

Electronic Supporting Information

Double complex salts based on tetraamminplatinum(II) and vanadyl(IV) bisoxalate for the preparation of bimetallic Pt-V alloy

Sofia N. Vorobyeva,^{*a} Zakhar V. Rudzis,^{a,b} Taisiya S. Sukhikh,^a Evgeny Yu. Filatov,^a Pavel E. Plusnin,^a Vladimir A. Nadolnny,^a Artem S. Bogomyakov,^c and Sergey V. Korenev^a

^{a.} *Nikolaev Institute of Inorganic Chemistry, Siberian Branch of Russian Academy of Sciences, 3, Acad. Lavrentiev Ave., Novosibirsk 630090, Russia. E-mail: vorobyeva@niic.nsc.ru(Sofiya N. Vorobyeva)*

^{b.} *Novosibirsk State University, 1, Pirogova str., Novosibirsk 630090, Russia .*

^{c.} *International Tomography Center, SB RAS, Institutskaya str., 3a, Novosibirsk, Russian Federation.*

Table of Contents

Table S1.....	6
Figure S1.....	7
Figure S2.....	7
Figure S3.....	7
Figure S4.....	8
Figure S5.....	8
Figure S6.....	8
Figure S7.....	9
Figure S8.....	9
Figure S9.....	9
Figure S10.....	10
Figure S11.....	10
Figure S12.....	10
IR spectra.....	11
Figure S13.....	11
Figure S14.....	11
Figure S15.....	12
Figure S16.....	12
Figure S17.....	13
Figure S18.....	13
Figure S19.....	14
Figure S20.....	14
Figure S21.....	15
Figure S22.....	15
EPR.....	16
Figure S23.....	16
TG.....	17
Figure S24.....	17
Figure S25.....	18
Figure S26.....	19
Figure S27.....	20
Figure S28.....	21
Figure S29.....	22

Table S1. Crystal data and structure refinement for **(Bu₄N)₂[VO(C₂O₄)₂] (I)**, **{(Bu₄N)(VO₂(C₂O₄))_n (II)}**, **[Pt(NH₃)₄][VO(H₂O)(C₂O₄)₂]·2H₂O (III)** and **{[Pt(NH₃)₄][VO(C₂O₄)₂]}_n (IV)**.

Complex	(Bu₄N)₂[VO(C₂O₄)₂] (I)	{(Bu₄N)(VO₂(C₂O₄))_n (II)}	[Pt(NH₃)₄][VO(H₂O)(C₂O₄)₂]·2H₂O (III)	{[Pt(NH₃)₄][VO(C₂O₄)₂]}_n (IV)
Empirical formula	C ₃₆ H ₇₂ N ₂ O ₉ V	C ₁₈ H ₃₆ NO ₆ V	C ₄ H ₁₈ N ₄ O ₁₂ PtV	C ₄ H ₁₂ N ₄ O ₉ PtV
Formula weight	727.89	413.42	560.25	506.21
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group, Z	C2/c, 4	P2 ₁ /n, 4	P-1, 2	C2/c, 8
<i>a</i> (Å)	18.9092(19)	8.8694(5)	7.27950(10)	19.603(8)
<i>b</i> (Å)	13.9416(12)	14.9160(6)	8.24340(10)	7.945(3)
<i>c</i> (Å)	18.272(3)	16.6499(7)	12.9863(2)	15.358(6)
<i>α</i> /°	90	90	108.1350(10)	90
<i>β</i> /°	120.899(3)	103.309(2)	97.3040(10)	97.242(13)
<i>γ</i> /°	90	90	95.7430(10)	90
<i>V</i> (Å ³)	4133.4(8)	2143.56(17)	726.455(18)	2372.8(16)
<i>d</i> Calc(g/cm ³)	1.170	1.281	2.561	2.834
<i>μ</i> /mm ⁻¹	0.289	0.493	10.331	12.618
<i>F</i> (000)	1588.0	888.0	534.0	1896.0
Crystal size (mm)	0.09 × 0.09 × 0.07	0.09 × 0.06 × 0.05	0.1 × 0.09 × 0.04	0.05 × 0.03 × 0.01
2 θ range for data collection/°	5.022– 56.558	4.81-54.978	3.348 - 66.264	5.348-46.522
Index ranges	-25 ≤ <i>h</i> ≤ 2 -18 ≤ <i>k</i> ≤ 18 -24 ≤ <i>l</i> ≤ 23	-11 ≤ <i>h</i> ≤ 11 -19 ≤ <i>k</i> ≤ 19 -20 ≤ <i>l</i> ≤ 21	-10 ≤ <i>h</i> ≤ 11 -12 ≤ <i>k</i> ≤ 12 -19 ≤ <i>l</i> ≤ 19	-21 ≤ <i>h</i> ≤ 21 -8 ≤ <i>k</i> ≤ 8 -17 ≤ <i>l</i> ≤ 10
Reflections collected	25901	23280	15497	4516
Independent reflections (<i>R</i> _{int})	5125 [<i>R</i> _{int} = 0.0738, <i>R</i> _{sigma} = 0.0543]	4914 [<i>R</i> _{int} = 0.0771, <i>R</i> _{sigma} = 0.0698]	5492 [<i>R</i> _{int} = 0.0258, <i>R</i> _{sigma} = 0.0279]	1703 [<i>R</i> _{int} = 0.1196, <i>R</i> _{sigma} = 0.1500]
Completeness to theta = 50.5°	99.9 %	99.8 %	100 %	99.8 %
Data / restraints / parameters	5125/0/222	4914/0/239	5492/0/213	1703/78/179
Goodness-of-fit on <i>F</i> ²	1.040	1.035	1.065	0.950
Final <i>R</i> indices (<i>I</i> ≥ 2σ (<i>I</i>))	<i>R</i> ₁ = 0.0449, <i>wR</i> ₂ = 0.1022	<i>R</i> ₁ = 0.0473, <i>wR</i> ₂ = 0.0951	<i>R</i> ₁ = 0.0192, <i>wR</i> ₂ = 0.0414	<i>R</i> ₁ = 0.0561, <i>wR</i> ₂ = 0.0987
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0648, <i>wR</i> ₂ = 0.1157	<i>R</i> ₁ = 0.0729, <i>wR</i> ₂ = 0.1098	<i>R</i> ₁ = 0.0252, <i>wR</i> ₂ = 0.0433	<i>R</i> ₁ = 0.0996, <i>wR</i> ₂ = 0.1190
Largest diff. peak and hole (e/Å ³)	0.41/-0.32	0.32/-0.33	0.61/-1.58	1.33/-1.55

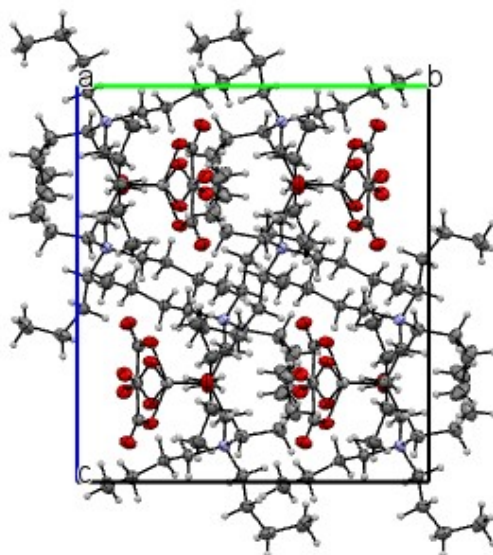


Figure S1. Packing of $(\text{Bu}_4\text{N})_2[\text{VO}(\text{C}_2\text{O}_4)_2]$ (**I**) (view along the a axis).

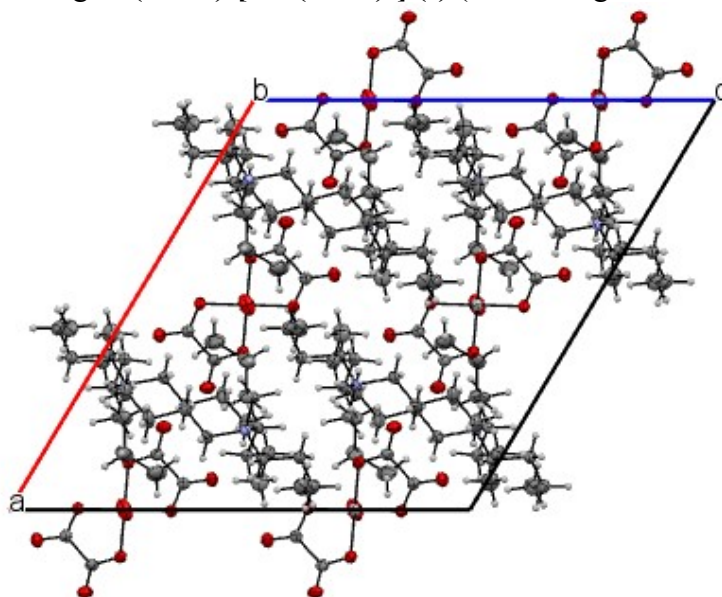


Figure S2. Packing of $(\text{Bu}_4\text{N})_2[\text{VO}(\text{C}_2\text{O}_4)_2]$ (**I**) (view along the b axis).

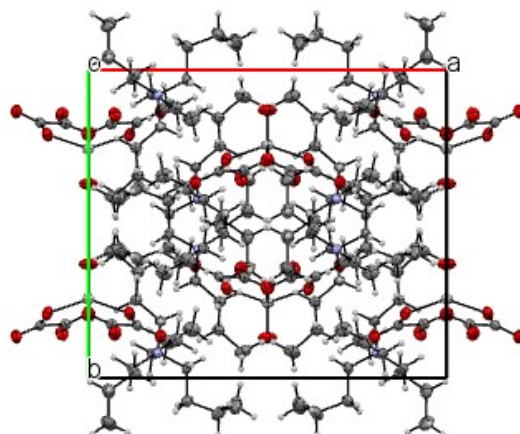


Figure S3. Packing of $(\text{Bu}_4\text{N})_2[\text{VO}(\text{C}_2\text{O}_4)_2]$ (**I**) (view along the c axis).

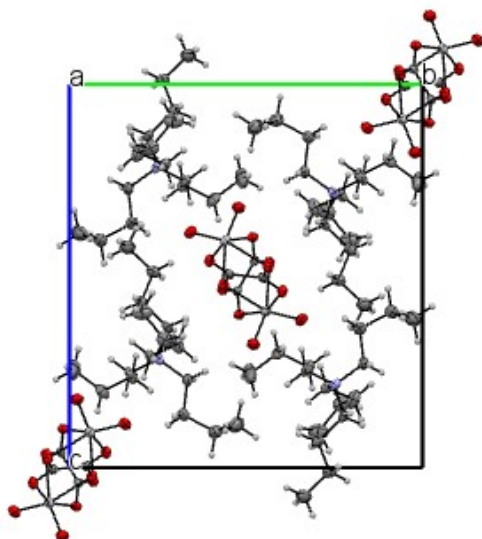


Figure S4. Packing of $\{(\text{Bu}_4\text{N})(\text{VO}_2(\text{C}_2\text{O}_4))\}_n$ (II) (view along the *a* axis).

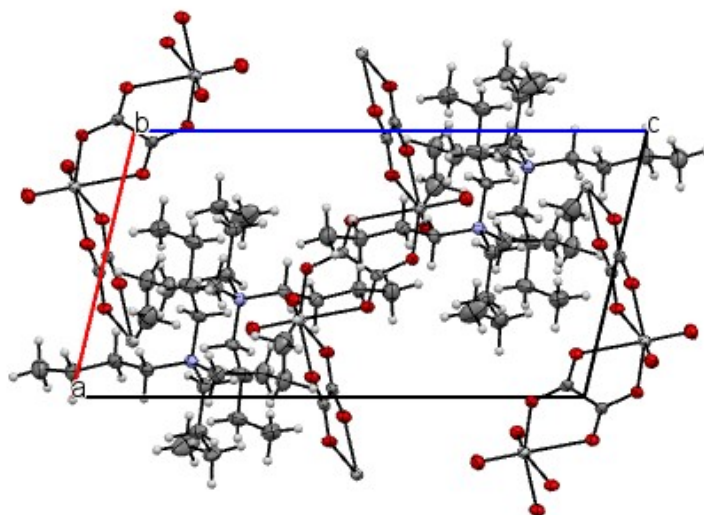


Figure S5. Packing of $\{(\text{Bu}_4\text{N})(\text{VO}_2(\text{C}_2\text{O}_4))\}_n$ (II) (view along the *b* axis).

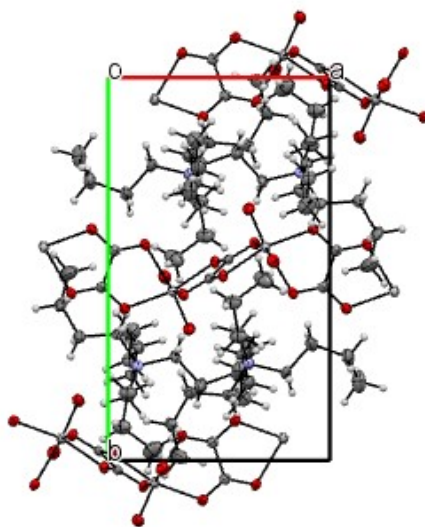


Figure S6. Packing of $\{(\text{Bu}_4\text{N})(\text{VO}_2(\text{C}_2\text{O}_4))\}_n$ (II) (view along the *c* axis).

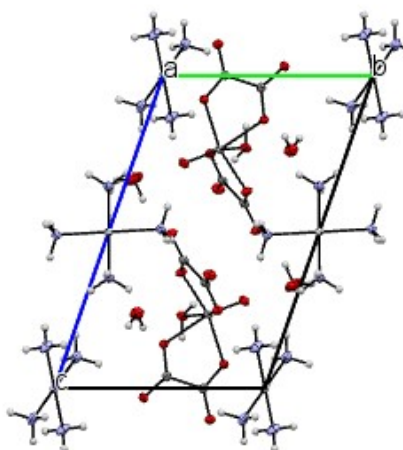


Figure S7. Packing of $[\text{Pt}(\text{NH}_3)_4][\text{VO}(\text{H}_2\text{O})(\text{C}_2\text{O}_4)_2]\cdot 2\text{H}_2\text{O}$ (III) (view along the a axis).

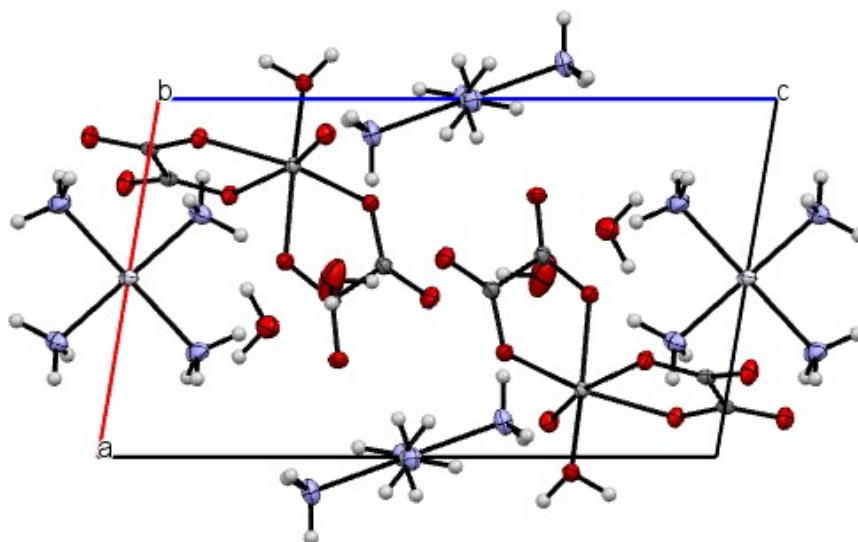


Figure S8. Packing of $[\text{Pt}(\text{NH}_3)_4][\text{VO}(\text{H}_2\text{O})(\text{C}_2\text{O}_4)_2]\cdot 2\text{H}_2\text{O}$ (III) (view along the b axis).

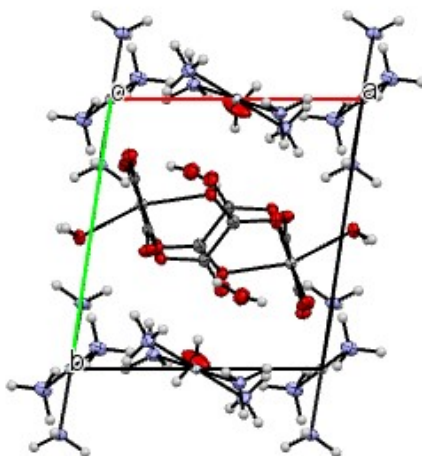


Figure S9. Packing of $[\text{Pt}(\text{NH}_3)_4][\text{VO}(\text{H}_2\text{O})(\text{C}_2\text{O}_4)_2]\cdot 2\text{H}_2\text{O}$ (III) (view along the c axis).

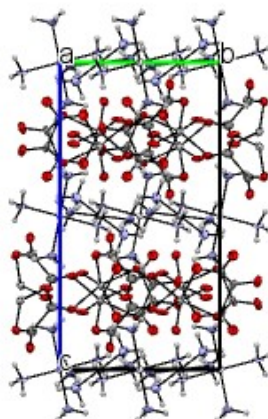


Figure S10. Packing of $\{[\text{Pt}(\text{NH}_3)_4][\text{VO}(\text{C}_2\text{O}_4)_2]\}_n$ (IV) (view along the a axis).

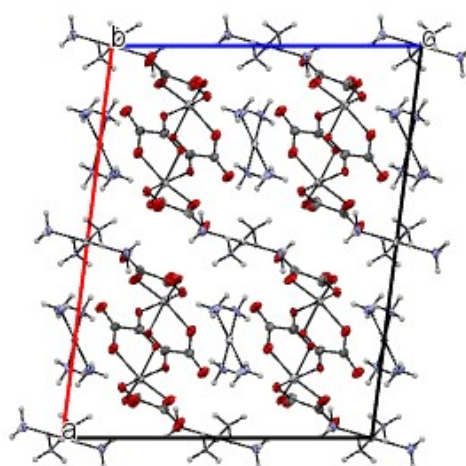


Figure S11. Packing of $\{[\text{Pt}(\text{NH}_3)_4][\text{VO}(\text{C}_2\text{O}_4)_2]\}_n$ (IV) (view along the b axis).

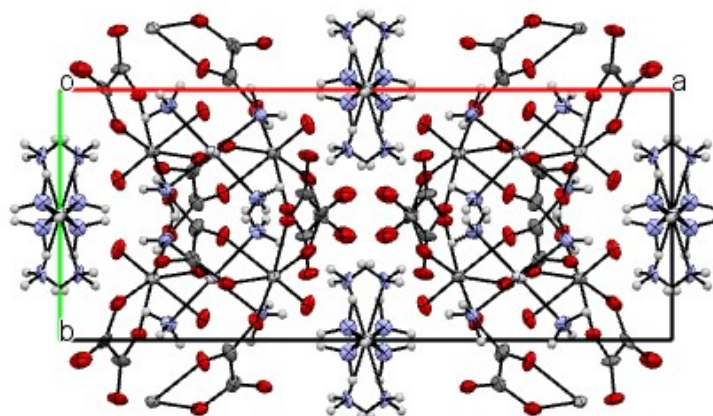


Figure S12. Packing of $\{[\text{Pt}(\text{NH}_3)_4][\text{VO}(\text{C}_2\text{O}_4)_2]\}_n$ (IV) (view along the c axis).

IR spectra

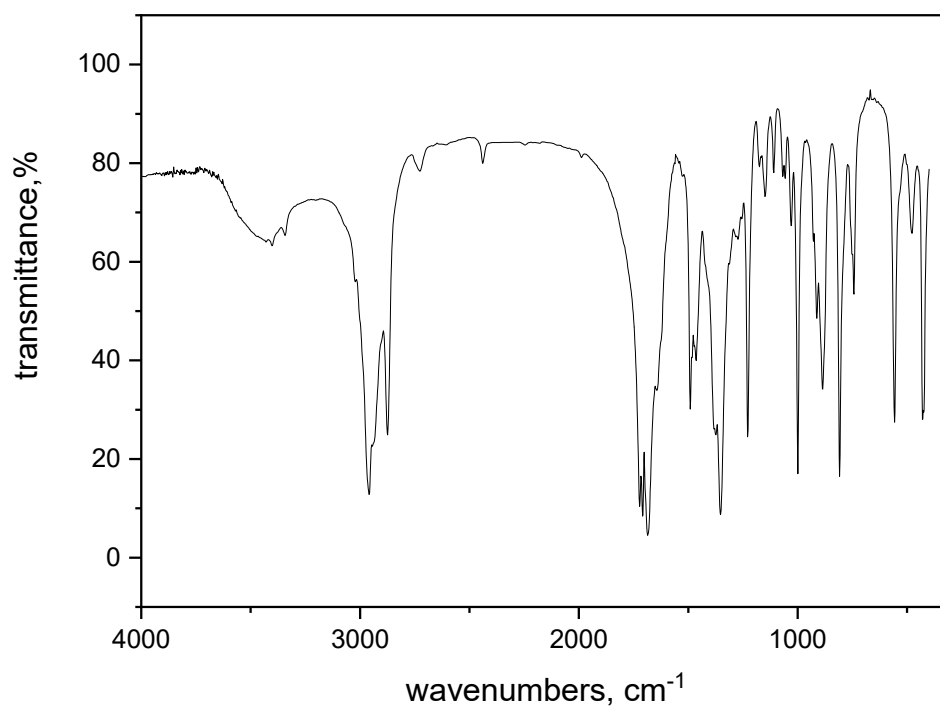


Figure S13. IR spectrum of $(\text{Bu}_4\text{N})_2[\text{VO}(\text{C}_2\text{O}_4)_2]$ (I).

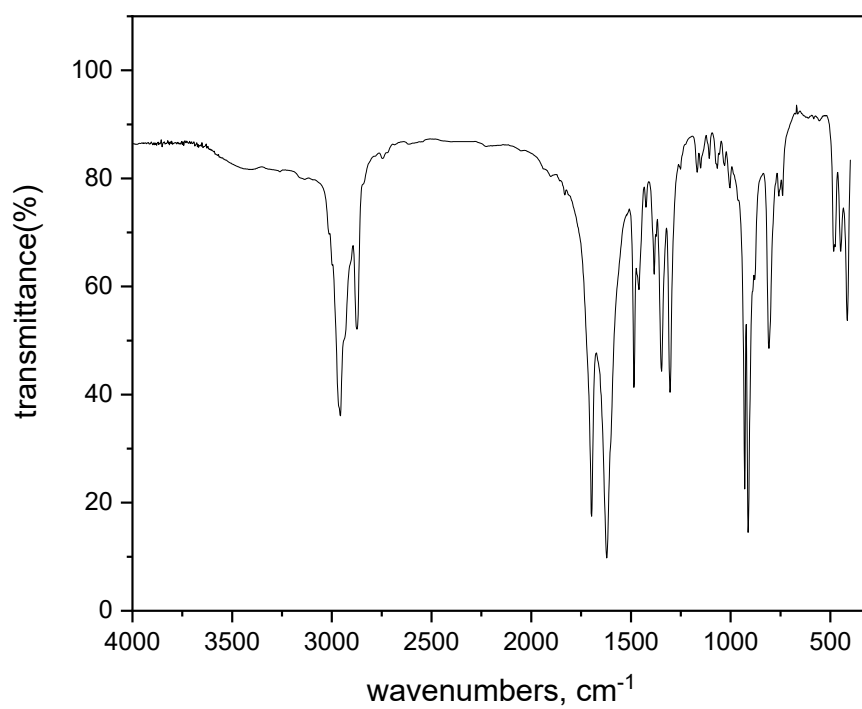


Figure S14. IR spectrum of $\{(\text{Bu}_4\text{N})(\text{VO}_2(\text{C}_2\text{O}_4))\}_n$ (II).

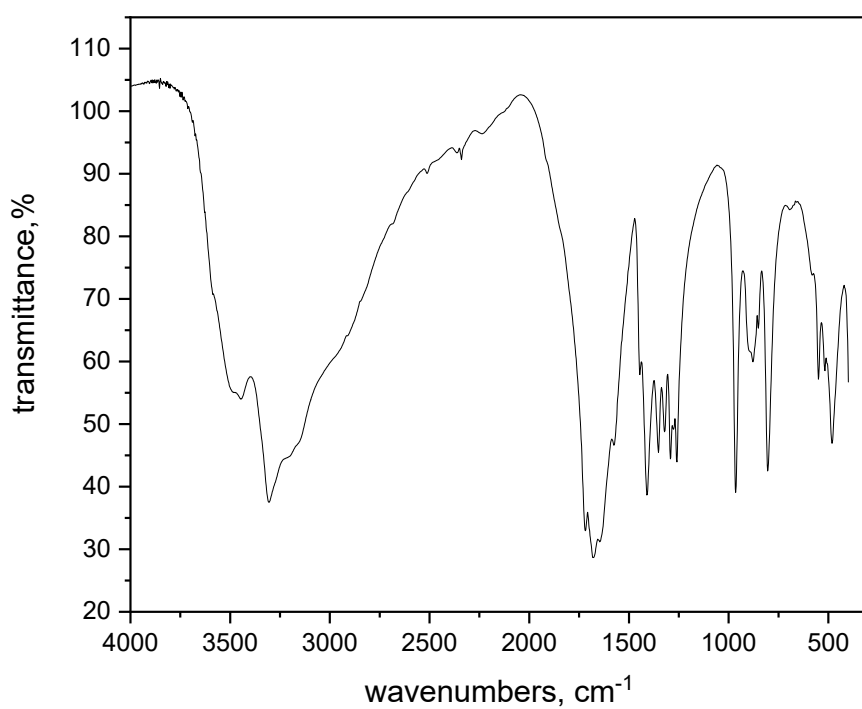


Figure S15. IR spectrum of $[\text{Pt}(\text{NH}_3)_4][\text{VO}(\text{H}_2\text{O})(\text{C}_2\text{O}_4)_2] \cdot 2\text{H}_2\text{O}(\text{III})$.

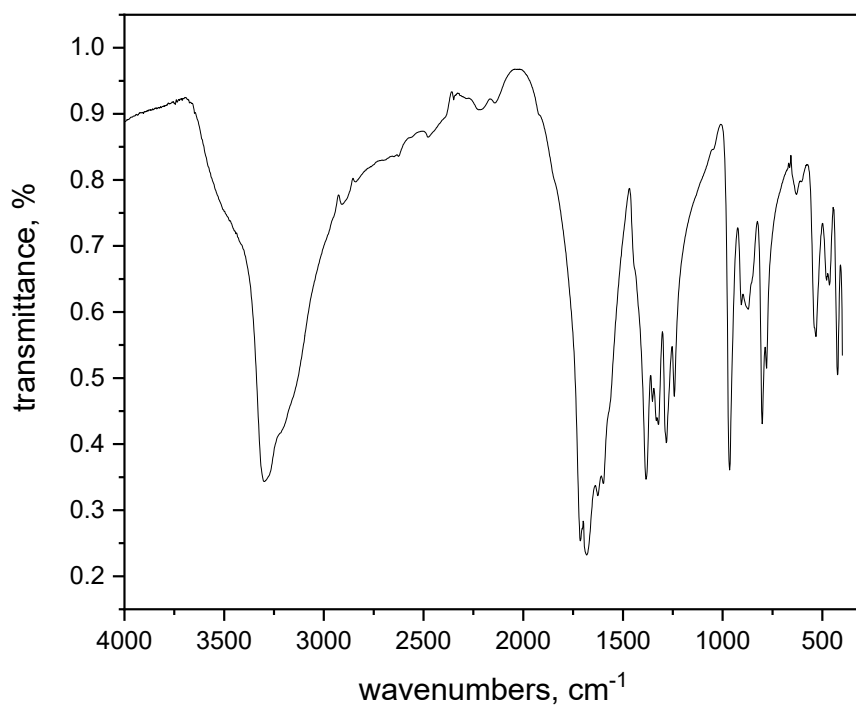


Figure S16. IR spectrum of $\{[\text{Pt}(\text{NH}_3)_4][\text{VO}(\text{C}_2\text{O}_4)_2]\}_n(\text{IV})$.

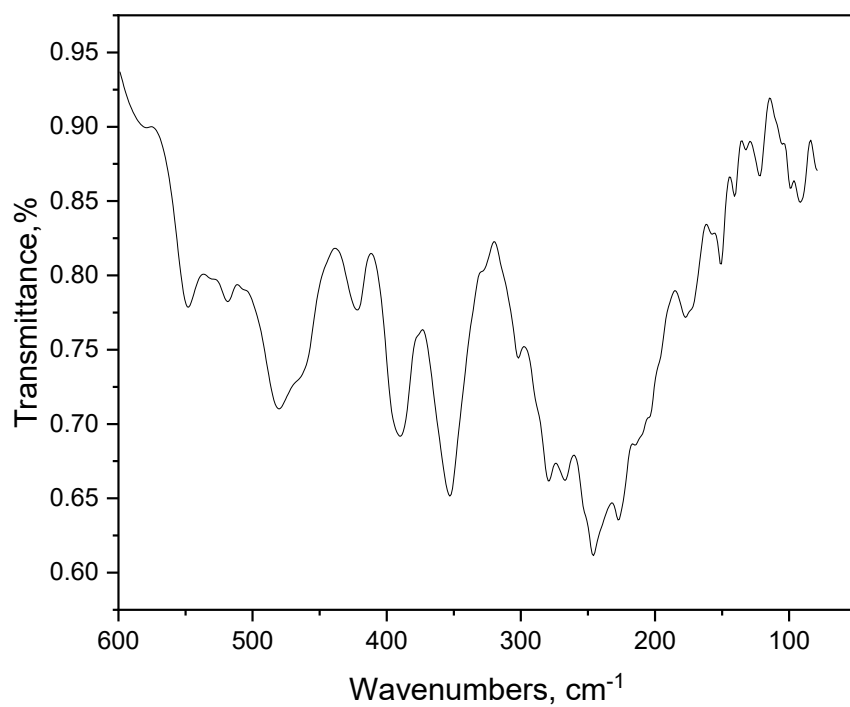


Figure S17. IR spectrum of $[\text{Pt}(\text{NH}_3)_4][\text{VO}(\text{H}_2\text{O})(\text{C}_2\text{O}_4)_2] \cdot 2\text{H}_2\text{O}(\text{III})$.

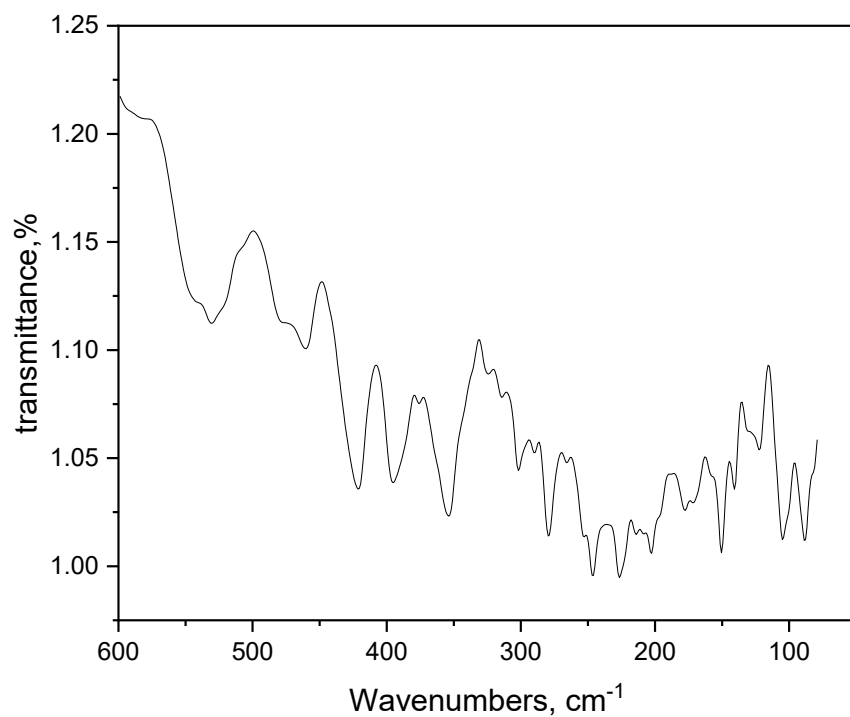


Figure S18. IR spectrum of $\{[\text{Pt}(\text{NH}_3)_4][\text{VO}(\text{C}_2\text{O}_4)_2]\}_n(\text{IV})$.

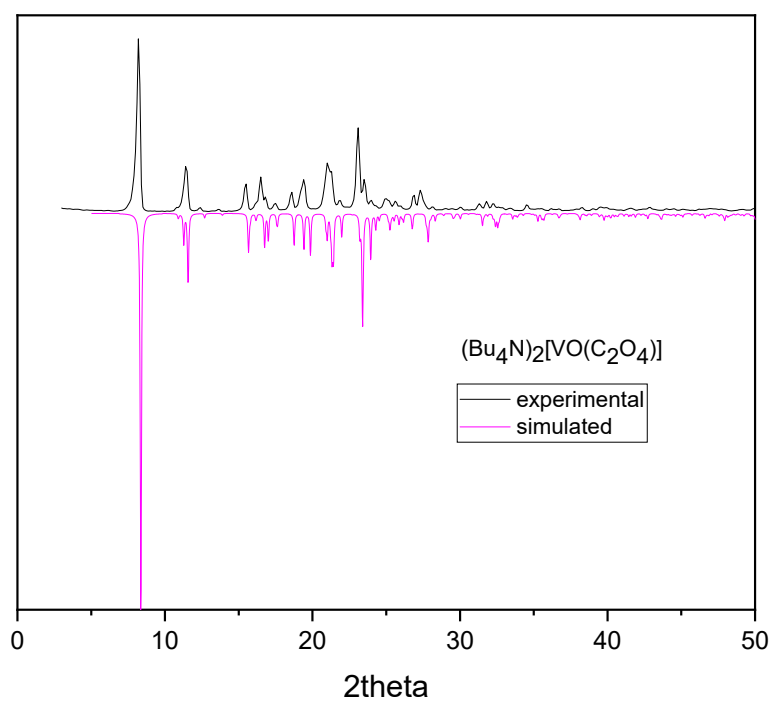


Figure S19. X-ray powder diffraction pattern of $(\text{Bu}_4\text{N})_2[\text{VO}(\text{C}_2\text{O}_4)_2](\text{I})$.

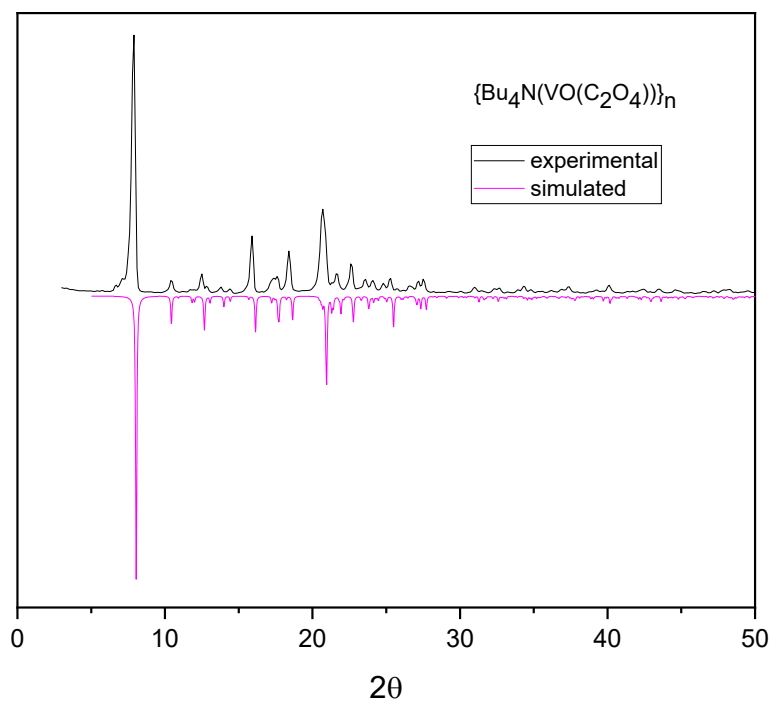


Figure S20. X-ray powder diffraction pattern of $\{(\text{Bu}_4\text{N})(\text{VO}_2(\text{C}_2\text{O}_4))\}_n(\text{II})$.

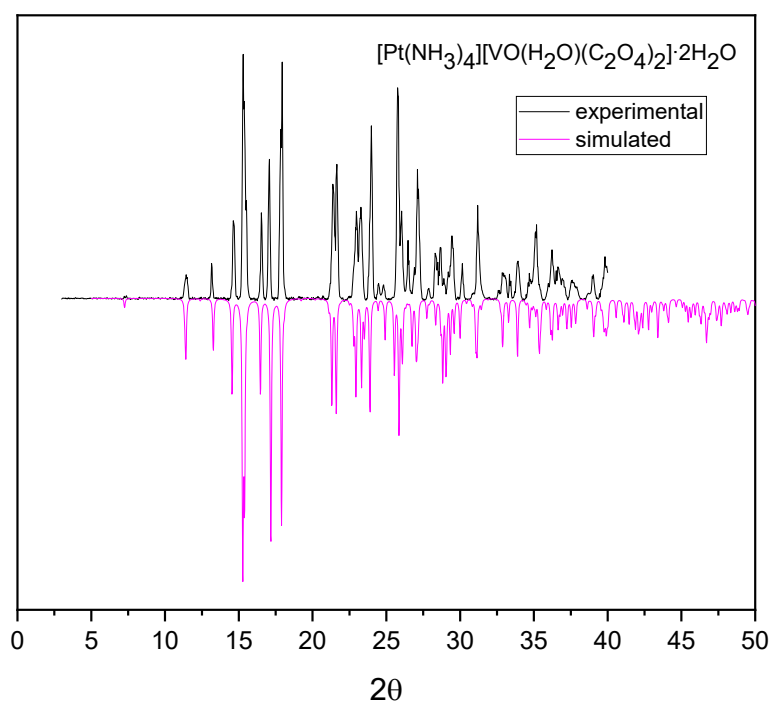


Figure S21. X-ray powder diffraction pattern of $[\text{Pt}(\text{NH}_3)_4][\text{VO}(\text{H}_2\text{O})(\text{C}_2\text{O}_4)_2] \cdot 2\text{H}_2\text{O}$ (III).

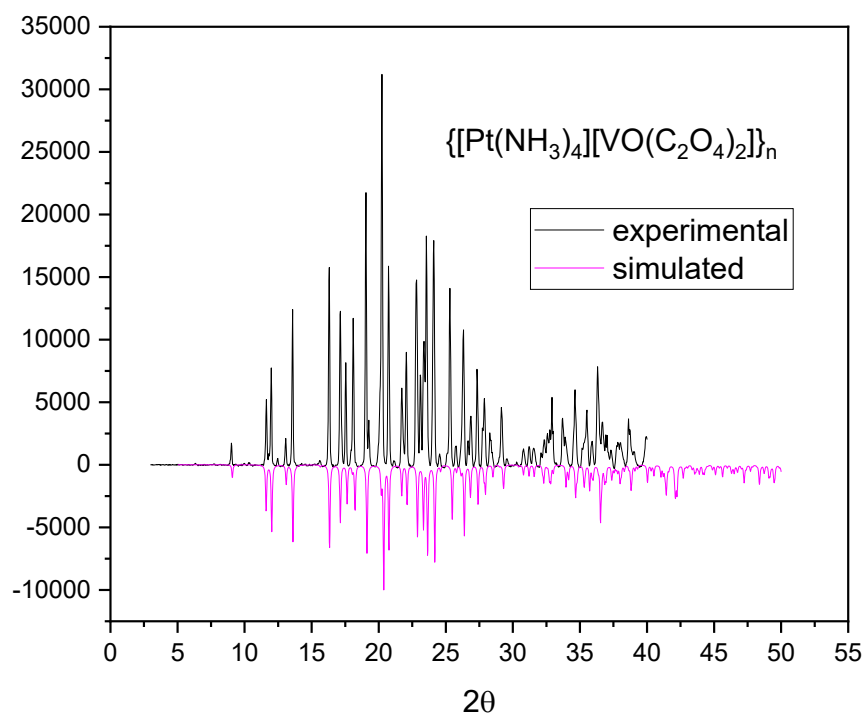


Figure S22. X-ray powder diffraction pattern of $\{[\text{Pt}(\text{NH}_3)_4][\text{VO}(\text{C}_2\text{O}_4)_2]\}_n$ (IV).

EPR

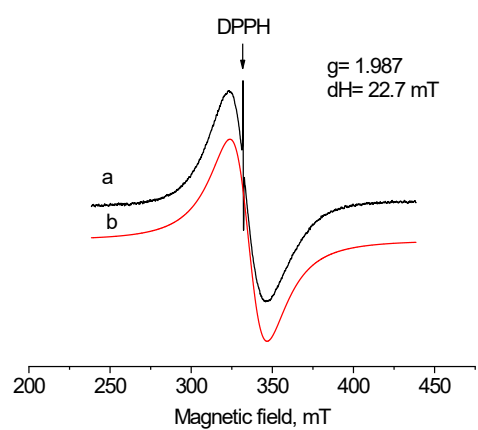


Figure S23. EPR spectra of $\{[\text{Pt}(\text{NH}_3)_4][\text{VO}(\text{C}_2\text{O}_4)_2]\}_n$ (IV): a- experimental, b- simulated.

TG

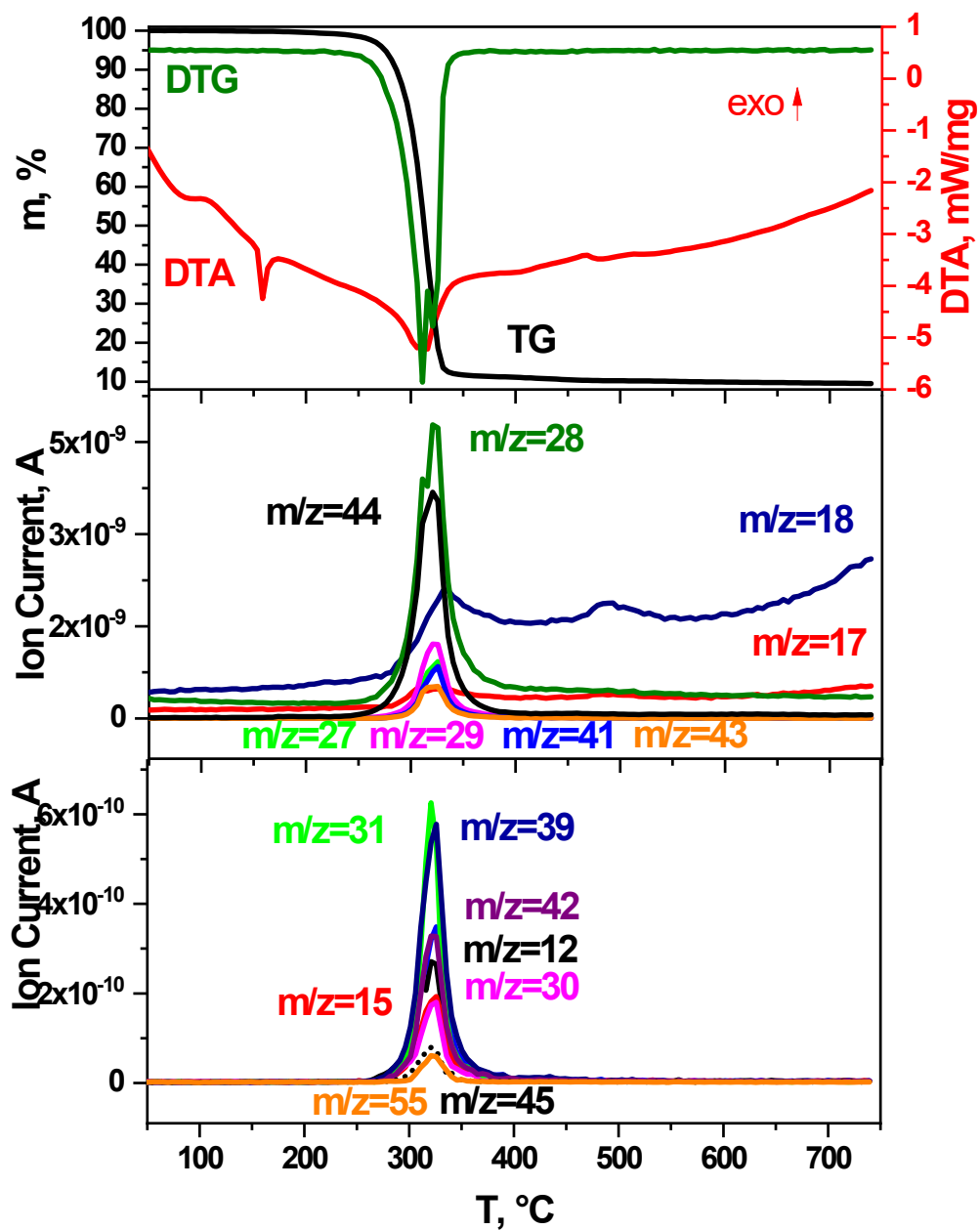


Figure S24. TG curves of $(\text{Bu}_4\text{N})_2[\text{VO}(\text{C}_2\text{O}_4)_2](\text{I})$ obtained in reducing atmosphere at a heating rate of 10 deg/min.

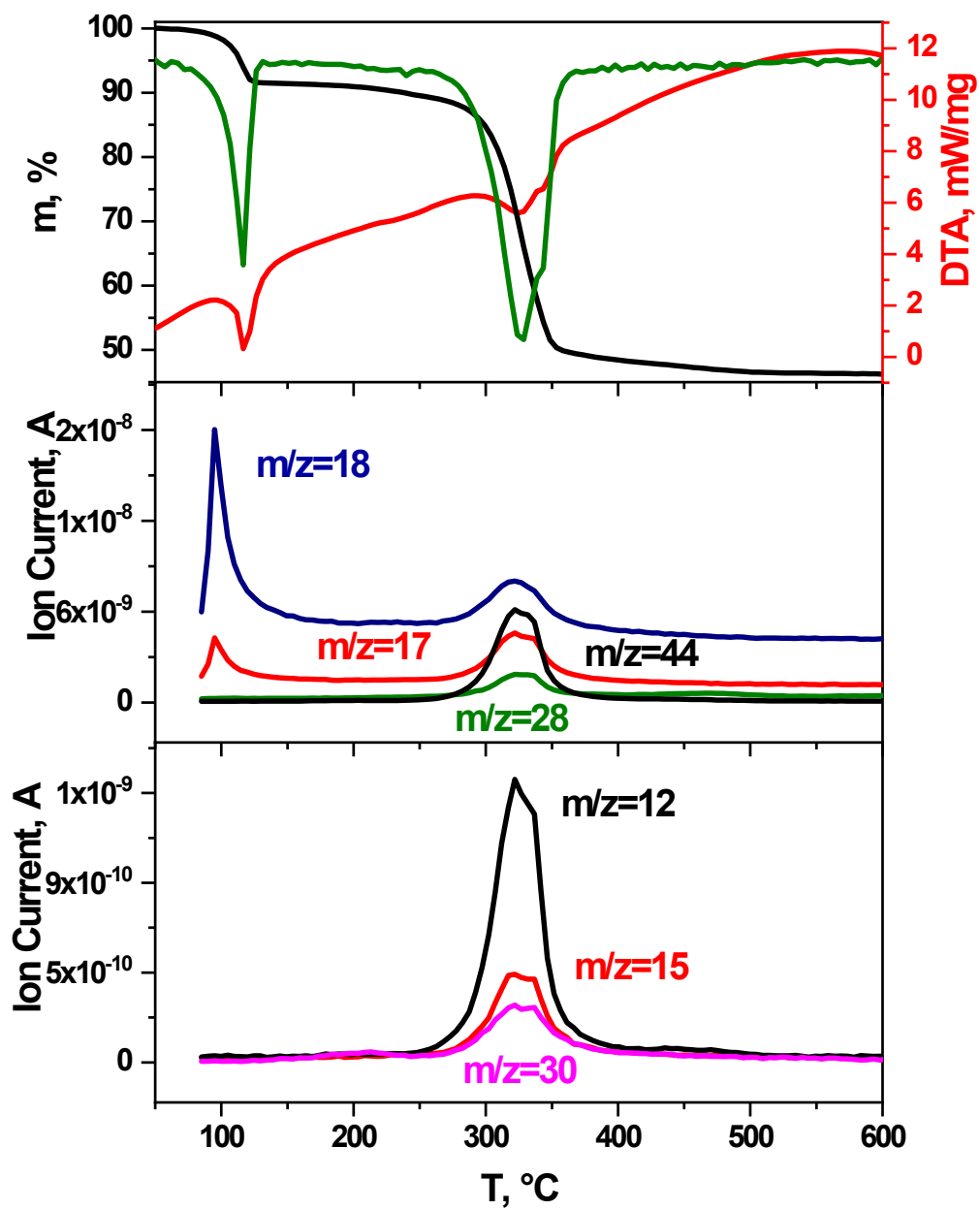


Figure S25. TG curves of $[\text{Pt}(\text{NH}_3)_4][\text{VO}(\text{H}_2\text{O})(\text{C}_2\text{O}_4)_2] \cdot 2\text{H}_2\text{O}(\text{III})$ obtained in inert (He) atmosphere at a heating rate of 10 deg/min.

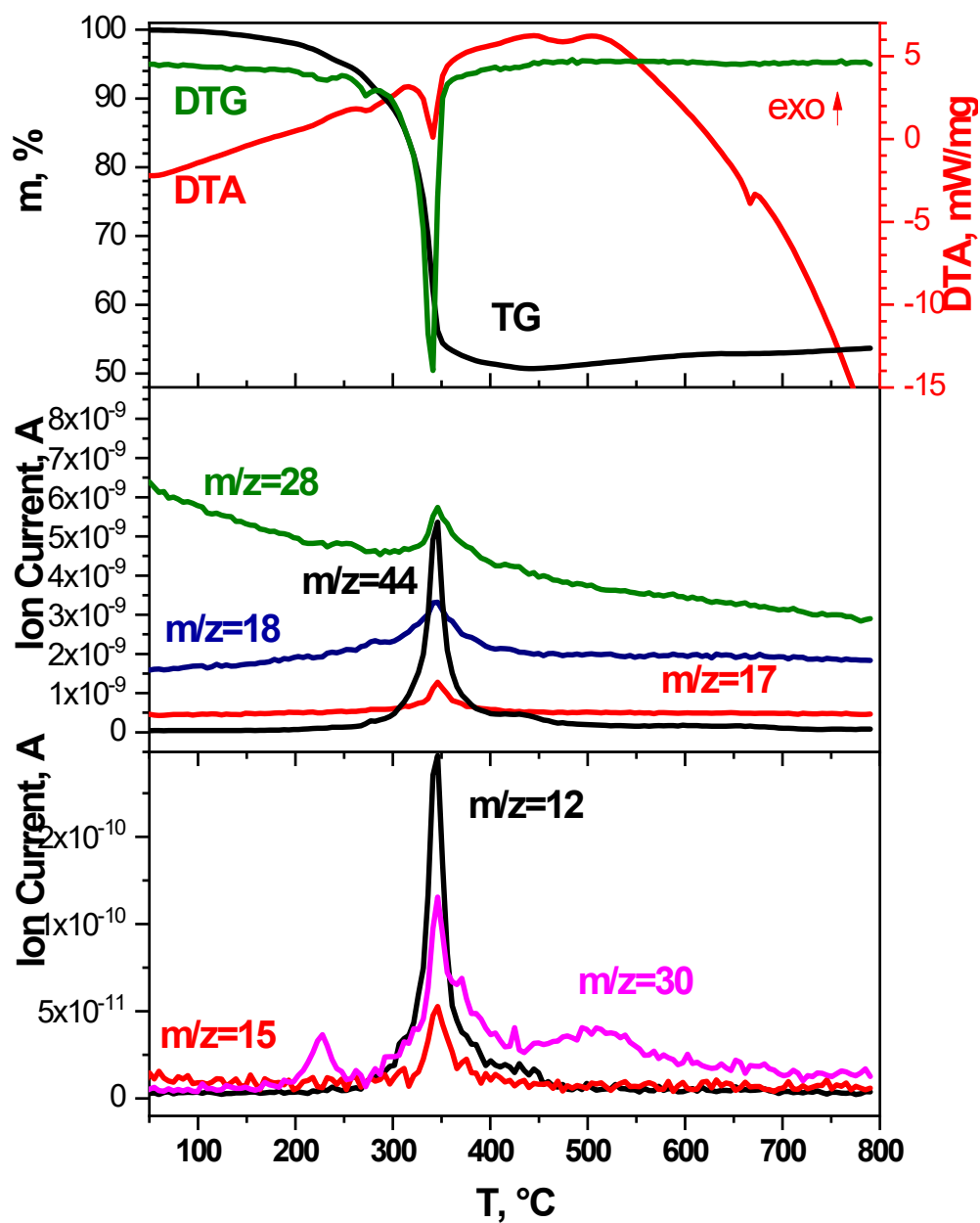


Figure S26. TG curves of $\{[\text{Pt}(\text{NH}_3)_4][\text{VO}(\text{C}_2\text{O}_4)_2]\}_n$ (IV) obtained in inert atmosphere at a heating rate of 10 deg/min.

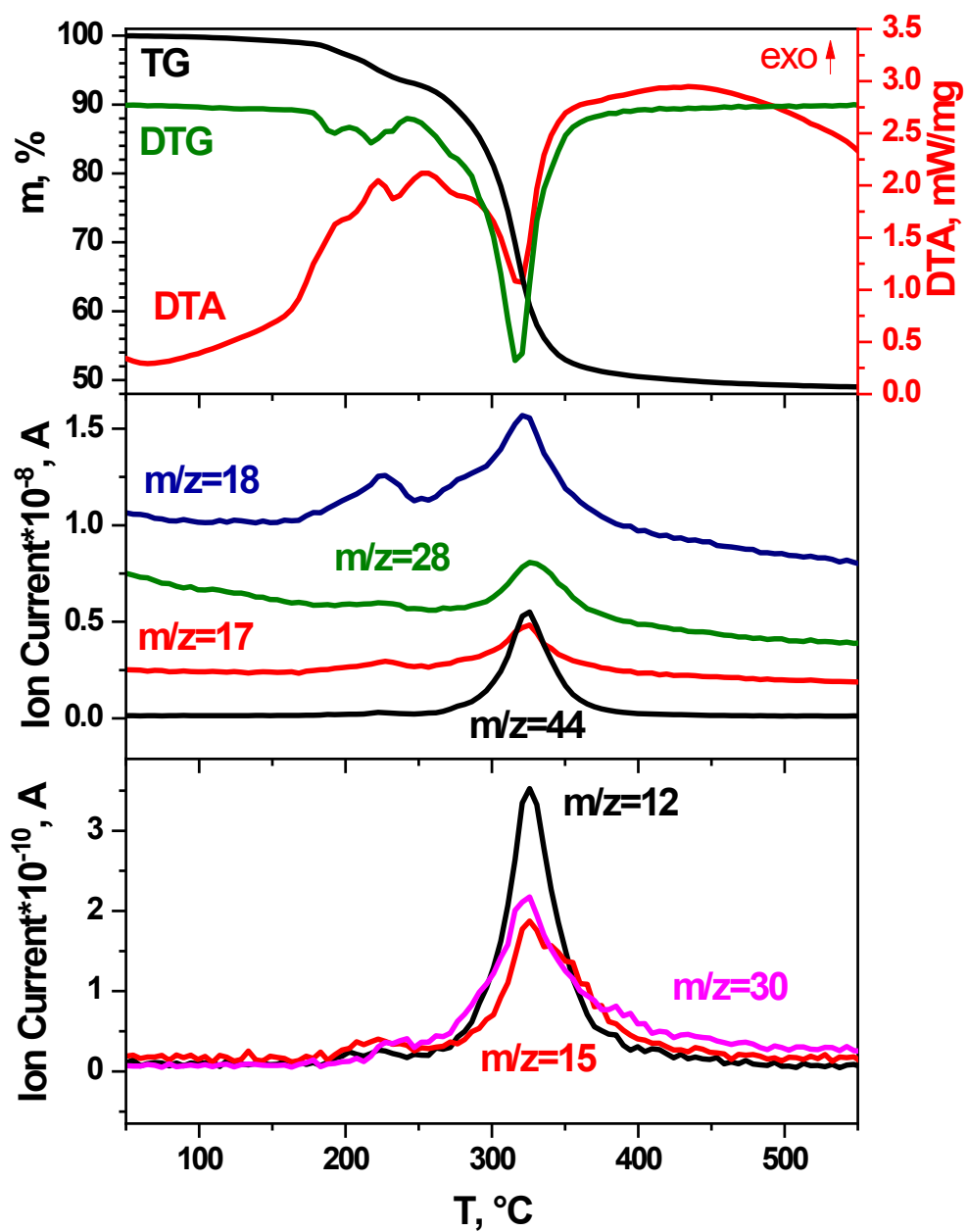


Figure S27. TG curves of of $\{[\text{Pt}(\text{NH}_3)_4][\text{VO}(\text{C}_2\text{O}_4)_2]\}_n$ (IV) obtained in reducing atmosphere at a heating rate of 10 deg/min.

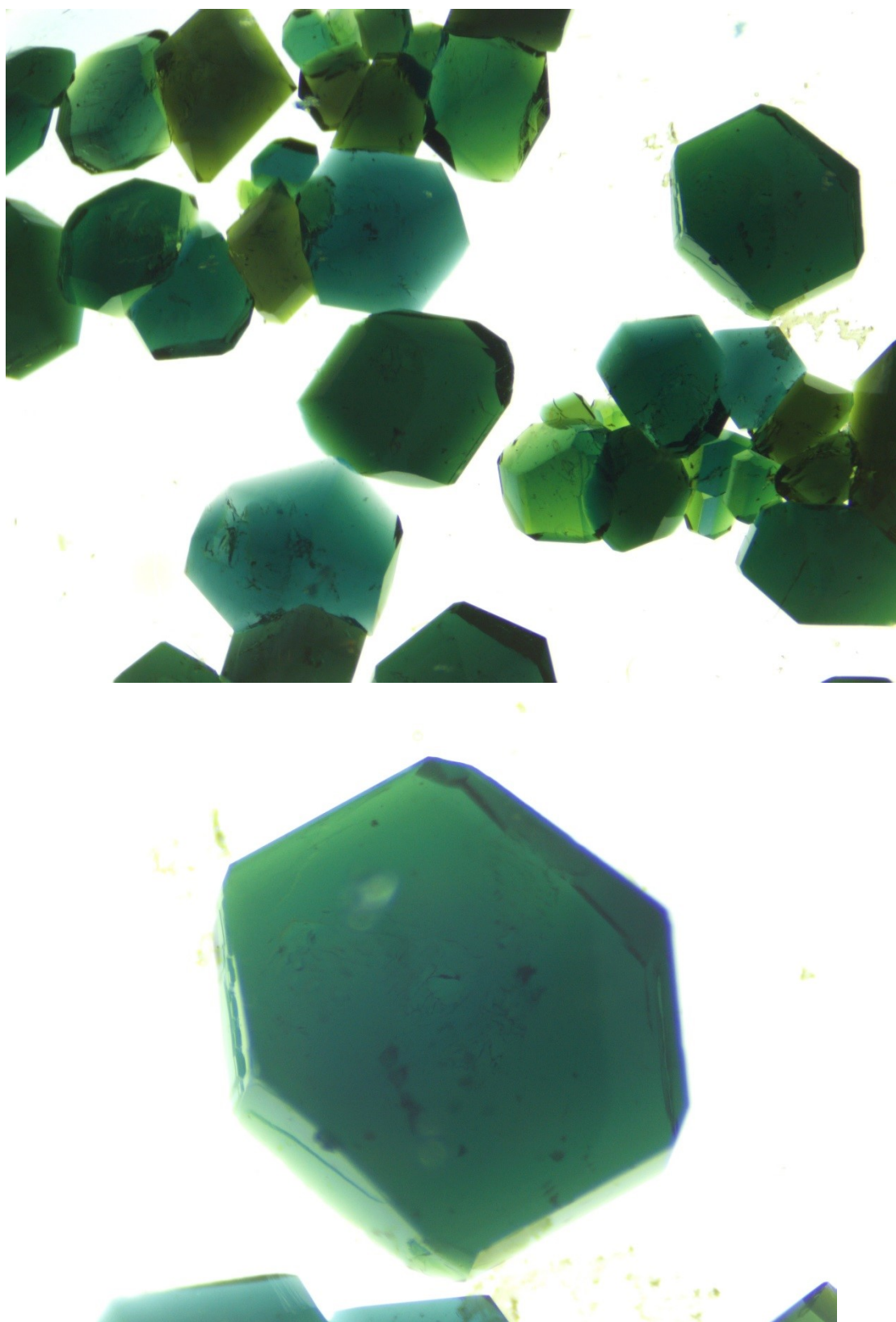


Figure S28. Microscope image of $(\text{Bu}_4\text{N})_2[\text{VO}(\text{C}_2\text{O}_4)_2](\text{I})$.

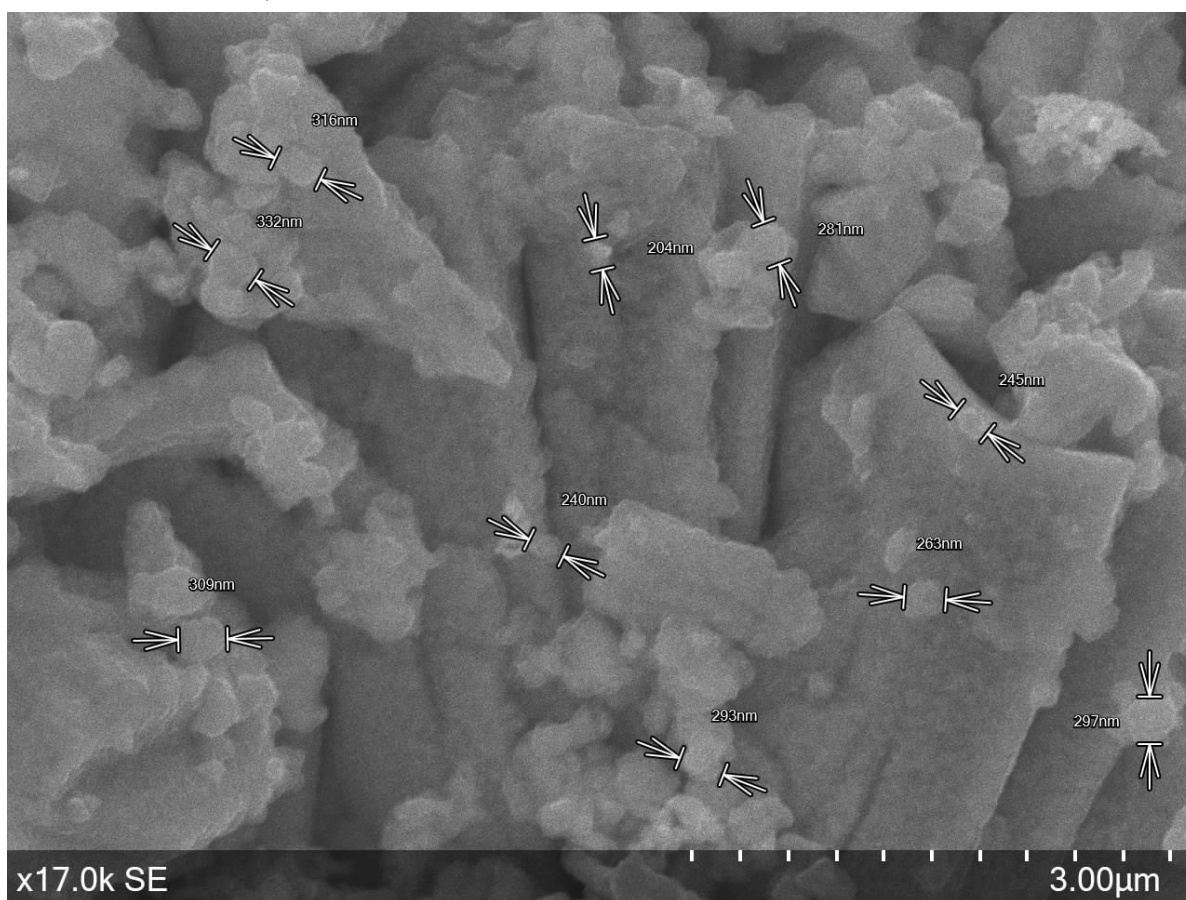
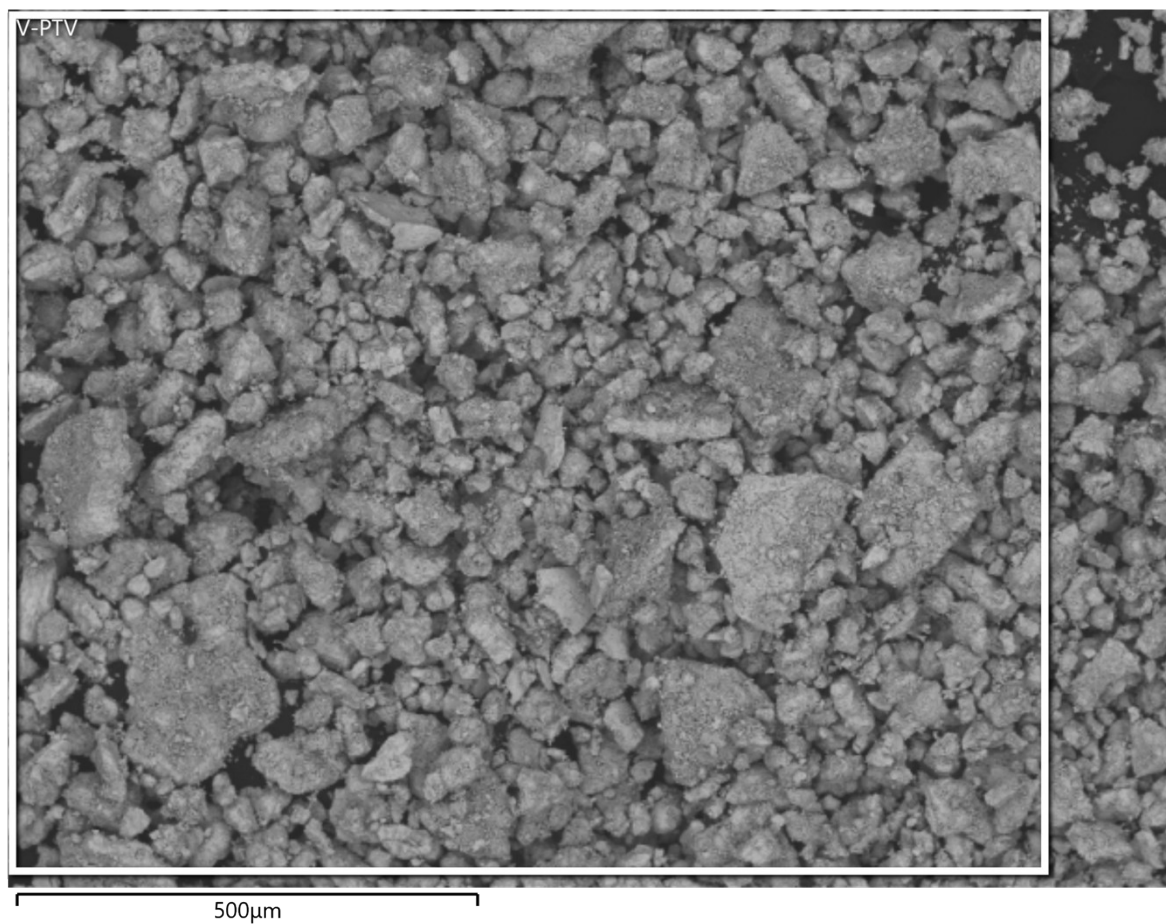


Figure S29. SEM pictures of IV thermolysis product at 700°C for 1 hour at two different scales.

