Supporting Information

Designing High Energy Density Flow Batteries by

Tuning Active-Material Thermodynamics

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a: $R_1 = H$, $R_2 = CH_3$ b: $R_1 = R_2 = H$ Figure S1. Amavadin, a naturally occurring vanadium chelate, isolated from mushrooms in the *Amanita* genus (a) and the related, proteo- analog, [VBH].



Figure S2. Standard UV-VIS spectra of fully reduced (V4) and fully oxidized V(5) species expressed as molar absorptivity at each wavelength from 950 nm to 450 nm. VBH²⁻ and VBH¹⁻ concentrations at each electrode can be extracted by simulating the observed spectrum as a linear combination of the reference spectra.



Figure S3. Plot of Viscosity Vs different concentration of oxidised (Red) and Reduced (black) active material at room temperature.

Dielectric Constant	Refractive Index
80.40	1.330
47.20	1.479
38.30	1.430
36.60	1.344
32.63	1.329
24.30	1.361
20.70	1.359
12.50	1.510
10.30	1.421
9.08	1.424
7.25	1.407
4.90	1.450
2.40	1.497
2.28	1.501
2.24	1.466
2.02	1.425
1.89	1.375
	Dielectric Constant 80.40 47.20 38.30 36.60 32.63 24.30 20.70 12.50 10.30 9.08 7.25 4.90 2.40 2.28 2.24 2.22 2.24 2.02 1.89

<u>Table S1. SMD solvents used in ΔG_{sol}^* calculations.</u>



Figure S4. Calibration curve from UV-VIS spectroscopy to determine molar extinction coefficient of oxidized [VBH]⁻¹ species at 485 nm.



Figure S5. Calibration curve from UV-VIS spectroscopy to determine molar extinction coefficient of reduced [VBH]²⁻ species at 825 nm.



Figure S6. Digital image of reduced (V⁴⁺BH) species (blue) and oxidized (V⁵⁺BH) species (red).

¹H and ¹³C Spectra







Figure S9. ¹H NMR spectrum of [N4444]VBH in acetonitrile-d3.



IR spectra



Figure S11 . ATR-FTIR spectrum of compound ZinHIDA ligand.



Figure S12 . ATR-FTIR spectrum of CaVBH.



Figure S13 . ATR-FTIR spectrum of compound $[N_{1111}]_2$ VBH.



Figure S14 . ATR-FTIR spectrum of compound $[N_{2222}]_2 VBH.$



Figure S15 . ATR-FTIR spectrum of compound [N₃₃₃₃]₂VBH.



Figure S16. ATR-FTIR spectrum of compound $[N_{4444}]_2$ VBH.



Figure S17. ATR-FTIR spectrum of compound $[N_{3333}]VBH$.



Single crystal X-ray diffraction

General: Single crystals obtained by the method as explained in experimental section were mounted on a Cryoloop with oil. Data were collected at the temperature as indicated in the table S2 on a Bruker D8 Venture X-ray instrument using Mo K alpha radiation and data were corrected for absorption with SADABS. Structure was solved by direct methods and all non-hydrogen atoms were refined anisotropically by full matrix least squares on F². Hydrogen atoms for the water molecule were found from a Fourier difference map and were allowed to refine isotropcially with O-H distances of 0.88(0.01) angstroms and with H – H distance of 1,43(0.02) angstroms and 1.50Ueq of parent O atom. All other hydrogen atoms were placed in calculated positions with appropriate riding parameters. The t-butyl groups for both ammonium cations were disordered. For carbons C9-C12, C13-C16, C17- C20 (0.666/0.334 ratio) for carbons C25-C28, C29-C32, C33-C36 (0.367/0.633 ratio) for for carbons C37-C40 (0.404/596 ratio). Each sequence of carbon atoms were refined using distance restraints (SADI), rigid body restraints (DELU), and isotropic restraints (ISOR restraints). In addition carbon atom C5 and oxygen atom O7 (0.457/543 ratio) and O2 (0.889/0.111 ratio) were also disordered and were treated using fixed distances (DFIX) and rigid body isotropic restraints. Further Refinement and molecular graphics were obtained using Bruker Suite of structural programs, OLEX2 and Mercury 3.7.

Compound	[N ₂₂₂₂] ₂ VBH	[N ₄₄₄₄] ₂ VBH	[N ₃₃₃₃]VBH	[N ₄₄₄₄]VBH
Formula	C24 H50 N4 O11 V	C40 H82 N4 O11 V	C20 H36 N3 O10 V	C26 H47 N4 O10 V
$D_{calc.}$ / g cm ⁻³	1.428	1.170	1.400	1.253
μ/mm^{-1}	0.407	0.262	0.452	0.353
Formula Weight	621.62	846.03	529.46	626.61
Colour	blue	blue	red-brown	orange
Shape	block	block	block	block
Size/mm ³	0.23×0.21×0.20	0.33×0.26×0.18	0.38×0.20×0.18	0.35×0.30×0.25
T/K	200(2)	200(2)	294(2)	297(2)
Crystal System	orthorhombic	monoclinic	triclinic	monoclinic
Space Group	$P2_{1}2_{1}2_{1}$	$P2_{1}/c$	P-1	$P2_1/n$
a/Å	9.450(8)	12.0215(12)	9.5136(8)	14.6589(11)
b/Å	10.573(10)	17.5162(17)	11.4193(10)	9.2683(6)
c/Å	28.94(2)	22.902(2)	13.5999(11)	24.4521(16)
$\alpha/^{\circ}$	90	90	67.468(2)	90
$\beta/^{\circ}$	90	95.183(3)	79.634(2)	91.334(2)
$\gamma/^{\circ}$	90	90	67.087(2)	90
V/Å ³	2892(4)	4802.7(8)	1256.19(18)	3321.2(4)
Ζ	4	4	2	4
Ζ'	1	1	1	1
Wavelength/Å	0.71073	0.71073	0.71073	0.71073
Radiation type	MoK _α	MoK _α	MoK _α	MoK _α
$\Theta_{min}/^{\circ}$	2.975	3.062	3.034	2.721
$\Theta_{max}/^{\circ}$	25.538	25.378	25.417	25.793
Measured Refl's.	46827	104598	23487	72770
Indep't Refl's	5363	8799	4620	6306
Refl's I≥2 <i>σ</i> (I)	5021	6833	4000	5326
R _{int}	0.0401	0.0500	0.0312	0.0340
Parameters	377	799	312	375
Restraints	3	640	0	0
Largest Peak	0.386	1.15	1.038	1.085
Deepest Hole	-0.260	-0.45	-0.411	-0.430
GooF	1.054	1.070	1.055	1.096
wR2 (all data)	0.0740	0.2386	0.1059	0.1342
wR_2	0.0722	0.2120	0.0973	0.1223
R_1 (all data)	0.0368	0.1026	0.0525	0.0597
R_1	0.0323	0.0797	0.0428	0.0480

Table S2. Single crystal x-ray crystallography data

Reference:

- S. a. S. APEX3, Bruker AXS, INC, 2018.
- O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339-341.
- Sheldrick, G.M., A short history of ShelX, Acta Cryst., (2008), A64, 339-341.
- Sheldrick, G.M., Crystal structure refinement with ShelXL, *Acta Cryst.*, (2015), **C71**, 3-8.