*Supporting Information*

# Reductive Formation of a Vanadium(IV/V) Oxide Cluster Complex [$V_8O_{19}$(4,4′-$^t$Bubpy)$_3$] Having a $C_3$-Symmetric Propeller-Shaped Nonionic $V_8O_{19}$ Core

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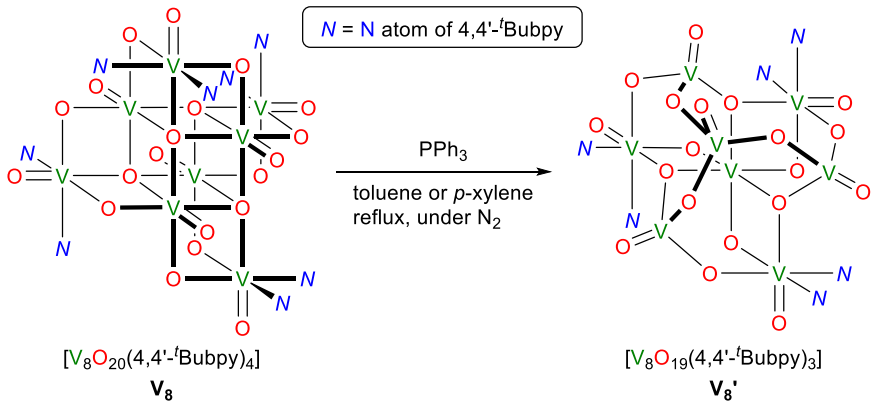
**Contents**

## General Considerations

Experimental manipulations for the reductive conversion of vanadium(V) oxide cluster complexes were carried out in a dried glass vessel under a nitrogen atmosphere by standard Schlenk techniques. $^{1}$H (500 MHz) and $^{31}$P{$^{1}$H} (202 MHz) NMR spectra were recorded on a JEOL ECA-500 spectrometer. Chemical shifts are reported in δ, referenced to the residual $^{1}$H signal of a deuterated solvent as an internal standard, to the $^{31}$P signal of $PPh_3$ (δ −5.65) as an external standard. IR spectra were recorded on a JASCO FT/IR-410 spectrometer using KBr pellets. Elemental analyses were conducted on a Perkin Elmer 2400 series II CHN analyzer. Magnetic susceptibility measurements were performed using a Quantum Design MPMS-XL superconducting quantum interference device (SQUID) magnetometer. Diamagnetic corrections were evaluated using Pascal's constants.[S1] Vanadium(V) oxide cluster complexes, $[V_8O_{20}(4,4'\text{-}^{t}\text{Bubpy})_4]$ (**$V_8$**), $[V_4O_8(OMe)_4(4,4'\text{-}^{t}\text{Bubpy})_2]$ (**$V_4$**), and $[V_7O_{17}(OEt)(4,4'\text{-}^{t}\text{Bubpy})_3]$ (**$V_7$-Et**), were synthesized according to the previously reported procedures.[S2] Unless otherwise noted, reagents were purchased from commercial source and used without further purification.

## Experimental Procedures

### *Reductive Formation of Octanuclear Vanadium(IV/V) Oxide Cluster Complex $V_8'$ from $V_8$*

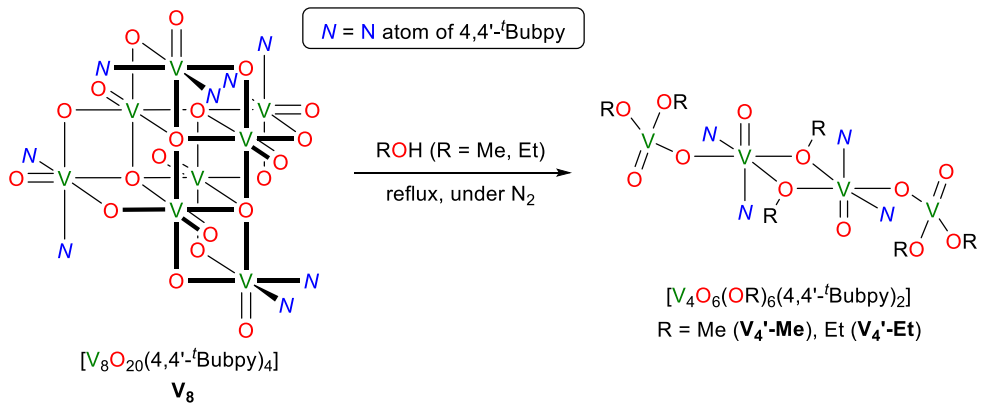



**$[V_8O_{19}(4,4'\text{-}^{t}\text{Bubpy})_3]\cdot 0.42C_7H_8$ ($V_8'\cdot 0.42C_7H_8$):** Complex **$V_8$**$\cdot CH_2Cl_2$ (568.9 mg, 0.30 mmol) and $PPh_3$ (632.1 mg, 2.41 mmol) in toluene (30.0 mL) were heated at reflux for 5 min under $N_2$ to form a dark green suspension. This suspension was filtered and allowed to stand overnight at room temperature to deposit dark blue crystals suitable for X-ray analysis. The crystals were collected by filtration, washed with toluene, and dried under vacuum to give **$V_8'$**$\cdot 0.42C_7H_8$ (an empirical formula)

(85.2 mg, 18% yield based on vanadium). Comparison of this empirical formula with the structure obtained by the X-ray analysis (**V₈′**·$3C_7H_8$) indicates that most parts of solvent molecules (toluene) in the crystals were lost during the drying process. IR (KBr, $cm^{-1}$) 2964 ($\nu_{CH}$), 1619 ($\nu_{C=C,\ C=N}$), 1413 ($\nu_{C=C,\ C=N}$), 979 ($\nu_{V=O}$), 849 ($\nu_{CH}$), 812 ($\nu_{CH}$), 770 ($\nu_{CH}$); Anal. Calcd for $C_{54}H_{72}N_6O_{19}V_8 \cdot 0.42C_7H_8$: C, 43.97; H, 4.88; N, 5.40. Found: C, 43.96; H, 4.80; N, 5.20%.

**[$V_8O_{19}$(4,4′-$^t$Bubpy)$_3$]·1.28$C_8H_{10}$ (V₈′·1.28$C_8H_{10}$):** This complex was obtained by a procedure similar to that for the synthesis of **V₈′**·0.42$C_8H_{10}$ using **V₈**·$CH_2Cl_2$ (565.5 mg, 0.30 mmol), $PPh_3$ (636.7 mg, 2.43 mmol), and *p*-xylene (30.0 mL). Dark blue crystals (33.8 mg, 7% yield based on vanadium) deposited from the filtered reaction mixture were collected by filtration, washed with *p*-xylene, and dried in vacuo to give **V₈′**·1.28$C_8H_{10}$ (an empirical formula). Comparison of this formula with the structure obtained by the X-ray analysis (**V₈′**·3$C_8H_{10}$) indicates that most parts of solvent molecules (*p*-xylene) in the crystals were lost during the drying process. IR (KBr, $cm^{-1}$) 2966 ($\nu_{CH}$), 1619 ($\nu_{C=C,\ C=N}$), 1413 ($\nu_{C=C,\ C=N}$), 980 ($\nu_{V=O}$), 848 ($\nu_{CH}$), 811 ($\nu_{CH}$), 767 ($\nu_{CH}$); Anal. Calcd for $C_{54}H_{72}N_6O_{19}V_8 \cdot 1.28C_8H_{10}$: C, 46.69; H, 5.17; N, 5.09. Found: C, 46.67; H, 5.25; N, 4.75%.

***Reductive Formation of Tetranuclear Vanadium(IV/V) Oxide Cluster Complex V₄′ from V₈***



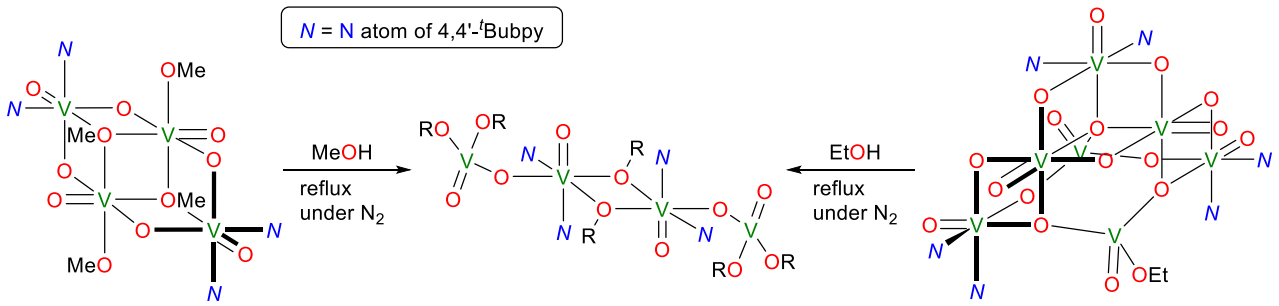

**[$V_4O_6$(OMe)$_6$(4,4′-$^t$Bubpy)$_2$] (V₄′-Me):** Complex **V₈**·$CH_2Cl_2$ (541.8 mg, 0.29 mmol) in MeOH (30.0 mL) was heated at reflux for 24 h under nitrogen to generate a green suspension. The green powder deposited was collected by filtration and washed with MeOH to afford **V₄′-Me** (329.5 mg, 56% yield based on vanadium). IR (KBr, $cm^{-1}$) 2963 ($\nu_{CH}$), 1617 ($\nu_{C=C,\ C=N}$), 1410 ($\nu_{C=C,\ C=N}$), 962

($\nu_{V=O}$), 956 ($\nu_{V=O}$), 886 ($\nu_{CH}$), 848 ($\nu_{CH}$), 800 ($\nu_{CH}$); Anal. Calcd for $C_{42}H_{66}N_4O_{12}V_4$: C, 49.32; H, 6.50; N, 5.48. Found: C, 49.07; H, 6.70; N, 5.47%.

Crystals of **$V_4'$-Me** suitable for X-ray analysis were obtained as follows: complex **$V_8$**·$CH_2Cl_2$ (44.6 mg, 0.024 mmol) in MeOH (5.0 mL) were heated at reflux for 19 h under nitrogen, and the resulting dark green suspension was filtered. The dark green filtrate was allowed to stand overnight at room temperature to deposit dark green crystals, which were suitable for X-ray analysis. The crystals were collected by filtration and washed with MeOH to afford **$V_4'$-Me** (4.9 mg, 10% yield based on vanadium).

**[$V_4O_6(OEt)_6(4,4'$-$^t$Bubpy$)_2$] ($V_4'$-Et):** Complex **$V_8$**·$CH_2Cl_2$ (542.0 mg, 0.29 mmol) in EtOH (30.0 mL) was heated at reflux for 24 h under nitrogen, and the resulting dark orange solution was filtered through a celite pad and allowed to stand for 4 days at room temperature to deposit dark orange crystals which were suitable for X-ray analysis. The crystals were collected by filtration and washed with EtOH to afford **$V_4'$-Et** (336.8 mg, 53% yield based on vanadium). IR (KBr, $cm^{-1}$) 2965 ($\nu_{CH}$), 1616 ($\nu_{C=C,\ C=N}$), 1410 ($\nu_{C=C,\ C=N}$), 968 ($\nu_{V=O}$), 956 ($\nu_{V=O}$), 888 ($\nu_{CH}$), 850 ($\nu_{CH}$), 799 ($\nu_{CH}$); Anal. Calcd for $C_{48}H_{78}N_4O_{12}V_4$: C, 52.08; H, 7.10; N, 5.06. Found: C, 51.97; H, 7.29; N, 5.01%.

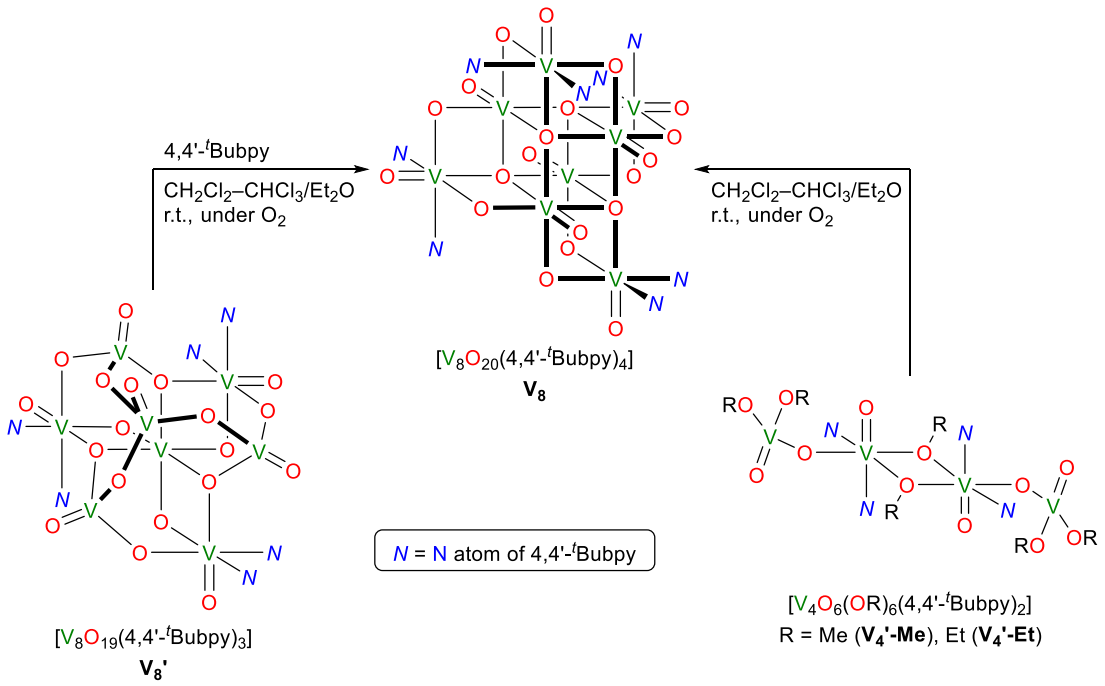
***Reductive Formation of $V_4'$ from $V_4$ or $V_7$-Et***




**Conversion of $V_4$ to $V_4'$-Me:** Complex **$V_4$**·$2H_2O$ (31.6 mg, 0.031 mmol) in MeOH (3.0 mL) was heated at reflux for 19 h under $N_2$. The resulting dark green solution was allowed to stand for 4 days at room temperature to deposit dark green crystals. The crystals were collected by filtration and washed with MeOH to afford **$V_4'$-Me** (13.6 mg, 43% yield based on vanadium).

**Conversion of $V_7$-Et to $V_4'$-Et:** Complex **$V_7$-Et** (149.9 mg, 0.10 mmol) in EtOH (5.0 mL) was heated at reflux for 21 h under $N_2$. The resulting dark orange solution was allowed to stand for 4 days at room temperature to deposit dark orange crystals. The crystals were collected by filtration and washed with EtOH to afford **$V_4'$-Et** (72.3 mg, 37% yield based on vanadium).

***Oxidative Formation of $V_8$ from $V_8'$ or $V_4'$***

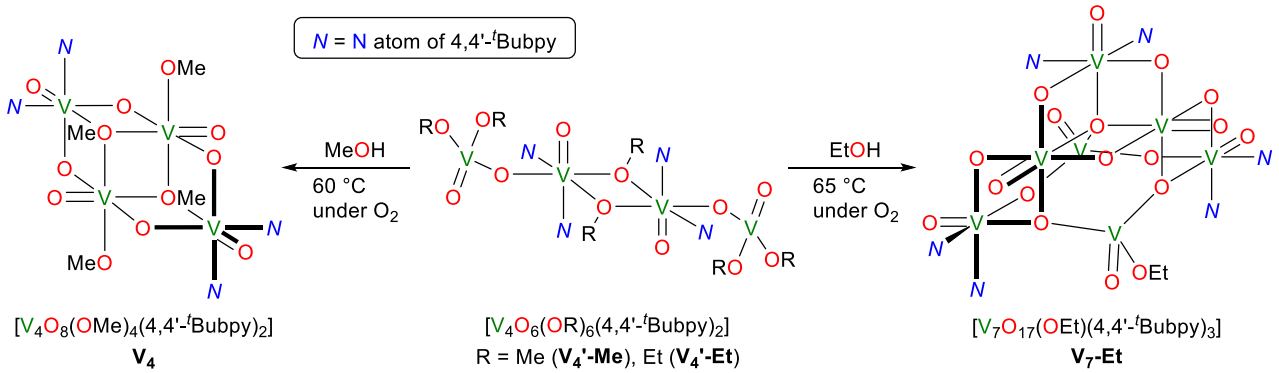



**Conversion of $V_8'$ to $V_8$:** To a $CHCl_3$–$CH_2Cl_2$ (7.0 mL) solution (v/v = 1:1) of **$V_8'$**·0.42toluene (75.2 mg, 0.048 mmol) and 4,4′-$^t$Bubpy (13.2 mg, 0.049 mmol) was added $Et_2O$ (14.0 mL), and the resulting brown suspension was stirred at room temperature for 2 days under $O_2$. The resulting yellow suspension was evaporated and dissolved in $CH_2Cl_2$–$Et_2O$ mixture (v/v = 1:1). The yellow powder thus obtained was collected and washed with $CH_2Cl_2$ to afford **$V_8$**·$CH_2Cl_2$ (70.0 mg, 77% yield based on vanadium).

**Conversion of $V_4'$-Me to $V_8$:** To a $CHCl_3$–$CH_2Cl_2$ (7.3 mL) solution (v/v = 1:1) of **$V_4'$-Me** (51.2 mg, 0.050 mmol) was added $Et_2O$ (14.6 mL), and the resulting brown solution was stirred at room temperature for 2 days under $O_2$. The yellow suspension was evaporated and dissolved in $CH_2Cl_2$–$Et_2O$ mixture (v/v = 1:1). The resulting yellow powder thus obtained was collected and washed with $CH_2Cl_2$ to afford **$V_8$**·$CH_2Cl_2$ (36.5 mg, 77% yield based on vanadium).

**Conversion of $V_4'$-Et to $V_8$:** To a $CHCl_3$–$CH_2Cl_2$ (7.3 mL) solution (v/v = 1:1) of **$V_4'$-Et** (55.3 mg, 0.050 mmol) was added $Et_2O$ (14.6 mL), and the resulting brown solution was stirred at room temperature for 2 days under $O_2$. The resulting yellow suspension was evaporated and dissolved in $CH_2Cl_2$–$Et_2O$ mixture (v/v = 1:1). The yellow powder thus obtained was collected and washed with $CH_2Cl_2$ to afford **$V_8$**·$CH_2Cl_2$ (30.5 mg, 65% yield based on vanadium).

### *Oxidative Formation of $V_4$ or $V_7$-Et from $V_4'$*




**Conversion of $V_4'$-Me to $V_4$: $V_4'$-Me** (51.0 mg, 0.050 mmol) in MeOH (2.5 mL) was heated at 60 °C for 2 days under $O_2$. The resulting brown solution was allowed to stand overnight at room temperature to deposit yellow crystals. The crystals were collected by filtration and washed with MeOH to afford **$V_4$** (13.0 mg, 26% yield based on vanadium).

**Conversion of $V_4'$-Et to $V_7$-Et: $V_4'$-Et** (110.4 mg, 0.10 mmol) in EtOH (2.5 mL) was heated at 65 °C for 2 days under $O_2$ to form a yellow-green suspension. The yellow-green crystalline precipitates were collected, washed with EtOH, and dried in vacuo to afford **$V_7$-Et** as a yellow-green powder (64.4 mg, 76% yield based on vanadium).

**X-ray Diffraction Studies**

Diffraction data for **V$_8$′**·3C$_7$H$_8$, **V$_8$′**·3C$_8$H$_{10}$, **V$_4$′-Me**, and **V$_4$′-Et** were collected on a Rigaku VariMax with a Saturn CCD diffractometer using multilayer mirror monochromated Mo-Kα radiation ($\lambda$ = 0.71075 Å) at −180 °C. Intensity data were corrected for Lorentz and polarization effects and for an empirical absorption.[S3] All calculations were performed using the *CrystalStructure*[S4] crystallographic software package except for refinements, which was performed using SHELXL Version 2016/6.[S5] The structures were solved by direct methods (SHELXS Version 2013/1)[S6] and expanded using Fourier techniques. Non-hydrogen atoms were refined on $F^2$ anisotropically by full-matrix least-squares techniques. Hydrogen atoms were placed at the calculated positions with fixed isotropic parameters. For **V$_8$′**·3C$_7$H$_8$, solvent molecules (toluene) were badly disordered, and the structure of **V$_8$′**·3C$_7$H$_8$ was refined without these solvents using PLATON Squeeze technique,[S6] which reported that the volume of total potential solvent accessible void is 574 Å$^3$ per unit cell, and estimated number of electrons within the void is 109 electrons/cell. Expected volumes for small molecules (e.g. toluene) are 100–300 Å$^3$, and toluene has 50 electrons per molecule. From these results, we assumed that the unit cell contains 2 molecules of toluene (100 electrons). There is a level B alert due to the disorder of a solvent molecule (toluene), but it does not affect the final structure determination. For **V$_8$′**·3C$_8$H$_{10}$, there is a level B alert: Missing # of FCF reflections below Theta(Min). However, data completeness of 96.3% is enough for structure determination. For **V$_4$′-Et**, hydrogen atoms of bridged ethoxide groups were not included in the refinements. Details of the X-ray diffraction study are summarized in Table S1. ORTEP drawings of **V$_8$′**·3C$_8$H$_{10}$, **V$_4$′-Me**, and **V$_4$′-Et** are shown in Figures S1–3 and selected interatomic distances and angles are listed in Tables S2–4. Results of bond valence sum (BVS) calculations for vanadium atoms of **V$_8$′**·3C$_7$H$_8$, **V$_8$′**·3C$_8$H$_{10}$, **V$_4$′-Me**, and **V$_4$′-Et** are shown in Table S5.

**Table S1.** X-ray crystallographic data for **V$_8$′**·3C$_7$H$_8$, **V$_8$′**·3C$_8$H$_{10}$, **V$_4$′-Me**, and **V$_4$′-Et**

| | **V$_8$′**·3C$_7$H$_8$ | **V$_8$′**·3C$_8$H$_{10}$ | **V$_4$′-Me** | **V$_4$′-Et** |
|---|---|---|---|---|
| CCDC | 1828015 | 1828016 | 1828017 | 1828019 |
| chemical formula | $C_{75}H_{96}N_6O_{19}V_8$ | $C_{78}H_{102}N_6O_{19}V_8$ | $C_{42}H_{66}N_4O_{12}V_4$ | $C_{48}H_{78}N_4O_{12}V_4$ |
| formula weight | 1793.14 | 1835.22 | 1022.77 | 1106.93 |
| dimension of crystals | 0.230×0.090×0.085 | 0.234×0.113×0.040 | 0.213×0.137×0.106 | 0.280×0.231×0.124 |
| crystal system | trigonal | triclinic | monoclinic | monoclinic |
| space group | P-3 (#147) | P-1 (#2) | P2$_1$/c (#14) | P2$_1$/c (#14) |
| $a$, Å | 20.323(3) | 11.6193(17) | 10.739(7) | 10.609(4) |
| $b$, Å | 20.323(3) | 15.836(3) | 21.314(12) | 22.256(7) |
| $c$, Å | 12.3450(18) | 23.758(3) | 10.433(7) | 11.793(4) |
| $\alpha$, deg | 90.0000 | 85.348(5) | 90.0000 | 90.0000 |
| $\beta$, deg | 90.0000 | 77.919(4) | 98.259(10) | 102.777(5) |
| $\gamma$, deg | 120.0000 | 87.030(5) | 90.0000 | 90.0000 |
| $V$, Å$^3$ | 4415.5(11) | 4257.8(11) | 2363(2) | 2715.5(16) |
| $Z$ | 2 | 2 | 2 | 2 |
| $\rho_{calcd}$, g cm$^{-3}$ | 1.349 | 1.431 | 1.437 | 1.354 |
| $F$(000) | 1848.00 | 1896.00 | 1068.00 | 1164.00 |
| $\mu$, cm$^{-1}$ | 8.719 | 9.059 | 8.283 | 7.265 |
| trans. factors range | 0.911–0.929 | 0.783–0.964 | 0.836–0.916 | 0.606–0.914 |
| index ranges | $-26 \le h \le 26$ | $-14 \le h \le 15$ | $-13 \le h \le 13$ | $-13 \le h \le 13$ |
| | $-26 \le k \le 26$ | $-20 \le k \le 20$ | $-24 \le k \le 27$ | $-27 \le k \le 27$ |
| | $-16 \le l \le 15$ | $-30 \le l \le 30$ | $-13 \le l \le 13$ | $-15 \le l \le 15$ |
| no. rflns measured | 36793 | 35310 | 18716 | 21853 |
| no. unique rflns | 6749 | 18777 | 5397 | 6117 |
| $R_{int}$ | 0.0875 | 0.0555 | 0.0868 | 0.0643 |
| no. rflns ($I > 2\sigma(I)$) | 5546 | 13300 | 4063 | 4576 |
| no. params refined | 325 | 1000 | 280 | 313 |
| $R1$ ($I > 2\sigma(I)$)[a] | 0.0793 | 0.0703 | 0.0916 | 0.0807 |
| $R$ (All cata) | 0.0965 | 0.1014 | 0.1199 | 0.1012 |
| $wR2$ (All cata)[b] | 0.1839 | 0.1619 | 0.2126 | 0.2500 |
| GOF[c] | 1.133 | 1.086 | 1.120 | 1.069 |
| max diff peak/hole, e Å$^{-3}$ | 0.60/–0.47 | 0.51/–0.68 | 0.73/–0.71 | 2.16/–1.37 |

[a] $R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. [b] $wR2 = [\Sigma\{w(F_o^2 - F_c^2)^2\} / \Sigma w(F_o^2)^2]^{1/2}$, $w = 1 / [\sigma^2 F_o^2 + (aP)^2 + bP]$ ($a$ and $b$ are constants suggested by the refinement program; $P = [\max(F_o^2,0) + 2F_c^2] / 3$). [c] $GOF = [\Sigma w(F_o^2 - F_c^2)^2 / (N_{obs} - N_{params})]^{1/2}$.

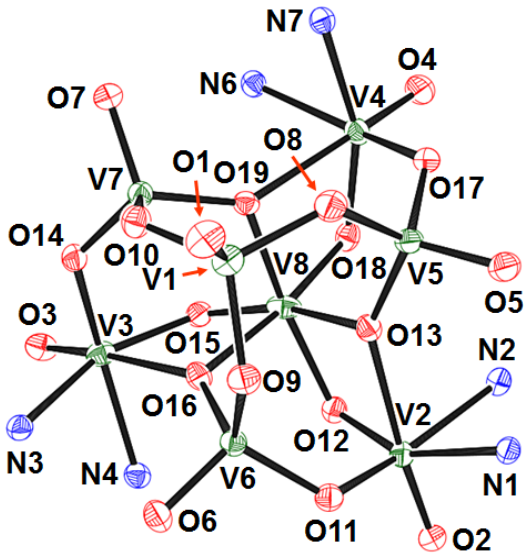



**Figure S1.** Crystal structure of $\mathbf{V_8'}\cdot 3C_8H_{10}$ with numbered atoms. Ellipsoids are shown at the 50% probability level. H and C atoms are omitted for clarity.

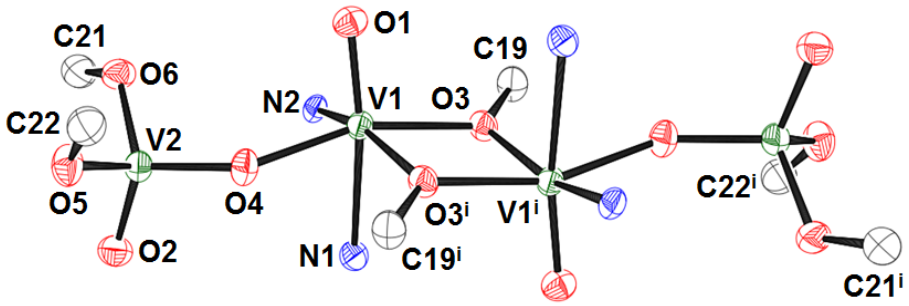



**Figure S2.** Crystal structure of $\mathbf{V_4'}$**-Me** with numbered atoms. Ellipsoids are shown at the 50% probability level. H and C atoms except for C19, C21, C22, C19$^{i}$, C21$^{i}$, and C22$^{i}$ are omitted for clarity. Symmetry operators: (i) – X + 1, – Y, – Z.

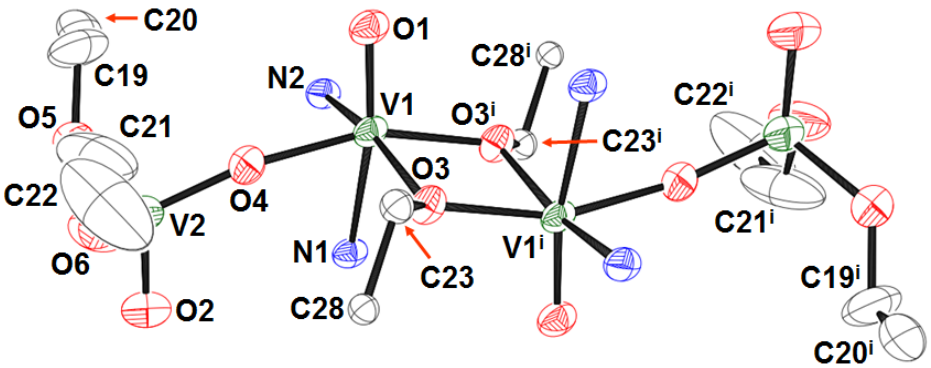



**Figure S3.** Crystal structure of $\mathbf{V_4'}$**-Et** with numbered atoms. Ellipsoids are shown at the 50% probability level. H and C atoms except for C19, C20, C21, C22, C23, C28, C19$^{i}$, C20$^{i}$, C21$^{i}$, C22$^{i}$, C23$^{i}$, and C28$^{i}$ are omitted for clarity. Symmetry operators: (i) – X + 1, – Y, – Z + 1.

**Table S2.** Selected interatomic distances (Å) and angles (deg) for $\mathbf{V_8'}\cdot 3C_8H_{10}$

| Interatomic distances (Å) | | | |
|---|---|---|---|
| V1−O1 | 1.598(3) | V1−O8 | 1.758(3) |
| V1−O9 | 1.770(3) | V1−O10 | 1.766(3) |
| V2−O2 | 1.607(3) | V2−O11 | 1.865(3) |
| V2−O12 | 1.734(3) | V2−O13 | 2.269(3) |
| V2−N1 | 2.169(4) | V2−N2 | 2.144(3) |
| V3−O3 | 1.602(3) | V3−O14 | 1.906(3) |
| V3−O15 | 1.860(3) | V3−O16 | 2.294(3) |
| V3−N3 | 2.143(4) | V3−N4 | 2.134(3) |
| V4−O4 | 1.592(3) | V4−O17 | 1.902(3) |
| V4−O18 | 1.879(3) | V4−O19 | 2.369(3) |
| V4−N5 | 2.139(3) | V4−N6 | 2.132(4) |
| V5−O5 | 1.601(3) | V5−O8 | 1.840(3) |
| V5−O13 | 1.746(3) | V5−O17 | 1.723(3) |
| V6−O6 | 1.602(3) | V6−O9 | 1.825(3) |
| V6−O11 | 1.766(2) | V6−O16 | 1.731(3) |
| V7−O7 | 1.615(3) | V7−O10 | 1.824(3) |
| V7−O14 | 1.729(3) | V7−O19 | 1.750(3) |
| V8−O12 | 1.951(2) | V8−O13 | 2.070(3) |
| V8−O15 | 1.805(3) | V8−O16 | 2.104(3) |
| V8−O18 | 1.794(3) | V8−O19 | 1.996(3) |
| V2⋯V8 | 3.0779(11) | V3⋯V8 | 3.0912(11) |
| V4⋯V8 | 3.0857(11) | | |
| **Angles (deg)** | | | |
| V1−O8−V5 | 128.23(16) | V2−O11−V6 | 124.05(16) |
| V2−O12−V8 | 113.13(15) | V2−O13−V5 | 144.40(15) |
| V2−O13−V8 | 90.26(11) | V3−O15−V8 | 115.01(16) |
| V3−O16−V8 | 89.19(11) | V4−O18−V8 | 114.29(15) |
| V4−O19−V8 | 89.57(10) | | |

**Table S3.** Selected interatomic distances (Å) and angles (deg) for **$V_4'$-Me**

| | | | |
|---|---|---|---|
| | Interatomic distances (Å) | | |
| V1−O1 | 1.609(4) | V1−O3 | 2.012(3) |
| V1−O3$^{i}$ | 1.968(4) | V1−O4 | 1.976(4) |
| V1−N1 | 2.309(4) | V1−N2 | 2.144(4) |
| V2−O2 | 1.617(4) | V2−O4 | 1.687(4) |
| V2−O5 | 1.792(4) | V2−O6 | 1.794(4) |
| V1···V1$^{i}$ | 3.140(2) | | |
| | Angles (deg) | | |
| O3−V1−O3$^{i}$ | 75.83(15) | V1−O3−V1$^{i}$ | 104.17(17) |
| V1−O4−V2 | 144.4(2) | | |

Symmetry operators: (i) − X + 1, − Y, − Z.

**Table S4.** Selected interatomic distances (Å) and angles (deg) for **$V_4'$-Et**

| | | | |
|---|---|---|---|
| | Interatomic distances (Å) | | |
| V1−O1 | 1.604(3) | V1−O3 | 1.970(3) |
| V1−O3$^{i}$ | 2.005(2) | V1−O4 | 1.973(3) |
| V1−N1 | 2.281(3) | V1−N2 | 2.164(3) |
| V2−O2 | 1.625(4) | V2−O4 | 1.688(3) |
| V2−O5 | 1.770(4) | V2−O6 | 1.792(4) |
| V1···V1$^{i}$ | 3.1411(13) | | |
| | Angles (deg) | | |
| O3−V1−O3$^{i}$ | 75.57(11) | V1−O3−V1$^{i}$ | 104.43(13) |
| V1−O4−V2 | 161.51(18) | | |

Symmetry operators: (i) − X + 1, − Y, − Z + 1.

**Table S5.** BVS calculations for vanadium atoms of **$V_8'$**·$3C_7H_8$, **$V_8'$**·$3C_8H_{10}$, **$V_4'$-Me**, and **$V_4'$-Et**[a]

| V complex | | V1 | V2 | V3 | V4 | V5 | V6 | V7 | V8 |
|---|---|---|---|---|---|---|---|---|---|
| **$V_8'$**·$3C_7H_8$ | V(IV) | 4.82 | 4.54 | 4.72 | **4.01** | – | – | – | – |
| | V(V) | **5.08** | 4.74 | **4.97** | 4.22 | – | – | – | – |
| **$V_8'$**·$3C_8H_{10}$ | V(IV) | 4.81 | 4.73 | 4.36 | 4.34 | 4.79 | 4.73 | 4.73 | **4.00** |
| | V(V) | **5.07** | **4.93** | 4.54 | 4.51 | **5.04** | **4.98** | **4.98** | 4.21 |
| **$V_4'$-Me** | V(IV) | **4.10** | 4.82 | – | – | – | – | – | – |
| | V(V) | 4.29 | **5.08** | – | – | – | – | – | – |
| **$V_4'$-Et** | V(IV) | **4.14** | 4.85 | – | – | – | – | – | – |
| | V(V) | 4.32 | **5.11** | – | – | – | – | – | – |

[a] BVS calculations were conducted using X-ray data of **$V_8'$**·$3C_7H_8$ (Figure 2 in the manuscript), **$V_8'$**·$3C_8H_{10}$ (Table S2), **$V_4'$-Me** (Table S3), and **$V_4'$-Et** (Table S4). Bond valence parameters: V(IV)−O (1.784 Å), V(V)−O (1.803 Å), and V−N (1.86 Å).[S7]

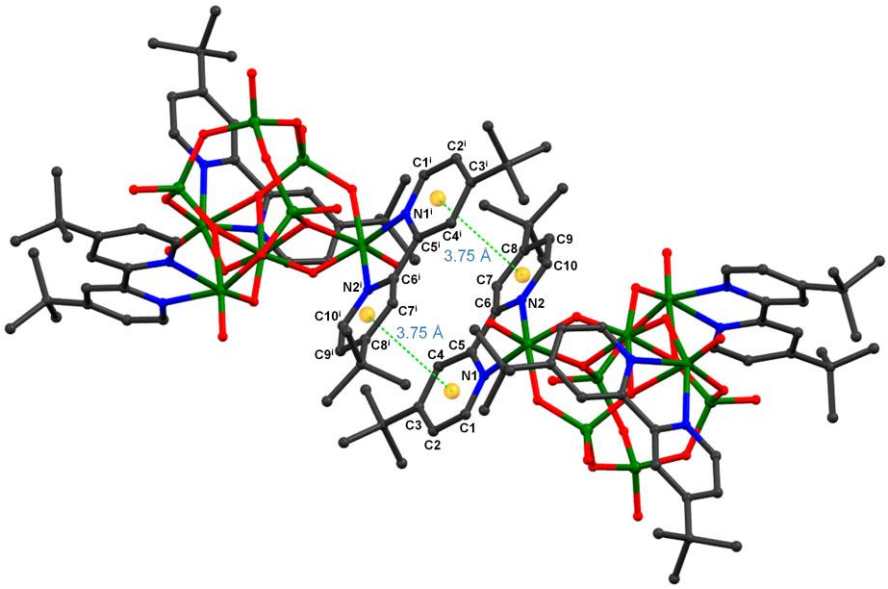



**Figure S4.** π-π interactions between pyridine rings of $\mathbf{V_8'}\cdot 3C_7H_8$ with a centroid–centroid distance of 3.75 Å. Symmetry operators: (i) 1 − X, 1 − Y, − Z.

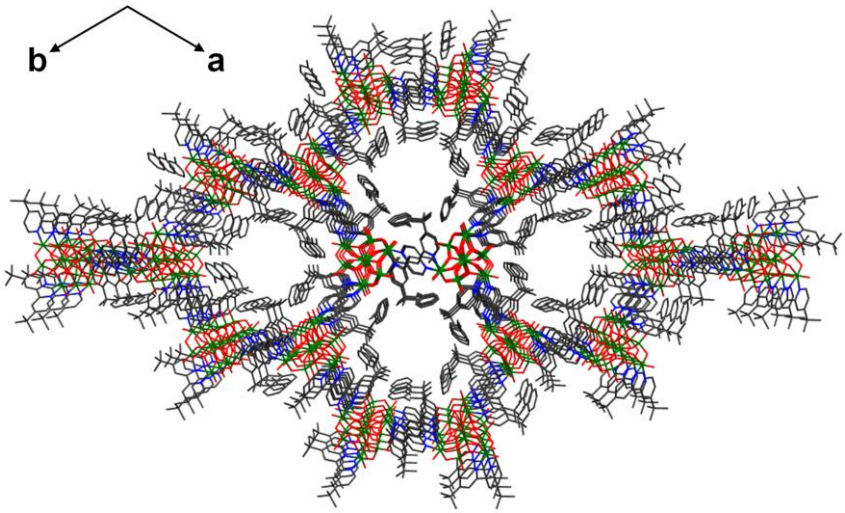



**Figure S5.** Crystal packing view of $\mathbf{V_8'}\cdot 3C_7H_8$ along the *c*-axis.

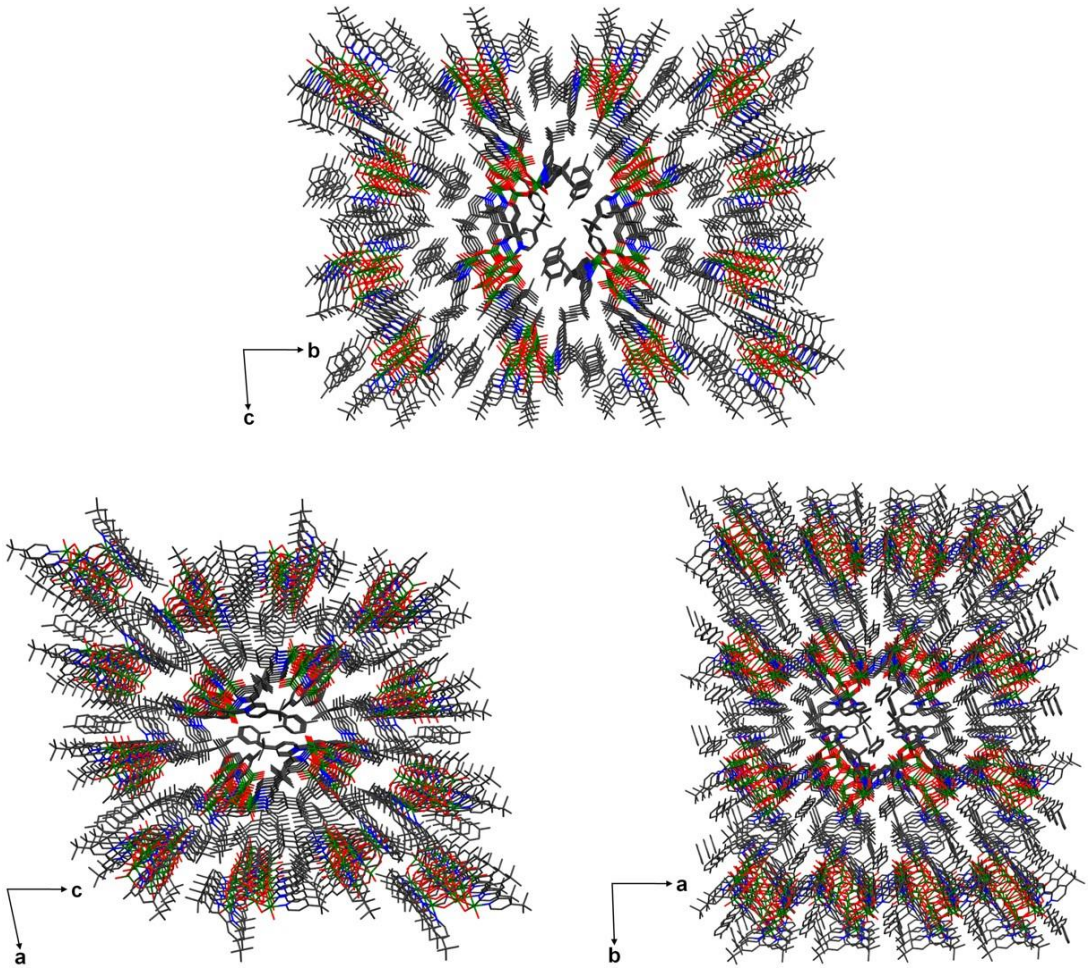



**Figure S6.** Crystal packing view of $\mathbf{V_8'}\cdot 3C_8H_{10}$ along the *a*-axis (top), *b*-axis (bottom left), and *c*-axis (bottom right).

**Results of SQUID Measurements**

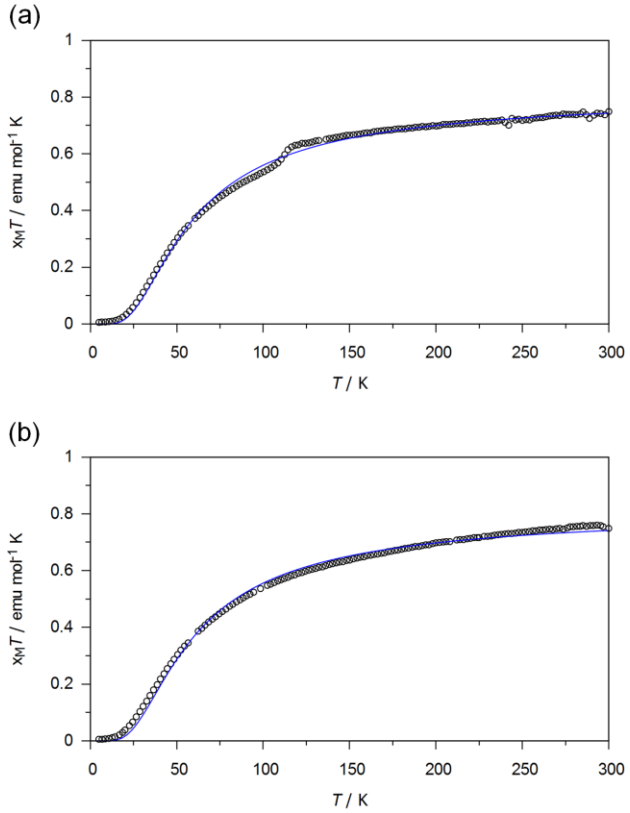



**Figure S7.** $\chi_M T$ versus $T$ plots for (a) **V$_4$′-Me** and (b) **V$_4$′-Et**. The solid blue lines represent the theoretical fitting with eq 1 in the manuscript.

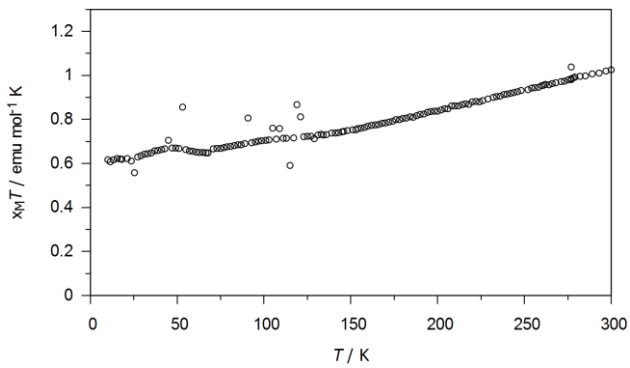



**Figure S8.** $\chi_M T$ versus $T$ plots for **V$_8$′**·1.28$C_8H_{10}$.

**Results of TG-DTA analysis**

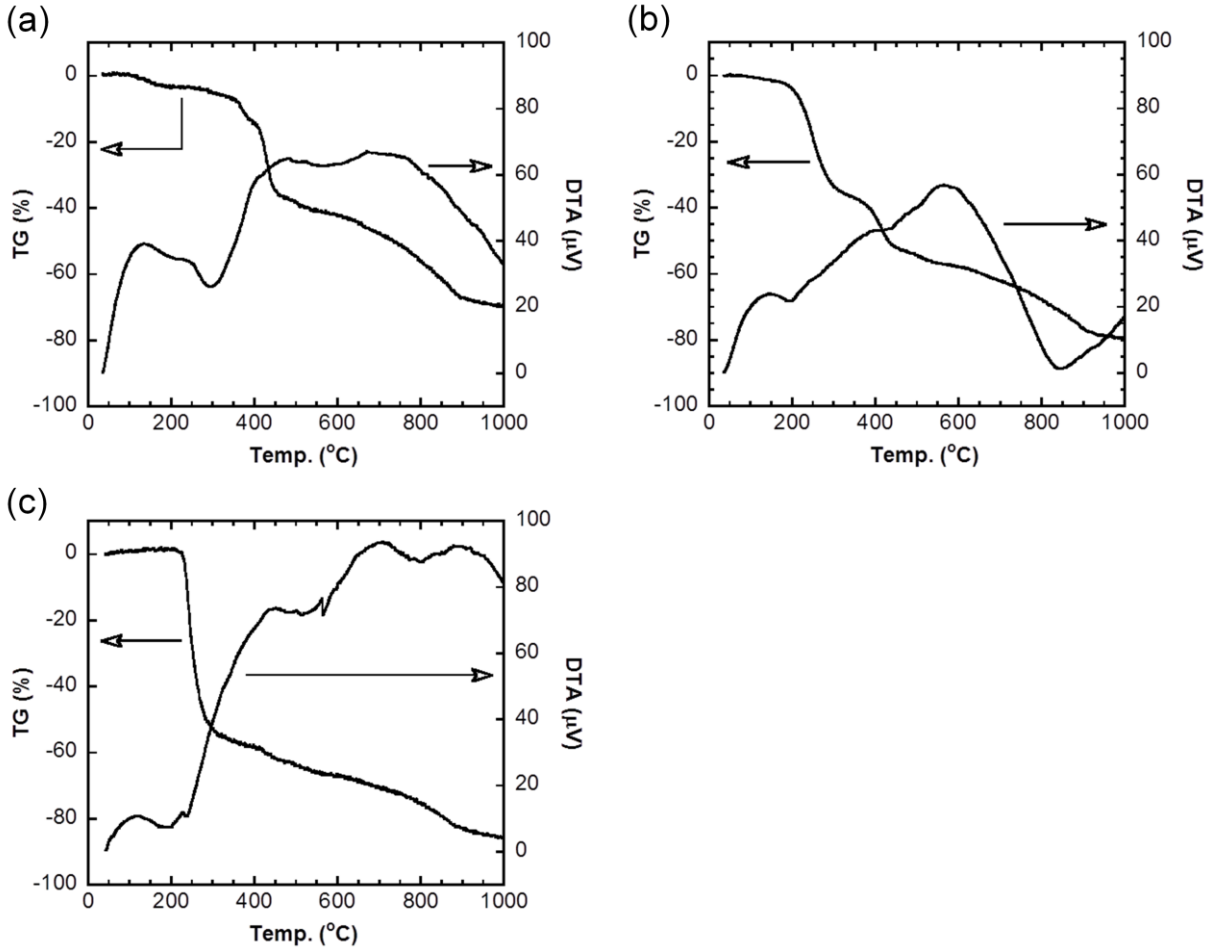



**Figure S9.** TG-DTA profile of (a) **V₈′**·0.42$C_7H_8$, (b) **V₄′-Me**, and (c) **V₄′-Et** measured in Ar gas atmosphere. Heating rate: 50 °C/min.

The weight loss of **V₈′**·0.42$C_7H_8$ (2.94%) observed at 100−170 °C is attributed to the release of 0.42 toluene molecules (calcd. 2.49%) per empirical formula unit. The next weight loss (32.29%) at 200−460 °C is considered to be due to the loss of two coordinated 4,4'-$^t$Bubpy molecules (calcd. 34.51%) (Figure S9a). In addition, the weight losses of **V₄′-Me** and **V₄′-Et** were observed at 150−450 °C (50.44%) and at 200−300 °C (54.16%), respectively, which may result from the loss of two 4,4'-$^t$Bubpy molecules (calcd. 52.48% for **V₄′-Me**; calcd. 48.49% for **V₄′-Et**) (Figures S9b and S9c).

**References**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