyl)pyridin-1-ium) bibromide – 2.

To a round-bottom flask were added 3-bromo-1-propanol (1.46 g, 10.49 mmol), **TDP** (0.5 g, 2.10 mmoL) and MeCN (100 mL), and the mixture was refluxed for 3 d. The resulting suspension was cooled, collected by vacuum filtration, washed with 3 x 10 mL MeCN and 3 x 10 mL ether, and then dried in vacuum to give **[(OHPr)**₂**TV]Br**₂. The product was exchanged for chloride by column anion exchange with Amberlite® IRA-900 chloride form anion exchange resin to give **2**. A red solid. Yield: 1.34 g (74%). ¹H NMR (400 MHz,

 D_2O) δ 8.78 (d, J = 6.9 Hz, 2H), 8.25 (d, J = 5.2 Hz, 2H), 8.05 (d, J = 2.9 Hz, 1H), 4.62 (t, J = 7.1 Hz, 2H), 3.64 (t, J = 5.9 Hz, 2H), 2.25 – 2.16 (m, 2H). ¹³C NMR (101 MHz, D_2O) δ 147.88, 144.54, 142.57 132.75, 123.42, 58.27, 57.66, 32.44. HRMS (ESI) m/z: [M-2CI]²⁺ calcd for $C_{20}H_{24}N_2O_2S$ 178.0773; found 178.0771.

Synthesis of (Ferrocenylmethyl)trimethylammonium Chloride – FcNCI.

FcNCI was synthesized according to the reported method.⁶ (Ferrocenylmethyl)dimethylamine (10 g, 41.2 mmol), methyl chloride (49.4 mL, 445.3 mmol) and 25 mL dry CH₃CN were added to a round-bottom flask, which was stirred at RT overnight. The product was collected by filtration, washed with 10mL ether for 3 times, and dried under vacuum. A yellow solid. Yield: 10.9 g (90%). ¹H NMR (400 MHz, D₂O) δ 4.49 (t, J = 1.8 Hz, 2H), 4.40 (t, J = 1.8 Hz, 2H), 4.37 (s, 2H), 4.25 (s, 5H), 2.92 (s, 9H).



3. X-ray Photoelectron Spectroscopy (XPS)

Figure S1. XPS of a) $[(NPr)_2TV]Br_4$ and b) 1, respectively.



Figure S2. XPS of a) $[(OHPr)_2TV]Br_2$ and b) 2, respectively.

4. Solubility tests

The solubility of thienoviologen derivatives was tested in the Deionized water or 1 M NaCl solutions by UV-Vis spectrum.⁷ Firstly, adding thienoviologen derivatives into the Deionized water or 1 M NaCl solutions until no further solid could be dissolved. A saturated solution of thienoviologen derivatives was obtained after centrifugation. Then take a small amount of the saturated solution and diluted it with a known magnification. The concentration was measured by the UV-Vis spectrum. Finally, the concentration was calculated according to a pre-calibrated absorbance-concentration curve of known concentrations of thienoviologen derivatives.



Figure S3. UV-Vis calibration lines for determination of the solubility of **1**. a) UV-Vis spectrum at different concentrations in deionized water. b) The absorbance versus the concentration at 376 nm. c) UV-Vis spectrum at different concentrations in NaCl (1 M). d) The absorbance versus the concentration at 376 nm.



Figure S4. UV-Vis calibration lines for determination of the solubility of **2**. a) UV-Vis spectrum at different concentrations in deionized water. b) The absorbance versus the concentration at 376 nm. c) UV-Vis spectrum at different concentrations in NaCl (1 M). d) The absorbance versus the concentration at 376 nm.

Compound	Solubility (M), (d	capacity, Ah L ⁻¹)	Fue(Vivs NHF)	cell voltage (V) Paired with FcNCI			
compound	H ₂ O	NaCI (1M)					
	1 26 (72 00)	1 20 (64 22)	-0.55	1.16			
I	1.30 (72.90)	1.20 (04.32)	-0.68	1.29			
2	1.44 (77.18)	1.30 (69.68)	-0.57	1.18			

Table S1. Solubility, capacity, and electrochemical data of 1 and 2.

5. Computed UV-Vis spectra



Figure S5. Computed, at the TD-B3LYP/6-311+G(d) level of theory in the H_2O , and experimental UV-Vis spectra of 1.



Figure S6. Computed, at the TD-B3LYP/6-311+G(d) level of theory in the H_2O , and experimental UV-Vis spectra of 2.

6. The cyclic voltammogram (CV) studies.

All electrochemical CV experiments were carried out in 0.5 M NaCl electrolyte solutions. Redox potentials were referenced to NHE. The glassy carbon electrode was used for the working electrode and counter electrode, which were polished using Al_2O_3 suspended in deionized H_2O , then rinsed with deionized H_2O and dried with air flow. The reference electrode consisted of a silver wire coated with a layer of AgCl and suspended in a solution of 3 M KCl electrolyte (Ag/AgCl, *vs.* NHE).



Figure S7. The cyclic voltammogram at different scan rates from 0.01 V/s to 1 V/s; conditions: 4.0 mM a) **1**, b) **2** in 0.5 M NaCl electrolyte; glassy carbon as working electrode; glassy carbon as counter electrode; Ag/AgCl as reference electrode.



Figure S8. The plot of i_c and i_a over the square root of scan rates for a) 1, b) 2.

7. SEM images and EDX spectrum.

The graphite felt was used as electrode during RFB operation. Pure graphite felt was used as the blank control group, and graphite felt after RFB operation was used as the experimental group. The scale bars of images are 30 µm.



Figure S9. SEM images of (a) the pure graphite felt and (c) the graphite felt after battery test for **[(OHPr)**₂**TV]Cl**₂. The scale bars of images are 30 µm. EDX spectrum of (b) the pure graphite felt and (d) the graphite felt after battery test for **[(OHPr)**₂**TV]Cl**₂.

8. UV-Vis spectra.



Figure S10. UV-Vis spectra of TDP, [(NPr)₂TV]Cl₄ and [(OHPr)₂TV]Cl₂. Extrapolated optical band gaps (Eg) are shown as insets.



9. Density Functional Theory (DFT) calculation

Figure S11. HOMO–LUMO plots and energy-level diagram of [(NPr)₂V]⁴⁺, [(NPr)₂TTz]⁴⁺, [APBPy]⁴⁺ by DFT calculation.



Figure S12. Conformation and dihedral angles of the optimized structures. (Note: Hydrogen bond is not shown for clarity.)

Table S2. The date of dihedral angle, molecular volume, kinetics (D and k ₀) for [(NPr) ₂ V]Cl ₄ , [(NPr) ₂ TTz]Cl ₄ , [APBPy]Cl ₄ , 1 and 2	2.
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Anolyte	Dihedral angle	Molecular volume (ų)	diffusion coefficient (D, *10 ⁻⁶ cm ² s ⁻¹)	electron transfer constant $(k_0, \text{ cm s}^{-1})$	
[(NPr) ₂ V]Cl ₄ ⁸	31.55°	496.21	3.80	>0.305	_
[(NPr)2TTz]Cl49	6.06°	621.24	3.15	>0.28	
[APBPy]Cl ₄ ¹⁰	55.33°	593.80	0.279	>0.0198	
[(NPr) ₂ TV]Cl ₄	18.37°	583.38	3.36	>0.31	
[(OHPr) ₂ TV]Cl ₂	25.81°	445.75	3.04	>0.17	



 Table S3. Bond length [Å] of 1⁴⁺, 1²⁺, 2²⁺ and 2⁰. (Note: Hydrogen bond is not shown for clarity, The R group stands for -NPr or -OHPr.

 R1, R2 and R3 stand for pyridinium ring, thiophene ring and pyridinium ring, respectively.)

Bond	1 ⁴⁺	1 ²⁺	Variation	2 ²⁺	2 ⁰	Variation
C1-C2	1.38411	1.4324	0.04829	1.38315	1.43229	0.04914
C2-C3	1.4044	1.367	-0.0374	1.4061	1.36733	-0.03877
C3-C4	1.38412	1.4324	0.04828	1.38326	1.43239	0.04913
C4-S5	1.74374	1.80017	0.05643	1.74325	1.80113	0.05788
C1-S5	1.74367	1.80017	0.0565	1.74328	1.80115	0.05787
C4-C6	1.45404	1.38115	-0.07289	1.45507	1.38146	-0.07361
C6-C7	1.45404	1.4525	-0.00154	1.40788	1.45241	0.04453
C7-C8	1.37411	1.35398	-0.02013	1.37514	1.35474	-0.0204
C8-N9	1.35406	1.38569	0.03163	1.3529	1.3841	0.0312
N9-C10	1.35321	1.38138	0.02817	1.35218	1.37934	0.02716
C10-C11	1.37443	1.35515	-0.01928	1.37512	1.35606	-0.01906
C11-C6	1.40829	1.45198	0.04369	1.40745	1.45187	0.04442
C1-C12	1.45414	1.45198	-0.00216	1.45511	1.38145	-0.07366
C12-C113	1.40884	1.4525	0.04366	1.40783	1.4523	0.04447
C13-C14	1.37409	1.35398	-0.02011	1.37504	1.35473	-0.02031
C14-N15	1.35407	1.38569	0.03162	1.35303	1.38399	0.03096
N15-C16	1.35316	1.38138	0.02822	1.35219	1.37936	0.02717
C16-C17	1.37442	1.35515	-0.01927	1.37502	1.35604	-0.01898
C17- C12	1.40823	1.45198	0.04375	1.40752	1.45196	0.04444

10. In-suit UV-Vis spectrum

In the glove box, the UV-Vis, PC, Neware instrument, and flow battery were connected together. Anolyte was stored in a customized cuvette (1 cm*1 cm*10 cm)and cathode electrolyte was stored in a sample bottle. The concentration of thienoviologens and FcNCl used are 10⁻⁵ M and 2*10⁻⁵ M for *in-situ* UV-Vis spectrum and their solution volume are 8mL and 20 mL, respectively. The flow rate was 30 ml min⁻¹. The current density was 0.5 mA cm⁻². The date was recorded quickly during charging and discharging.



Figure S13. The instrument set-up for In-suit UV-Vis spectrum.



Figure S14. *In-situ* UV-Vis spectrum of 2 during a) charge and b) discharge process at 100% SOC. c) The EPR spectrum of radical species of 2^{1+•}. d) the reaction structure of 2.

11. The electrochemical kinetics studies.

All linear sweep voltammetry (LSV) studies were conducted using a CHI660E and a Pine in a three-electrode configuration. A glassy carbon rotating electrode (5 mm diameter) was used as the working electrode along with a glassy carbon counter electrode and an Ag/AgCl reference electrode same as used in CV studies. Before data collection, the electrolyte was purged by argon gas for 20 minutes to remove the oxygen dissolved in the electrolyte. Linear sweep voltammetry (LSV) scans were recorded at a scan rate of 5 mV s⁻¹, with rotational speed between 300-2100 rpm with an increment of 300 rpm.

The diffusion coefficient (*D*) was determined by the slope of fitted Levich equation: $i = 0.620 nFAcD^{2/3}v^{-1/6}\omega^{1/2}$, where n was the electron transfer number, Faraday's constant F = 96485 C mol⁻¹, electrode area A = 0.1963 cm², concentration c = 1×10⁻⁶ mol cm⁻³, kinetic viscosity v = 9×10⁻³ cm² s⁻¹ (0.5 M NaCl aqueous solution), ω represented rotate speed (rad/s).

The electron transfer constant (k_0) was calculated from the Nicholson's method. The peak(E_{pc})-peak(E_{pa}) separation, ΔE_p , was obtained from CV curves and used to calculate the kinetic parameter, Ψ. using the equation: $\Psi = (-0.6288 + 0.0021\Delta E_p)/(1 - 0.017\Delta E_p).$ And then, k_0 was calculated from the following equation: $\varphi = K^0 [\pi D n F/RT]^{-1/2} \vartheta^{-1/2}$, where F, D, and n were the same as described above, R = 8.314, T=298.16 K, and v represents the scan rate.

The CV of **1** displayed ΔE_p of 41 mV and 59 mV for the 1st and 2nd electron reduction under 0.3 V/s scan rate (Figure S10a), respectively, and the CV of **2** displayed ΔE_p of 61 mV for the two-electron reduction under 0.1 V/s scan rate (Figure S10b), confirming fast and reversible Nernst reduction processes. For Nicholson's method, ΔE_p has a limit value of 61 mV, corresponding to Ψ as 20. Corresponding diffusion constants, k_0 of **1** and **2** are greater than 0.31 cm s⁻¹ and 0.17 cm s⁻¹, respectively.



Figure S15. RDE studies of **1** (1 mM in 0.5 M NaCl). a) Current *versus* potential at rotation rates from 300 to 2100 rpm with an increment of 300 rpm and potential sweeping rate of 5 mV s⁻¹. b) Levich plot of limiting current *versus* square root of rotation rate ($\omega^{1/2}$).



Figure S16. RDE studies of **2** (1 mM in 0.5 M NaCl). a) Current *versus* potential at rotation rates from 300 to 2100 rpm with an increment of 300 rpm and potential sweeping rate of 5 mV s⁻¹. b) Levich plot of limiting current *versus* square root of rotation rate ($\omega^{1/2}$).



Figure S17. CV curves of 4.0 mM thienoviologen derivatives in a 0.5 M NaCl solution: a) for 1 with scan rate 0.3 V/s scan rate. b) for 2 with scan rate 0.1 V/s scan rate.

12. Area-specific resistance (ASR)

The area-specific resistance (ASR) of the membrane was measured through plane in 1 M NaCl solution.¹¹ The AMV anion-exchange membrane was installed in the flow battery device used in our experiments with an active area of 9 cm². Electrochemical Impedance analysis (EIS) was performed using an Autolab electrochemical workstation. Before the measurement, the membranes were equilibrated in a 1 M NaCl solution for 24 h. The ASR was determined by computing the difference of the cell resistance with (R_{mem}) and without (R_{bkg}) the membrane and by normalizing to the active area (A), following Equation : $ASR(\Omega \cdot cm^2) = (R_{mem} - R_{bkg}) \cdot A$

Therefore, ASR = 2.2 Ω cm².



Figure S18. Electrochemical impedance spectroscopy (EIS) of RFB with membrane and without membrane.

13. Full cell tests

A home-made full battery was assembled with two steel plates, two polytetrafluoroethylene insulation plates, two Cu plate collectors, two graphite plates, and two graphite-felts, which was separated by AMV anion-exchange membrane. The cell has an active area of 9 cm². For the two-electron storage, 0.1 M anolyte was dissolved in 1 M NaCl (8 mL) and 0.2 M catholyte was dissolved in 1 M NaCl (10 mL). The AORFB was also tested at a higher concentration (0.3 M). The electrolytes were pumped into the cell at a flow rate of 60 mL min⁻¹ through a peristaltic pump (BT100M, Baoding Chuang Rui Precision Pump Co., Ltd.). The reservoirs were purged with Ar to displace any O_2 in the system, and then sealed. The flow cell was galvanostatically charge-discharged between 1.8 V and 0.1 V using a Neware battery test system in the glove box at RT. The flow battery was conducted at current densities from 20 to 90 mA cm⁻².



Figure S19. The color change of the 0.1 M **1/FcNCI** AORFB during charge and discharge process (From orange to deep purple for **1**, From yellow to deep blue for **FcNCI**). The initial charging voltage and discharge voltages are 1.24 V and 1.14 V, respectively. The 0.1 M **1/FcNCI** AORFB has similar color changes. The initial charging voltage and discharge voltages are 1.26 V and 1.10 V, respectively.



Figure S20. a) 0.1 M **2/FcNCI**-based AORFB exhibited a) 1000 cycle of stability at a current density of 40 mA cm⁻². Inset: Representative charge and discharge curves from the experiment. b) Polarization and power density curves of the AORFB at 0.1 M after full charge using 10 mA cm⁻². From 20 mA cm⁻² to 90 mA cm⁻², c) plot of the battery capacity *versus* cycling numbers, d) representative charge and discharge curves, e) Plots of average Coulombic efficiency (CE), energy efficiency (EE), and voltage efficiency (VE).



Figure S21. Extended 100 cycle data of the 0.3 M **1/FcNCI** AORFB showing charge capacity, discharge capacity, and Coulombic efficiency versus cycle number at 40 mA cm⁻² current density. Conditions: anolyte: 0.3 M **1** in 1 M NaCl (8 mL); catholyte: 0.3 M FcNCl in 1.0 M NaCl (20 mL); AMV anion-exchange membrane, 25 °C.



Figure S22. Extended 200 cycle data of the 0.3 M 2/FcNCI AORFB showing charge capacity, discharge capacity, and Coulombicefficiency versus cycle number at 40 mA cm⁻² current density. Conditions: anolyte: 0.3 M 1 in 1 M NaCl (8 mL); catholyte: 0.3 M FcNClin1.0MNaCl(20mL);AMVanion-exchangemembrane,25°C.

14. Electrochemical Impedance Spectroscopy (EIS)



The Potentio-controlled Electrochemical impedance spectroscopy (EIS) of cells was obtained by Autolab electrochemical workstation with a frequency range from 0.01 Hz to 10 kHz.

Figure S23. Electrochemical impedance spectroscopy (EIS) of a) 0.1 M 1/FcNCI AORFB before and after 300 cycles. b) 0.1 M 2/FcNCI AORFB before and after 1000 cycles in full battery.

15. The cyclic voltammogram after cycle of the battery test.



Figure S24. CV curves of a) 0.1 M 1/FcNCI after 300 cycles. b) 0.1 M 2/FcNCI after 1000 cycles in full battery.



16. The ¹H NMR spectra after cycle of battery test.

Figure S25. ¹H spectra of a) 1 after 300 cycles. b) 2 after 1000 cycles in full battery. (inset: the suggested decomposition reaction)

17. Calculation of theoretical energy density

The theoretical energy density for the full battery was calculated by the following equation.

$$Energy \ Density \ \left(E_{d} \right) = \frac{n CFV}{\mu_{\vartheta}}$$

where n is the number of electron transfer involved in the reaction, C is the concentration of thienoviologen derivatives, F is the Faradic constant (26.8 Ah mol⁻¹), V is the cell voltage, and μ_{ϑ} is the volume factor. $\mu_{\vartheta} = 1+C_{Small}/C_{Large}$. For the **[(NPr)₂TV]Cl₄/FcNCI** based AORFB, $\mu_{\vartheta}=1+1.2/3=1.4$, V=1.29 v, E_d=59.27 Wh L⁻¹. For the **[(OHPr)₂TV]Cl₂/FcNCI** based AORFB, $\mu_{\vartheta}=1+1.3/3=1.43$, V=1.18 v, $E_d=57.50$ Wh L⁻¹.¹²

Anolyte/Catholyte	Concentration [M]	Capacity utilizationª [%]	Cycles	Capacity retention ^ь [%]	Number of electrons	Ref., Feature
	0.1	86.1	50	97.0		
	0.1		300	87.9		
	0.3	81.1	50	95.9		This
			100	92.6		work
	0.1	65.3	1000	93.5	Two-	
	0.3	41.5	200	99.7	electron	
[(Me)(NPr)V]Cl ₃ /FcNCl	0.25	92.5	50	91.4	storage	8
[(NPr) ₂ V]Cl ₄ /N ^{Me} -TEMPO	0.05	88.1	50	91		8
[(NPr) ₂ TTz]Cl ₄ /N ^{Me} -TEMPO	0.25	80.2	50	95.7		9
[APBPy] ₂ Cl ₄ /[TBABPy]Cl ₃	0.5	80.3	100	96		10
(2HO-V)Br ₂ /Br ₂	0.1	80°	200	no date		13
(SPr) ₂ V/KI	0.5	93°	300	98.8°		14
BHOP-Vi/FcNCI	0.1	104	300	95.9		2
BPP-Vi/K ₄ Fe(CN) ₆	1	99°	285	99.8°	One-	15
R-Vi/K ₄ Fe(CN) ₆	0.1	92	3200	77.6	electron	16
MV/4-HO-TEMPO	0.1	67°	100	99	storage	17
MV/N ^{Me} -TEMPO	0.5	71°	500	91.2	1	18
(NPr) ₂ V/N ^{Me} -TEMPO	0.5	67°	500	97.5	1	18

Table S4. Comparison of technical features of thienoviologen-based AORFBs.

a: (SPr)₂V/KI, MV/N^{Me}-TEMPO, (NPr)₂V/N^{Me}-TEMPO tested at 60 mA cm⁻², R-Vi/K₄Fe(CN)₆ tested at 50 mA cm⁻², other AORFBs tested at 40 mA cm⁻².

b: [(Me)(NPr)V]Cl₃/FcNCl, [(NPr)₂V]Cl₄/N^{Me}-TEMPO, (SPr)₂V/Kl, MV/N^{Me}-TEMPO, (NPr)₂V/N^{Me}-TEMPO tested at 60 mA cm⁻²; [APBPy]Cl₄/[TBABPy]Cl₃ tested at 80 mA cm⁻². R-Vi/K₄Fe(CN)₆ tested at 50 mA cm⁻², other AORFBs tested at 40 mA cm⁻².

c: Calculated based on the capacity utilization and capacity retention shown in the reference. The data of (2HO-V)Br₂/Br₂ from Figure S7, the data of (SPr)₂V/KI from Figure 4c, the data of BPP-Vi/K₄Fe(CN)₆ from Figure 5e, the data of MV/4-HO-TEMPO from Figure 4c, the data of (NPr)₂V/N^{Me}-TEMPO from Figure S3c, the data of (NPr)₂V/N^{Me}-TEMPO from Figure 3a.

18. ¹H, ¹³C NMR spectra

¹H NMR (DMSO-*d*₆, 400 MHz) and ¹³C NMR (DMSO, 101 MHz) spectra of **2,5-di(pyridin-4-yl)thiophene**:





¹H NMR (D₂O, 400 MHz) and ¹³C NMR (D₂O, 101 MHz) spectra of **[(NPr)₂TV]Cl₄:**

 $\substack{ 8.79 \\ 8.77 \\ 8.26 \\ 8.24 \\ 8.05 \\ 8.05 \\ \end{array}$ 4.79 4.64 4.61 3.65 3.64 3.64 $\overbrace{2.19}^{2.22}$ c CI но -3.99⊣ 2.00⊣ 4.00 3.98⊣ 3.99 3.99 8.0 5.5 5.0 4.5 f1 (ppm) 4.0 3.5 3.0 2.5 2.0 9.5 9.0 8.5 7.5 7.0 6.5 6.0 1.5 1.0 0.5 0.0 ~147.88 ~144.54 ~142.57 -132.75 -123.42 58.27 -32.44 CI CI он но 170 90 f1 (ppm) 160 150 140 130 120 110 100 80 70 60 50 40 30 20 10

¹H NMR (D₂O, 400 MHz) and ¹³C NMR (D₂O, 101 MHz) spectra of **[(OHPr)₂TV]Cl**₂:

¹H NMR (D₂O, 400 MHz) spectra of **FcNCI**:



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