Tetragonal Symmetric Shaped $\{V^{IV}_4O_8\}$ Cubane-Encasing Vanado-Phosphate Derivative: Prototype Liquid Configured Device Grade Supercapacitor with Enhanced Performance

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Supporting Information

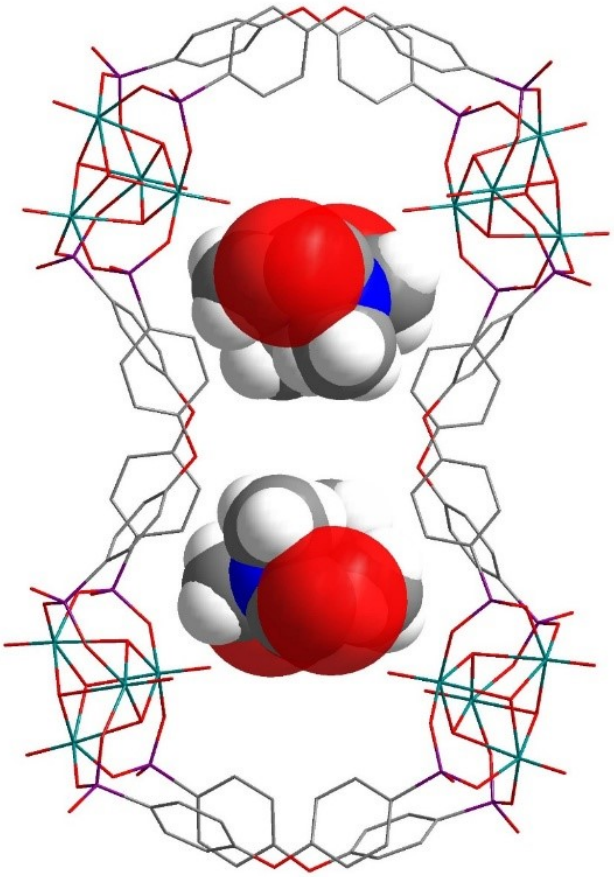


Figure S1. Wire frame representation of the polyanion $[H_{10}(V^{IV}_4O_8)_4\{O_3P\text{-}C_6H_4\text{-}O\text{-}C_6H_4\text{-}PO_3\}_8 \subset 4DMF \bullet 4H_2O]^{22-}$ **(1)**, including respective encapsulated DMF molecules (space filling representation). Color code: V green, P purple, O red, N blue, C black, H white.

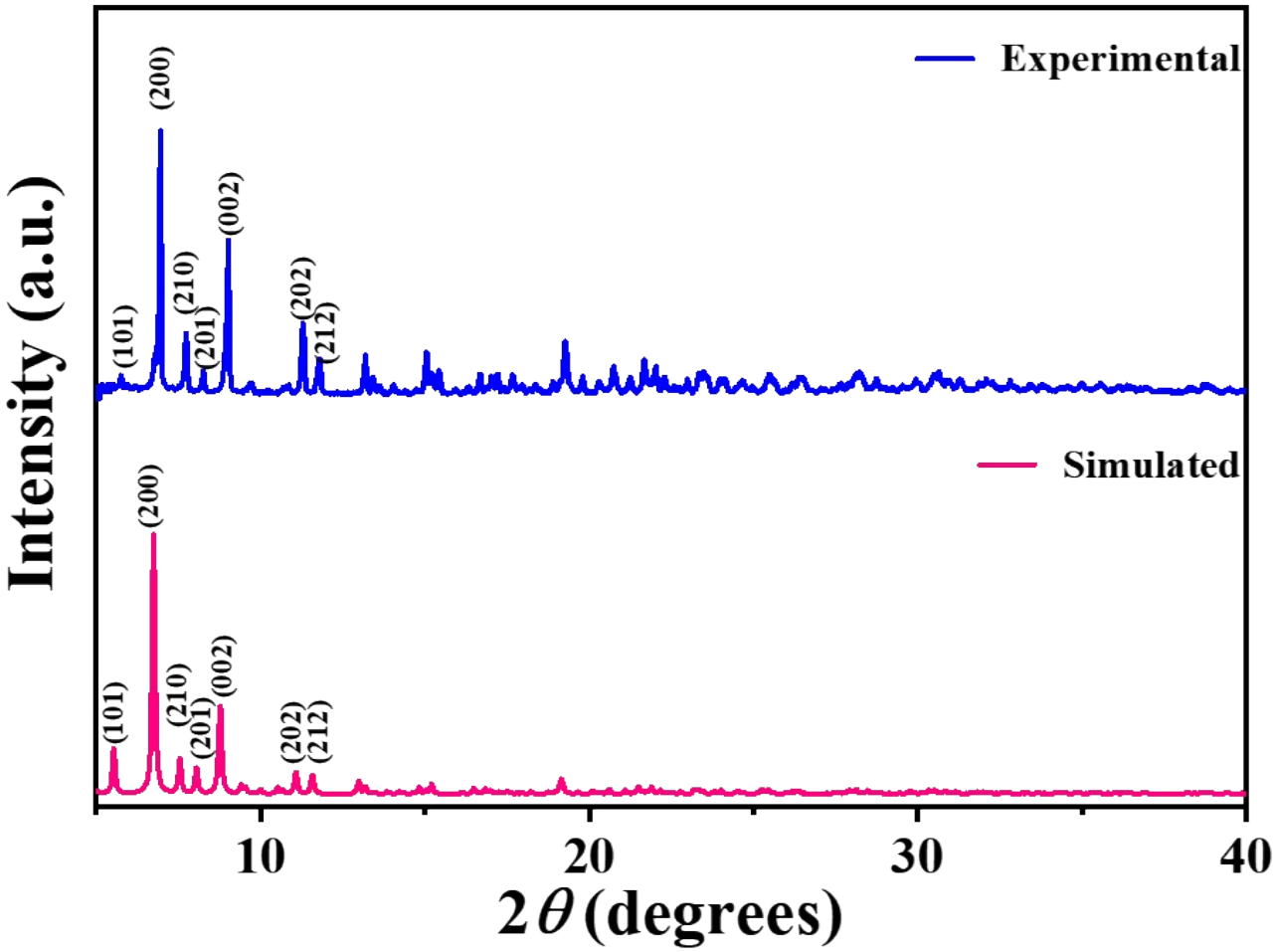


Figure S2. Comparative PXRD of compound **1a** (simulated vs experimental).

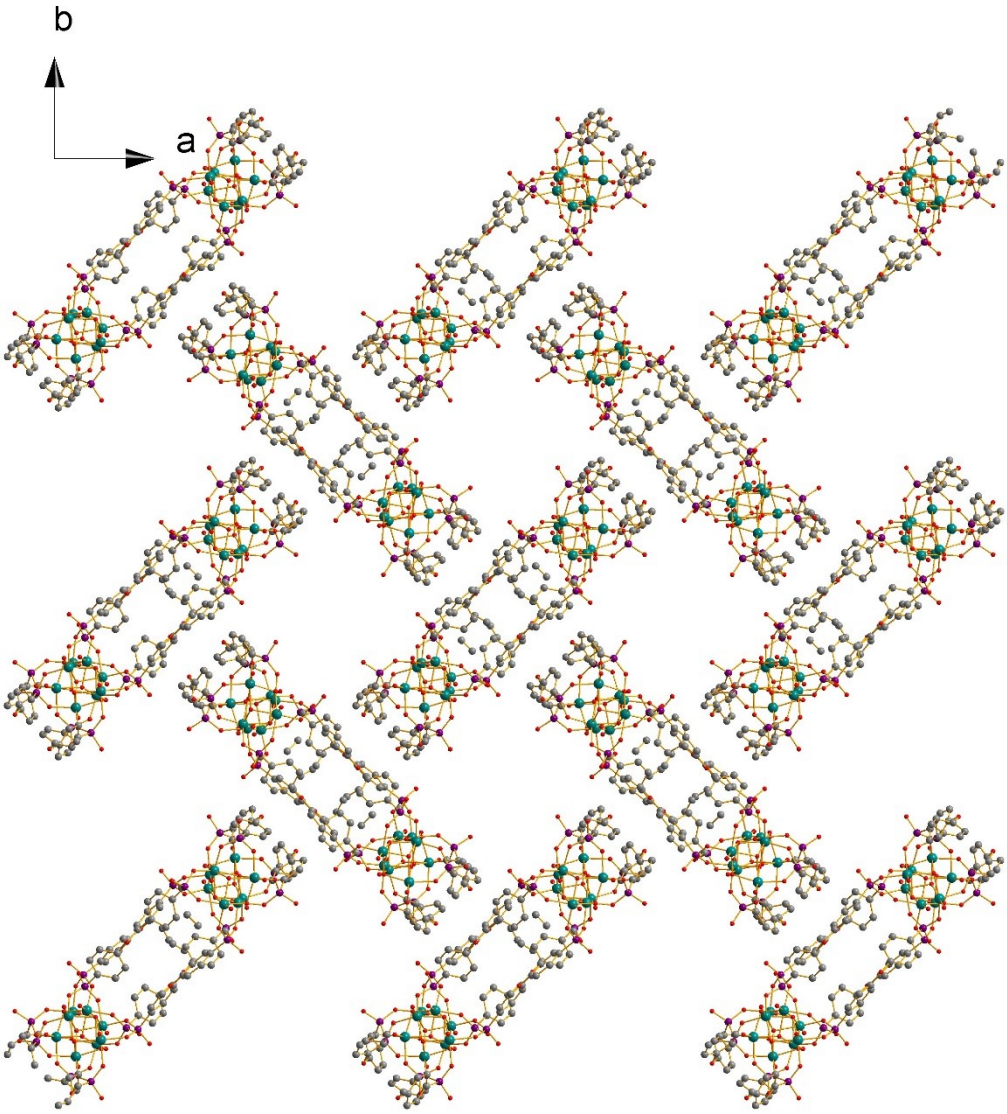


Figure S3. Crystal packing arrangement for polyanion **1** within compound **1a**, as viewed along the *c*-axis.

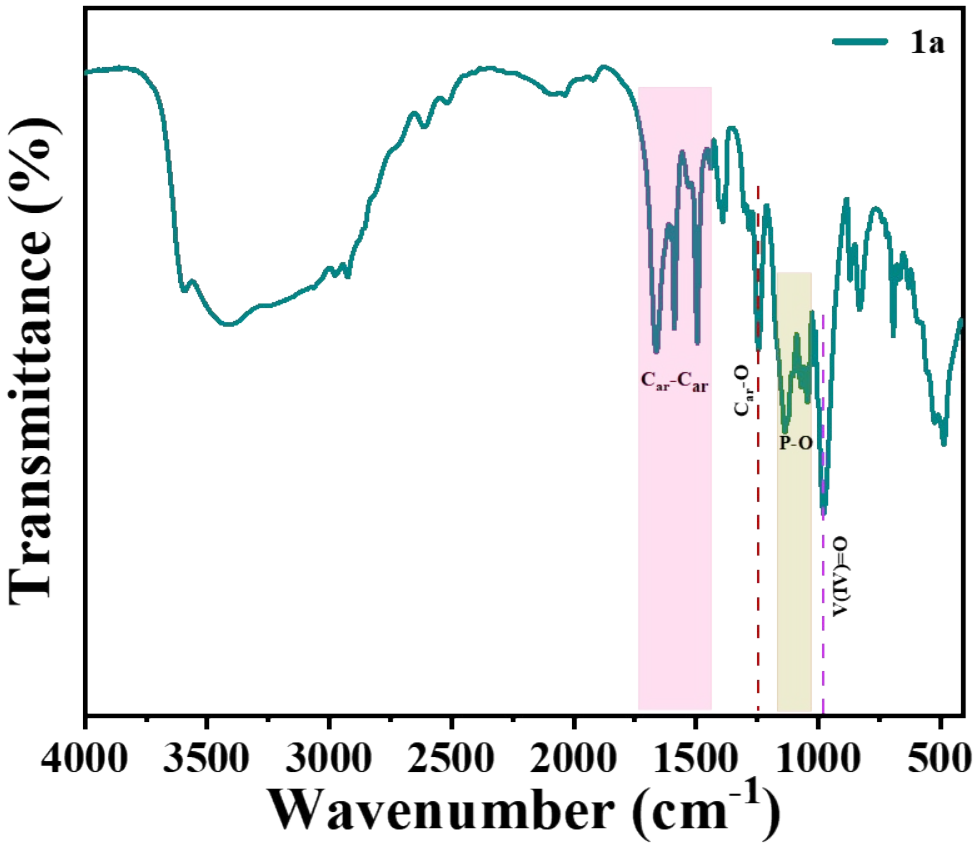


Figure S4. FTIR Spectrum of compound **1a**.

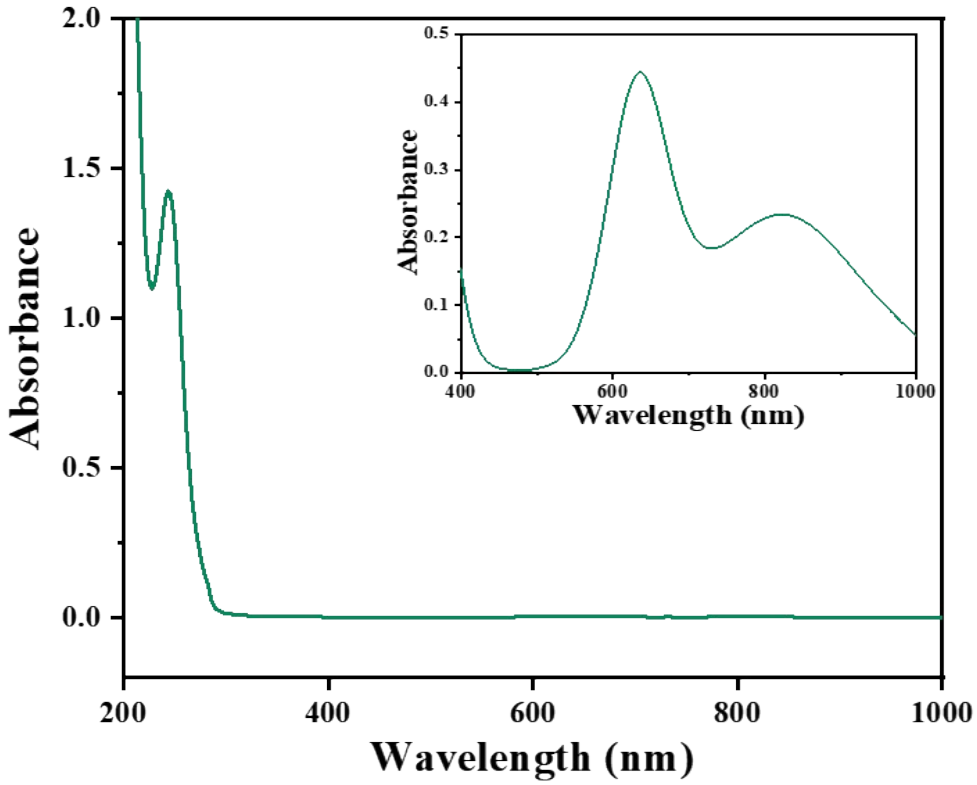


Figure S5. UV-Vis Spectra of polyanion **1** in aqueous solution. Inset shows the visible region.

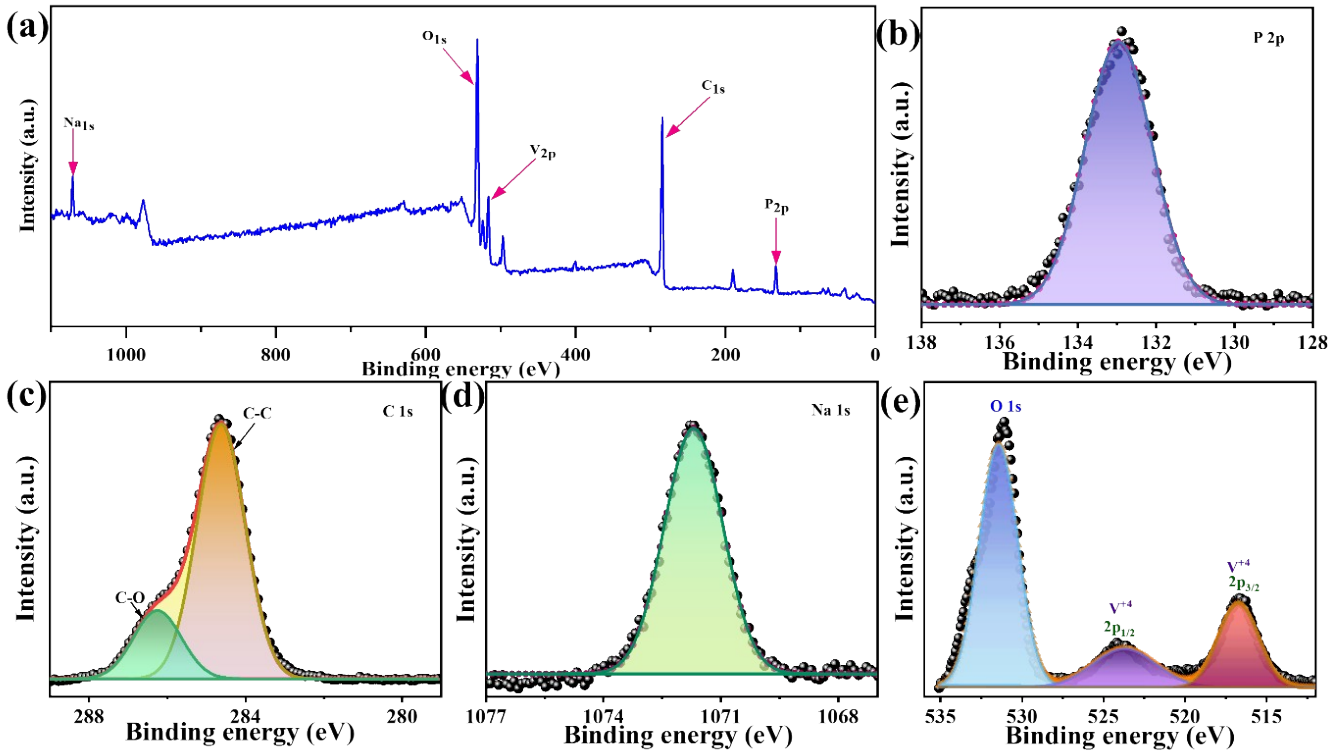


Figure S6. X-ray photoelectron spectrum of compound **1a**, **(a)** Survey spectrum **(b)** P 2p, **(c)** C1s, **(d)** Na 1s, and **(e)** vanadium-oxygen region.

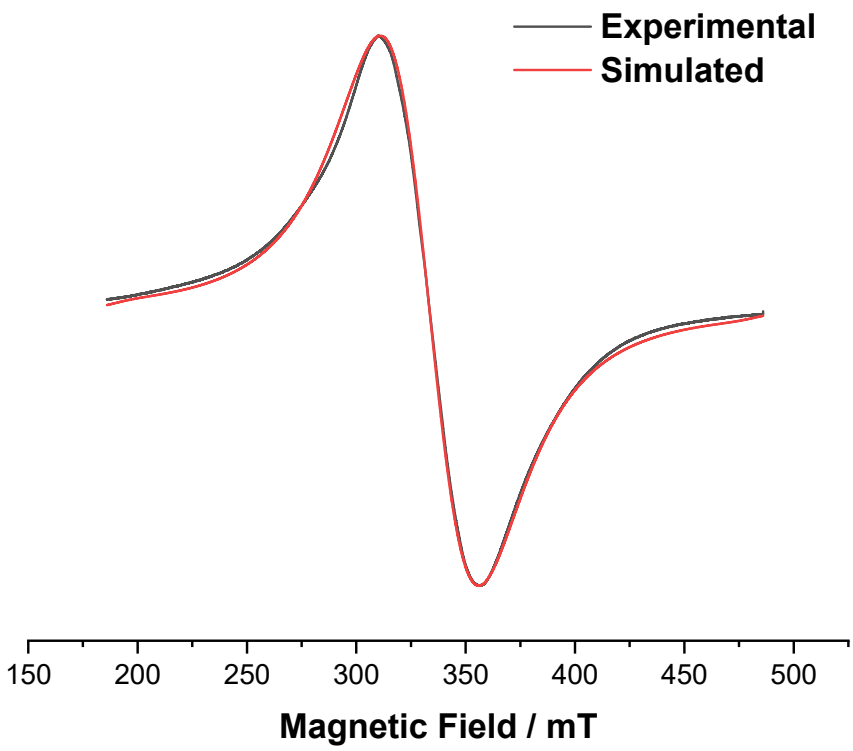


Figure S7. X-band EPR spectrum (black) of **1a** at liquid nitrogen temperature in the solid state. Red and black lines represent the simulated and the experimental spectra using the EasySpin program. [$\mathbf{g_{iso}}$ = 1.9674, LWPP (Gaussian broadening) = 18.2576 mT, LWPP (Lorentzian broadening) = 37.5348 mT, X-band experimental frequency = 9.182736 GHz].

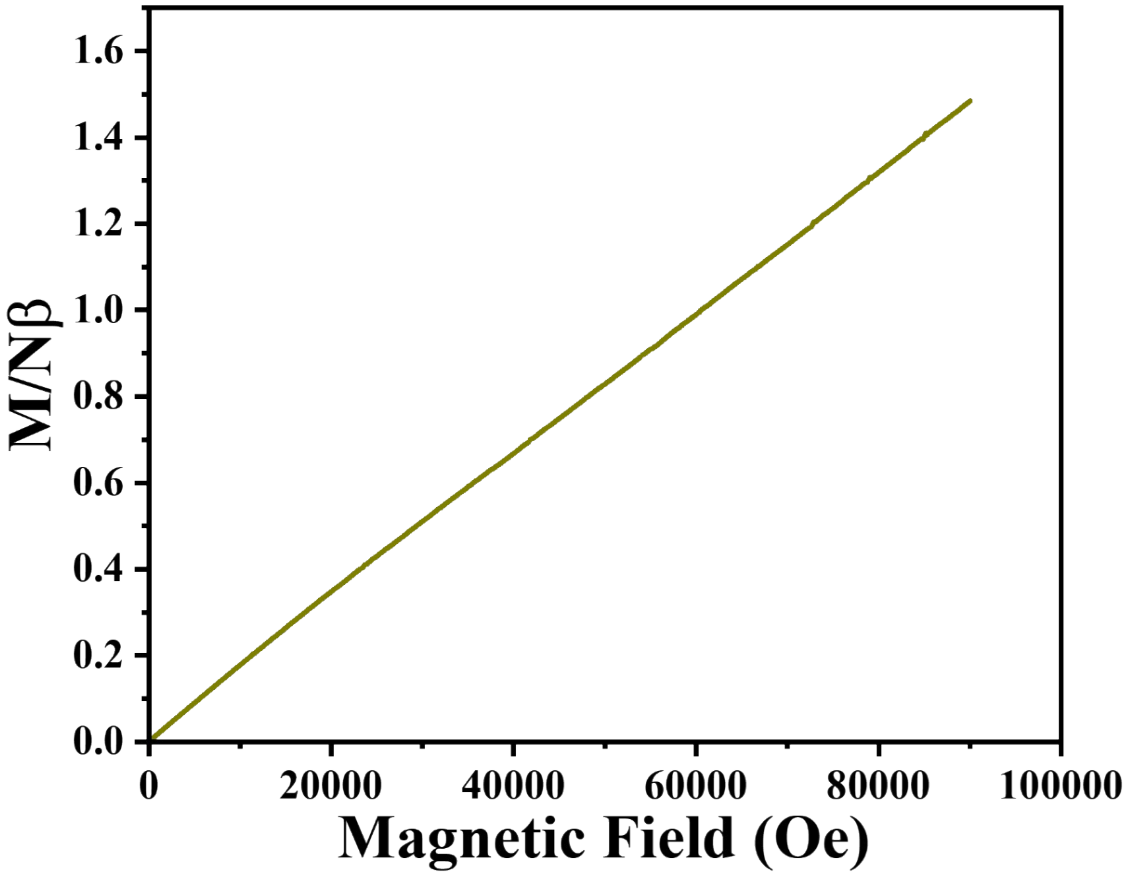


Figure S8. M *vs* H plot of each V^{IV} unit of complex **1a** suggesting the population of S = 0 and S = 1 at 3 K.

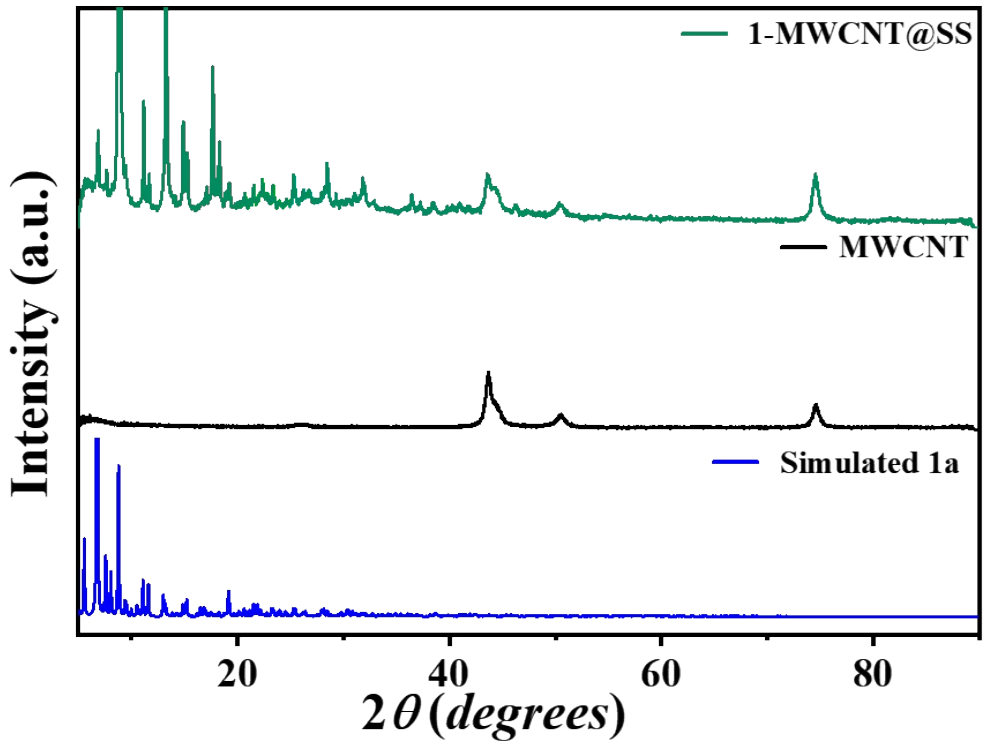


Figure S9. Comparative PXRD patterns of **1-MWCNT@SS**, MWCNT@SS and simulated pattern of **1a**.

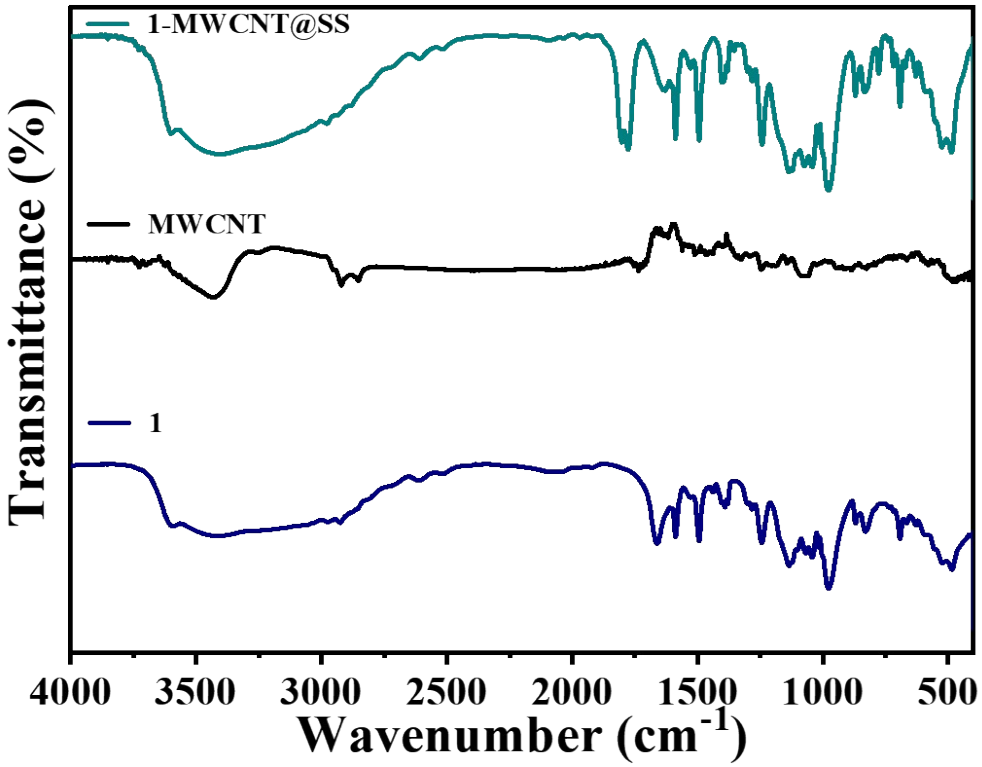


Figure S10. Comparative FTIR Spectra of **1a**, MWCNT@SS and **1-MWCNT@SS**.

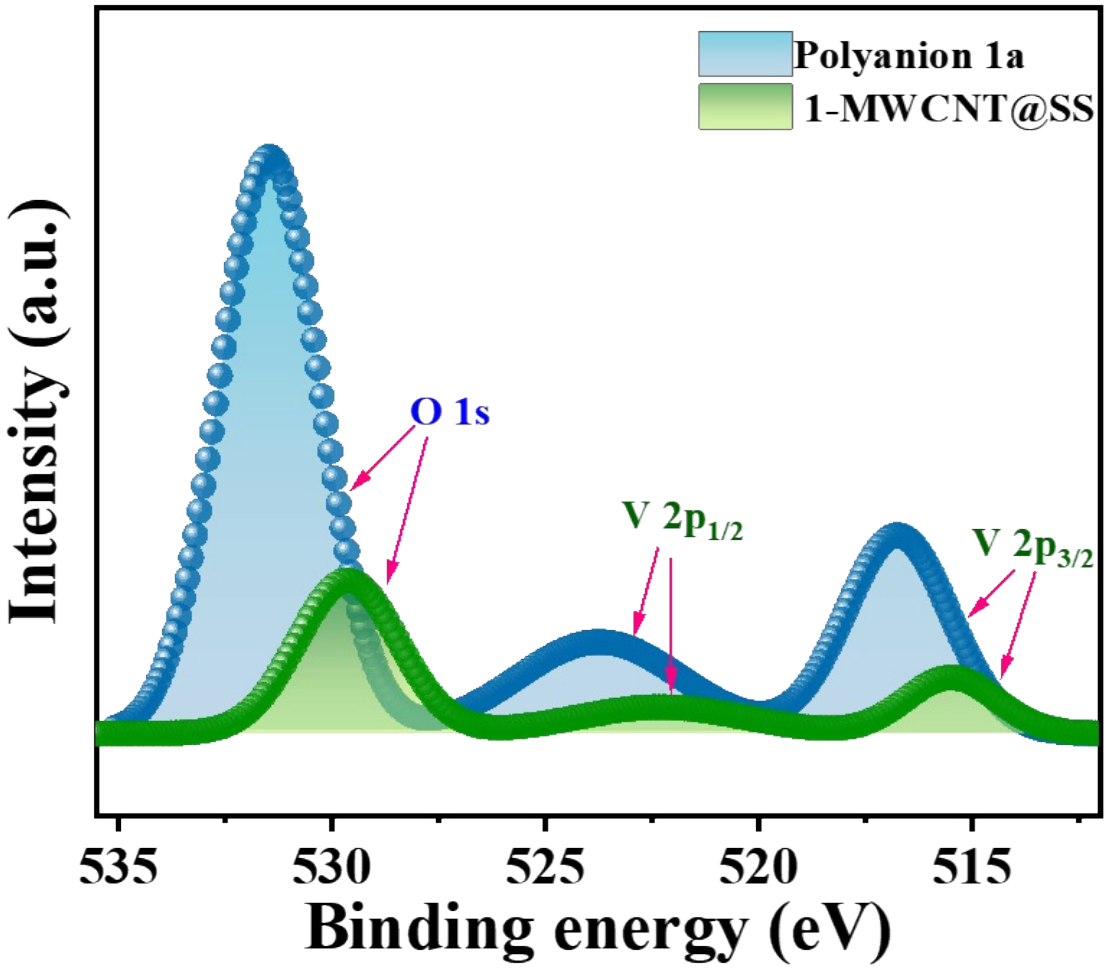


Figure S11. Comparative XPS spectrum of **1a** and **1-MWCNT@SS** [vanadium-oxygen region only].

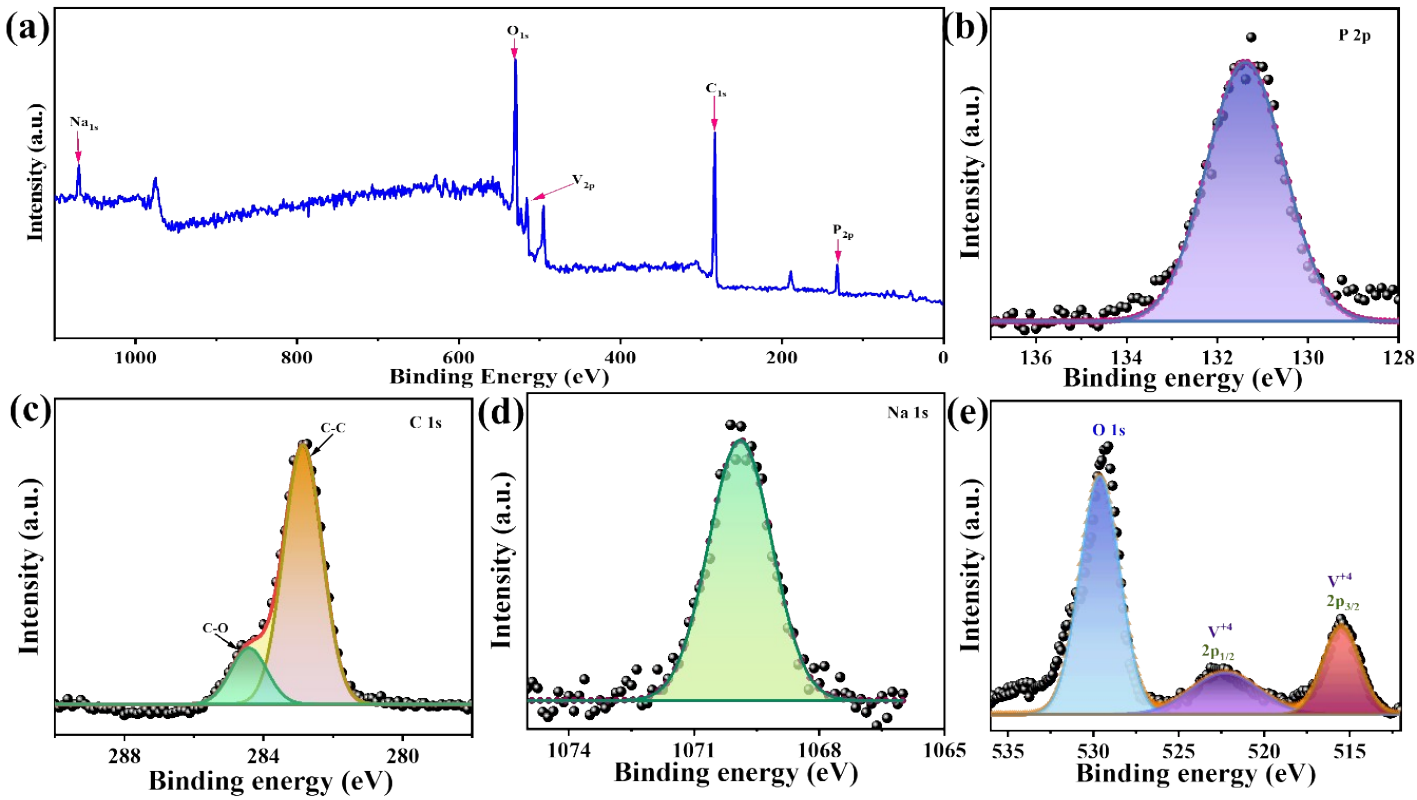


Figure S12. X-ray photoelectron spectrum of composite **1-MWCNT@SS**, **(a)** Survey spectrum, **(b)** P 2p, **(c)** C 1s, **(d)** Na 1s, and **(e)** vanadium-oxygen region.

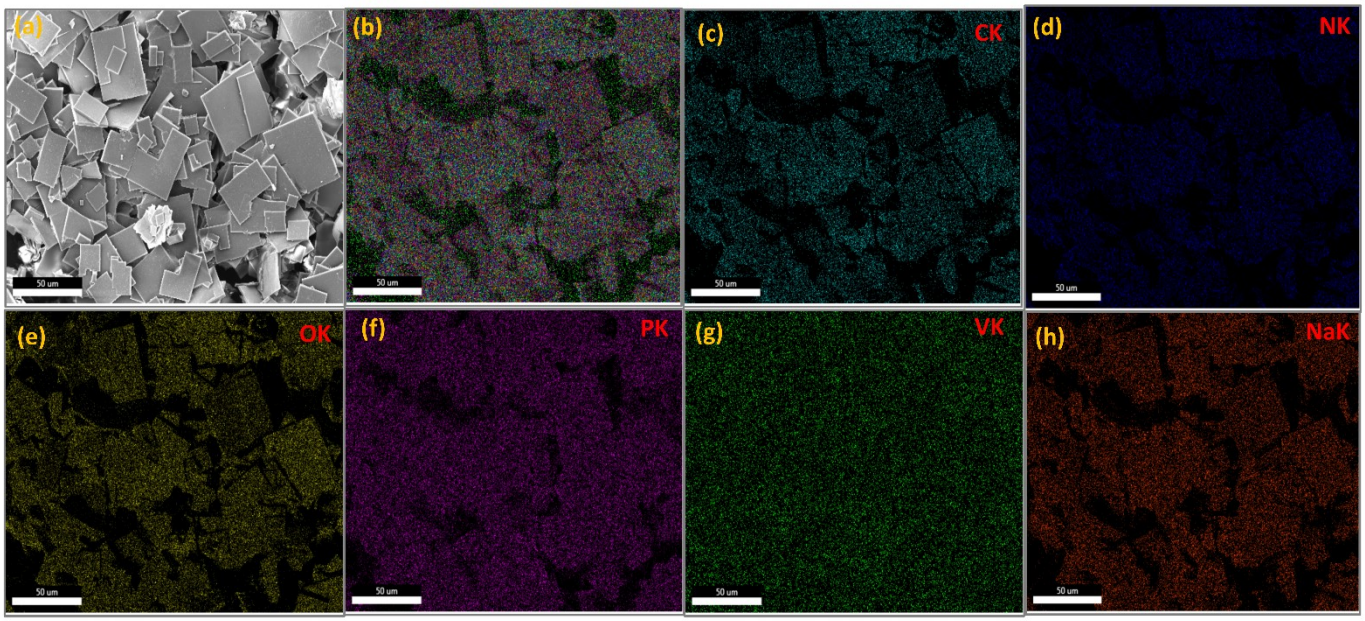


Figure S13. (a) FESEM images of **1-MWCNT@SS** at magnifications of 50 µm, respectively, and **(b-h)** Elemental mapping for **1-MWCNT@SS** with respective elements at 50 µm scale**.**

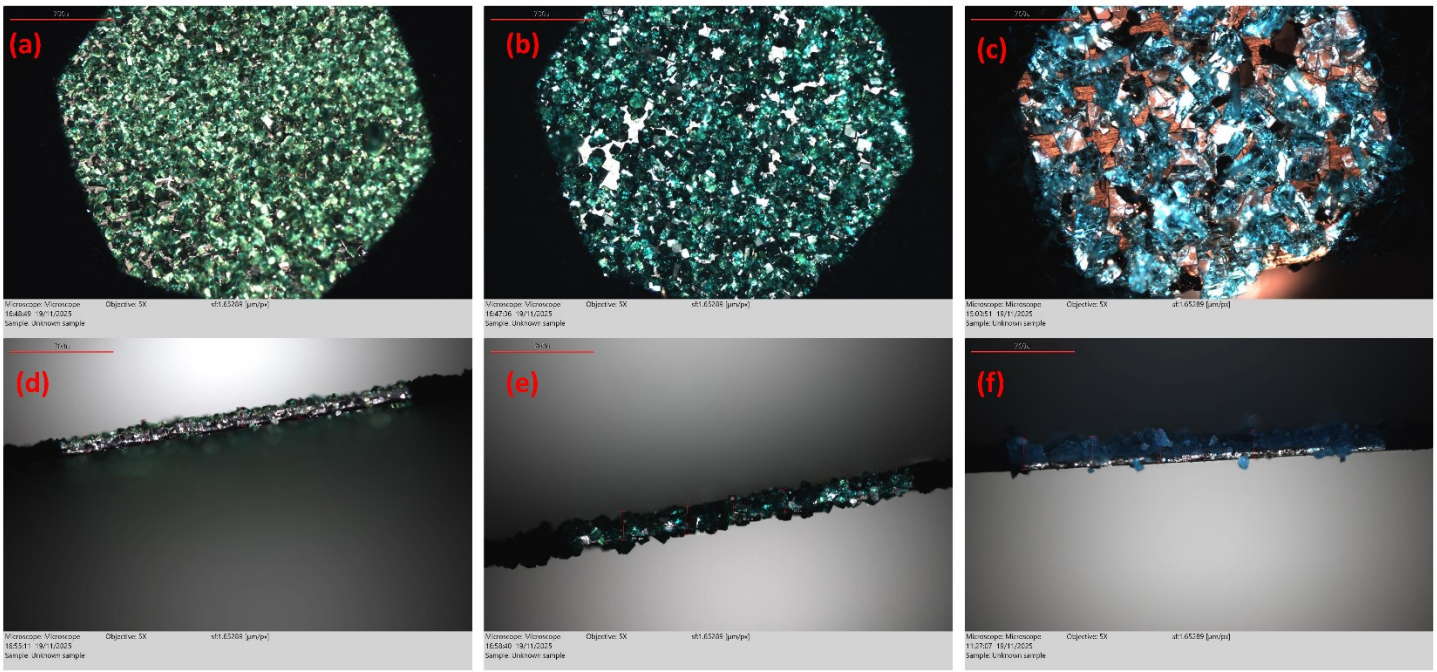


Figure S14. Cross – sectional optical micrograph of **Generation 1** and **Generation 2** electrodes over **MWCNT@SS**. **(a, b, and c)** Top-down view illustrating the crystalline morphology and surface distribution of the active material over **Generation 1 Electrode 1**, **Generation 1 Electrode 2**, and **Generation 2 Electrode 1-MWCNT@SS**, respectively. **(d, e, and f)** Side-on view showing the thickness of the deposited active layer over MWCNT@SS of the respective electrodes. Scale bar: 700 µm (Microscope: Polarized optical microscope; Objective: 5X; Scale factor: 1.65289 µm/px).

Table S1. Electrode Parameters of **Bare SS**, **MWCNT@SS**, and **Generation1** and **Generation 2** electrodes.

	Electrode Parameters		
Electrode type	**Film thickness**	**Electrode area**	**Volume of deposited layer**
Bare SS	60.06 µm ($\approx 0.0060\ cm$)	3.5 cm^2	2.10×10^{-2} cm^3
MWCNT@SS	70.9 µm ($\approx 0.00709\ cm$)	3.5 cm^2	2.48×10^{-2} cm^3
Generation 1 Electrode 1	126.2 µm ($\approx 0.01262\ cm$)	3.5 cm^2	4.41×10^{-2} cm^3
Generation 1 Electrode 2	175.2 µm ($\approx 0.01752\ cm$)	3.5 cm^2	6.13×10^{-2} cm^3
Generation 2 Electrode	210.5 µm ($\approx 0.02105\ cm$)	3.5 cm^2	7.37×10^{-2} cm^3

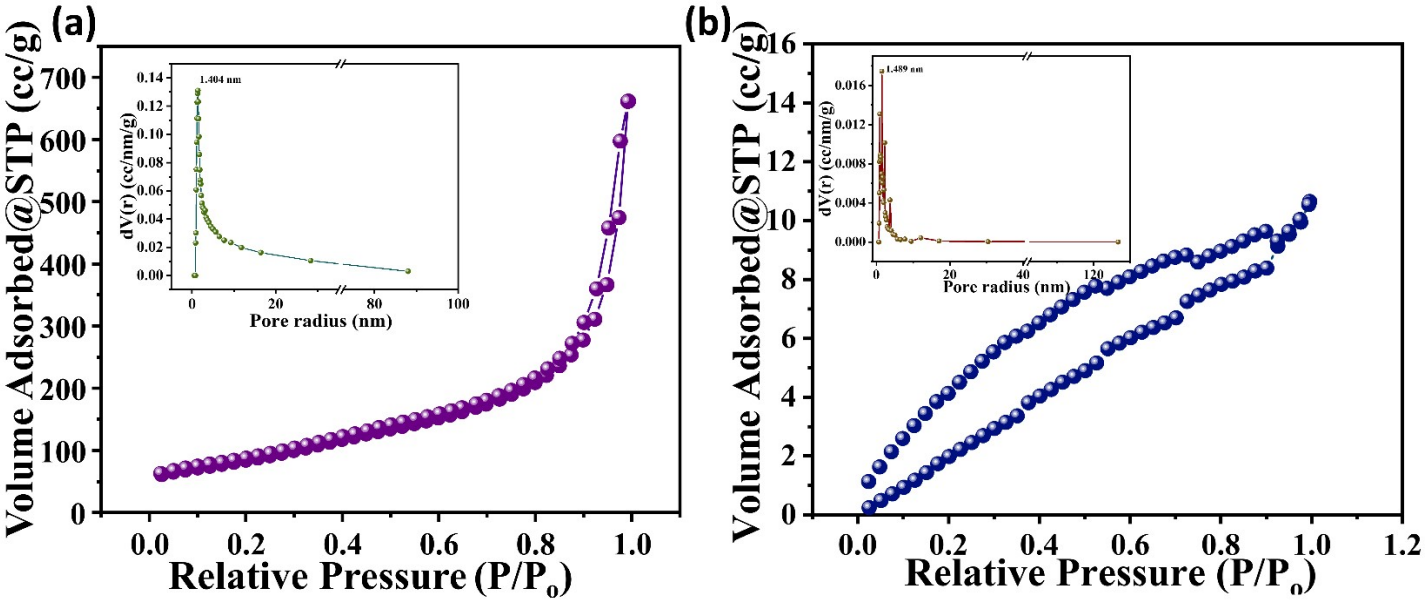


Figure S15. Nitrogen adsorption-desorption isotherm and BJH pore size distribution plots (insets) of **(a) MWCNT@SS**, and **(b) 1-MWCNT@SS**.

Table S2. Specific surface area and pore diameter of **MWCNT@SS** and **1-MWCNT@SS**.

Material	S_{BET} (m^2/g)	Pore Radius (nm)	Pore Volume (cm^3/g)
MWCNT@SS	85.110	1.404	1.020
1-MWCNT@SS	1.419	1.489	0.0218

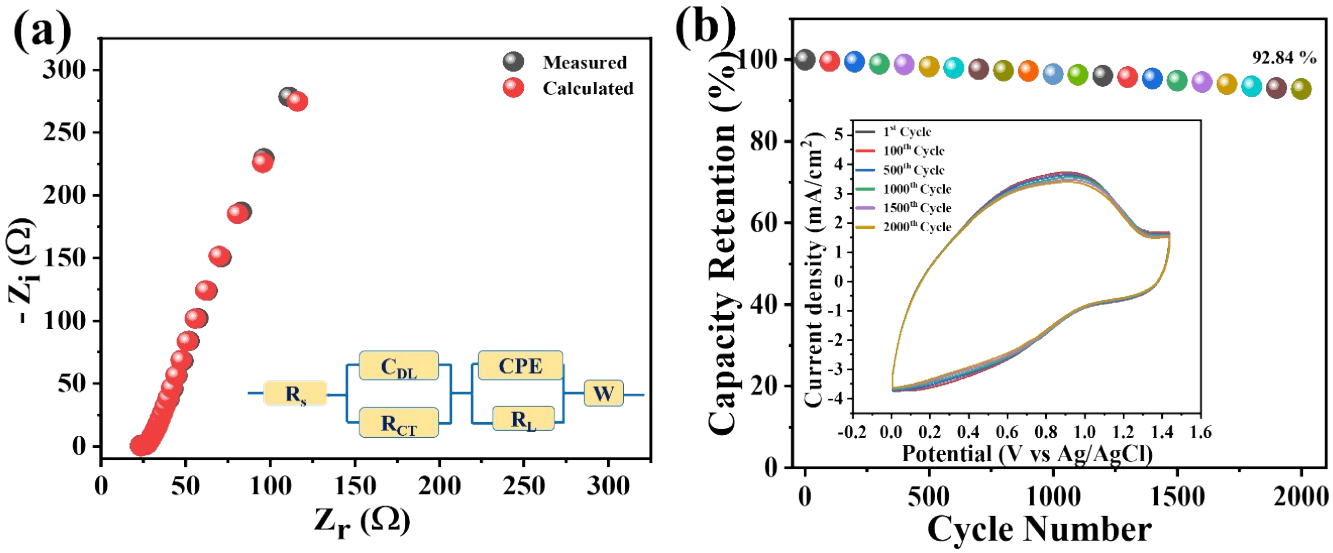


Figure S16. Electrochemical impedance spectroscopy (EIS) analysis and Stability Plot of prepared electrode **1-MWCNT@SS** in 0.5 M $NaClO_4$ electrolyte solution. **(a)** Nyquist plot (inset showing fitting circuit), and **(b)** Stability plot.

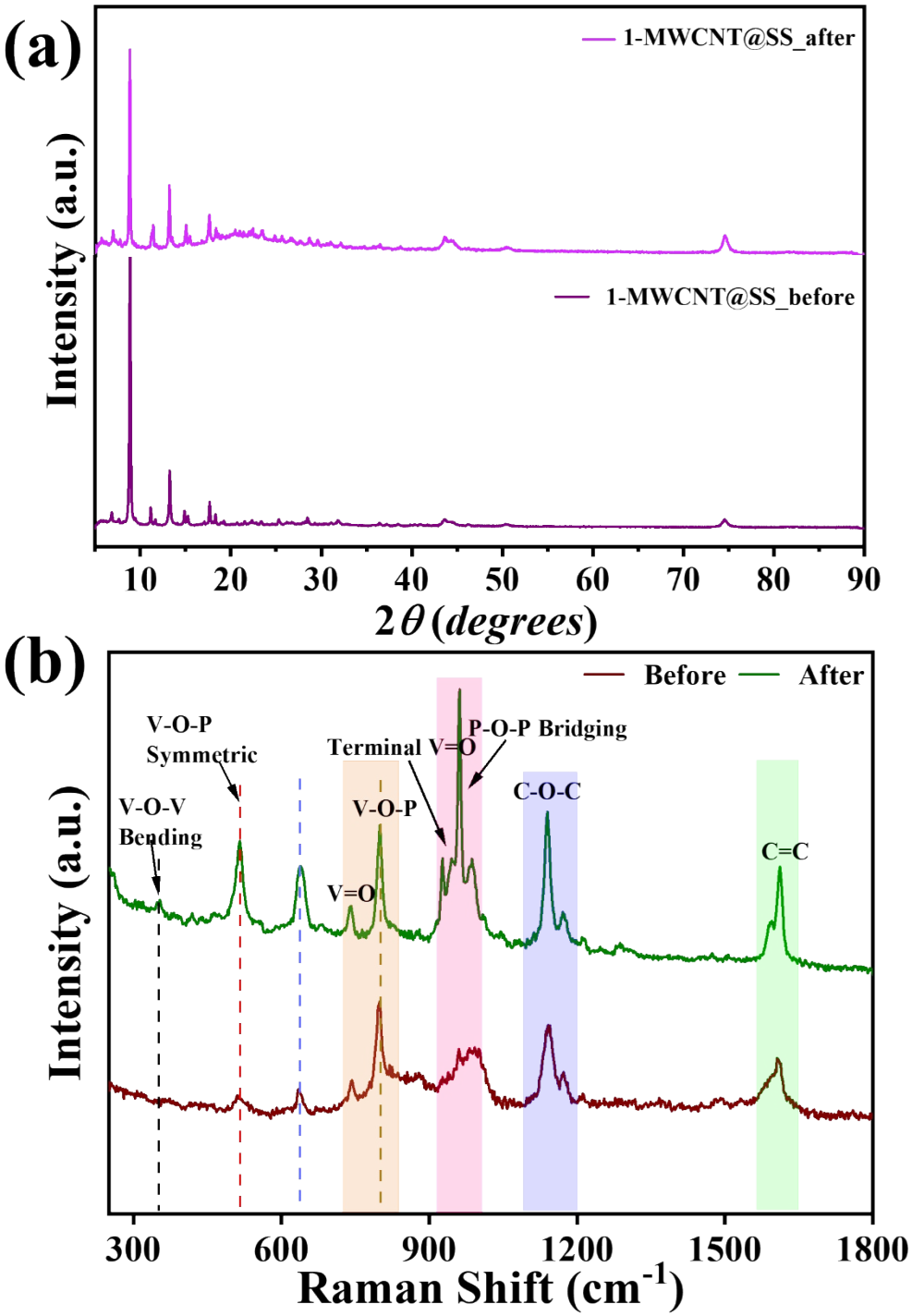


Figure S17. Comparative **(a)** PXRD, and **(b)** Raman Spectra of **1-MWCNT@SS** electrode, before and after electrochemical analysis, respectively.

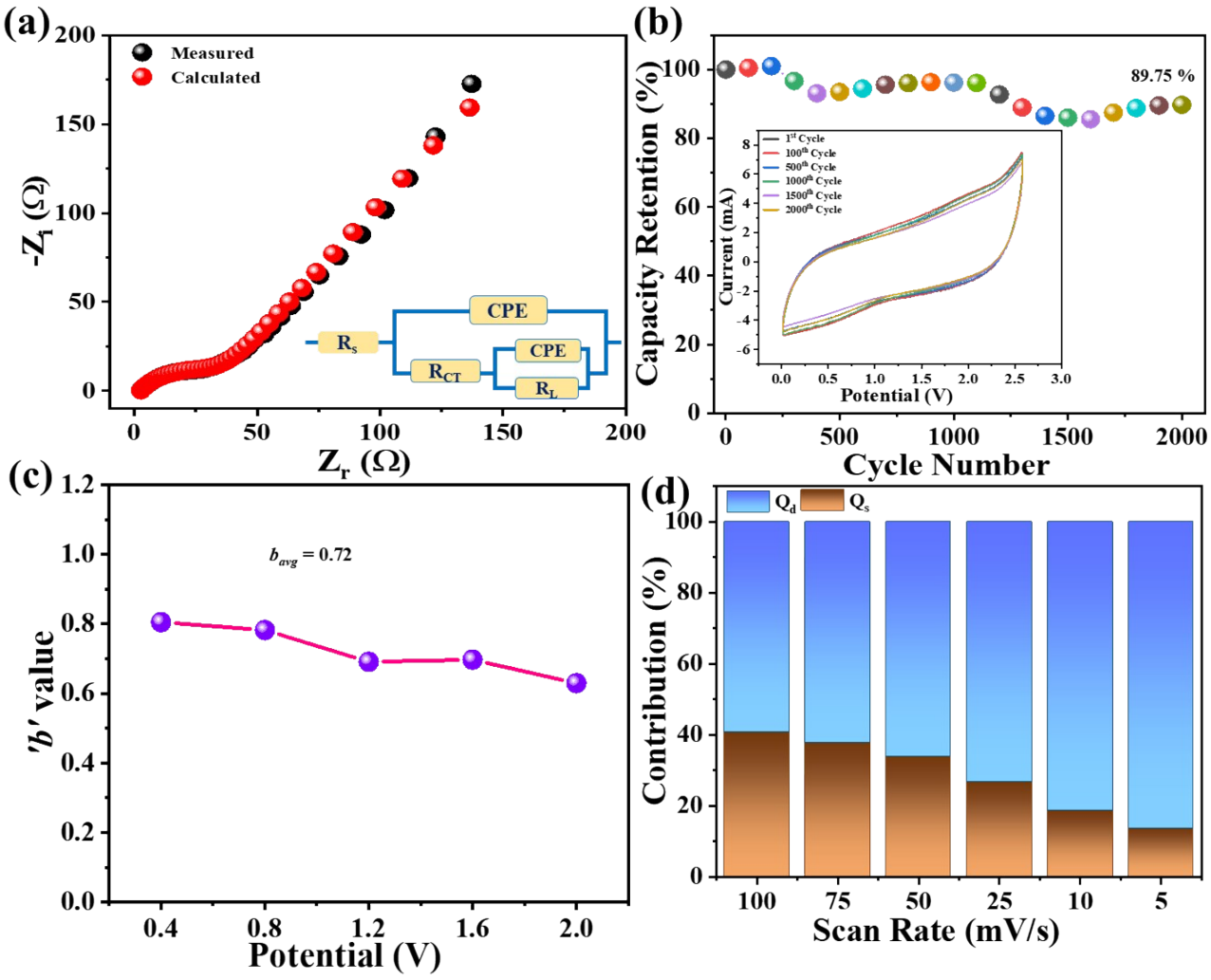


Figure S18. **(a)** Nyquist plot for the **Generation 2** device inset showing fitting circuit for Nyquist plot), (**b)** Stability plot, **(c)** $b-value$ at various potentials of **Generation 2** Device, and **(d)** Capacitive contribution at different scan rate.

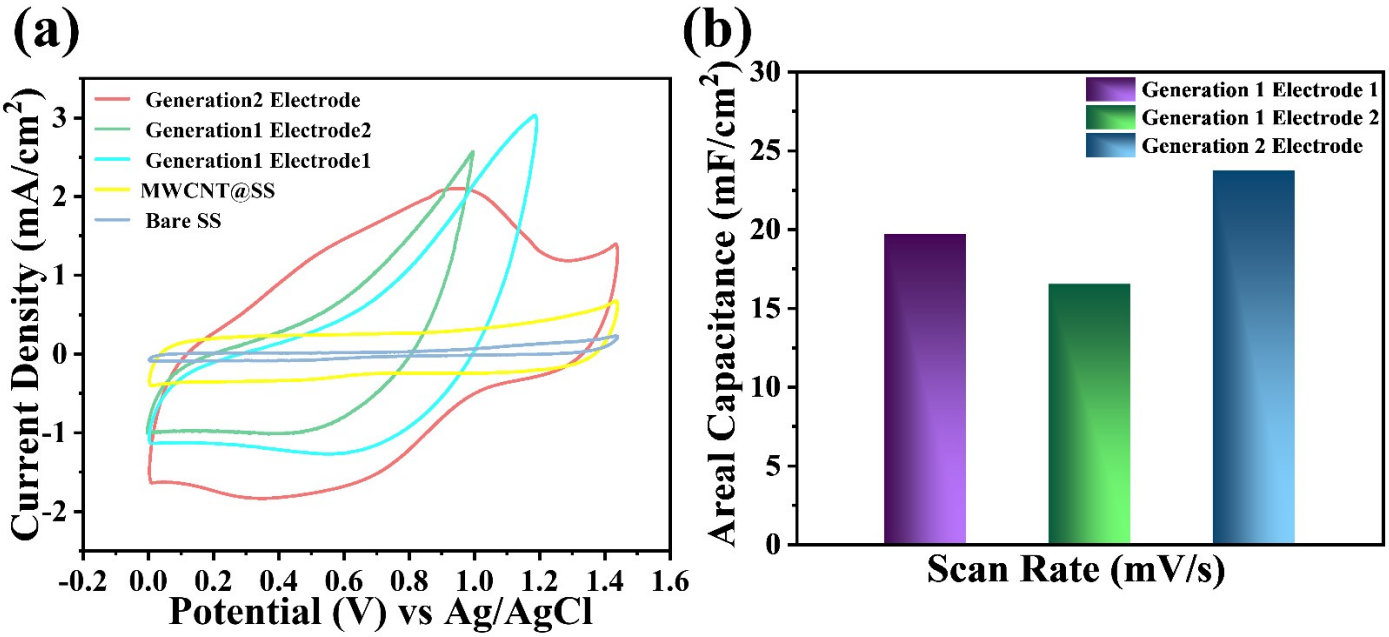
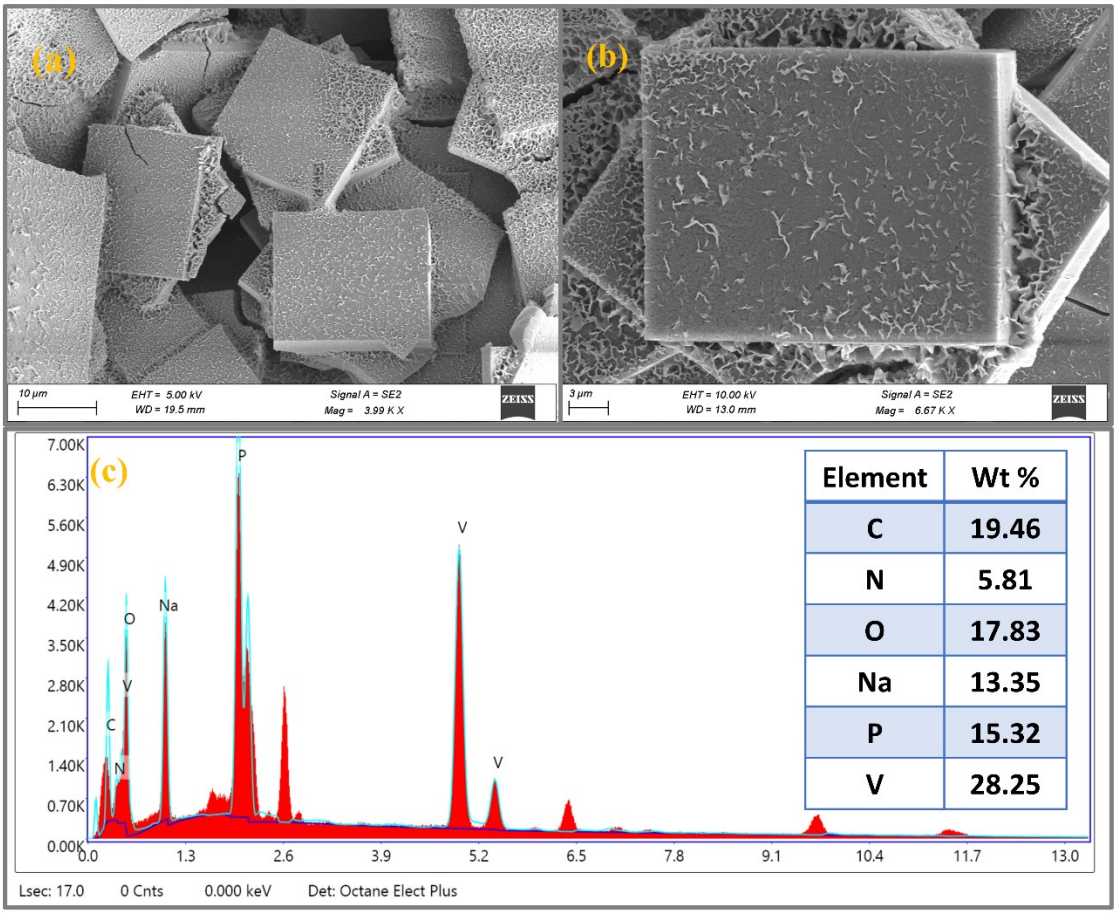


Figure S19. Comparative Supercapacitor performance of electrodes in a 0.5 M $NaClO_4$ electrolyte solution. **(a)** CV plots of **Bare SS**, **MWCNT @SS**, **Generation 1 Electrodes 1** and **2**, and **1-MWCNT@SS** at 100mV/s scan rate, and **(b)** Areal Capacitance Comparison of **Generation 1 Electrodes 1** and **2**, and **1-MWCNT@SS** at 100mV/s scan rate.



Element	Wt %
C	19.46
N	5.81
O	17.83
Na	13.35
P	15.32
V	28.25

Figure S20. FESEM images of **(a) 1-MWCNT@SS** at 10 µm**, (b) 1-MWCNT@SS** at 3 µm, and **(c)** EDX Spectra of **1-MWCNT@SS** after Electrochemical Studies. Elemental composition in wt% is displayed as a table in the inset.

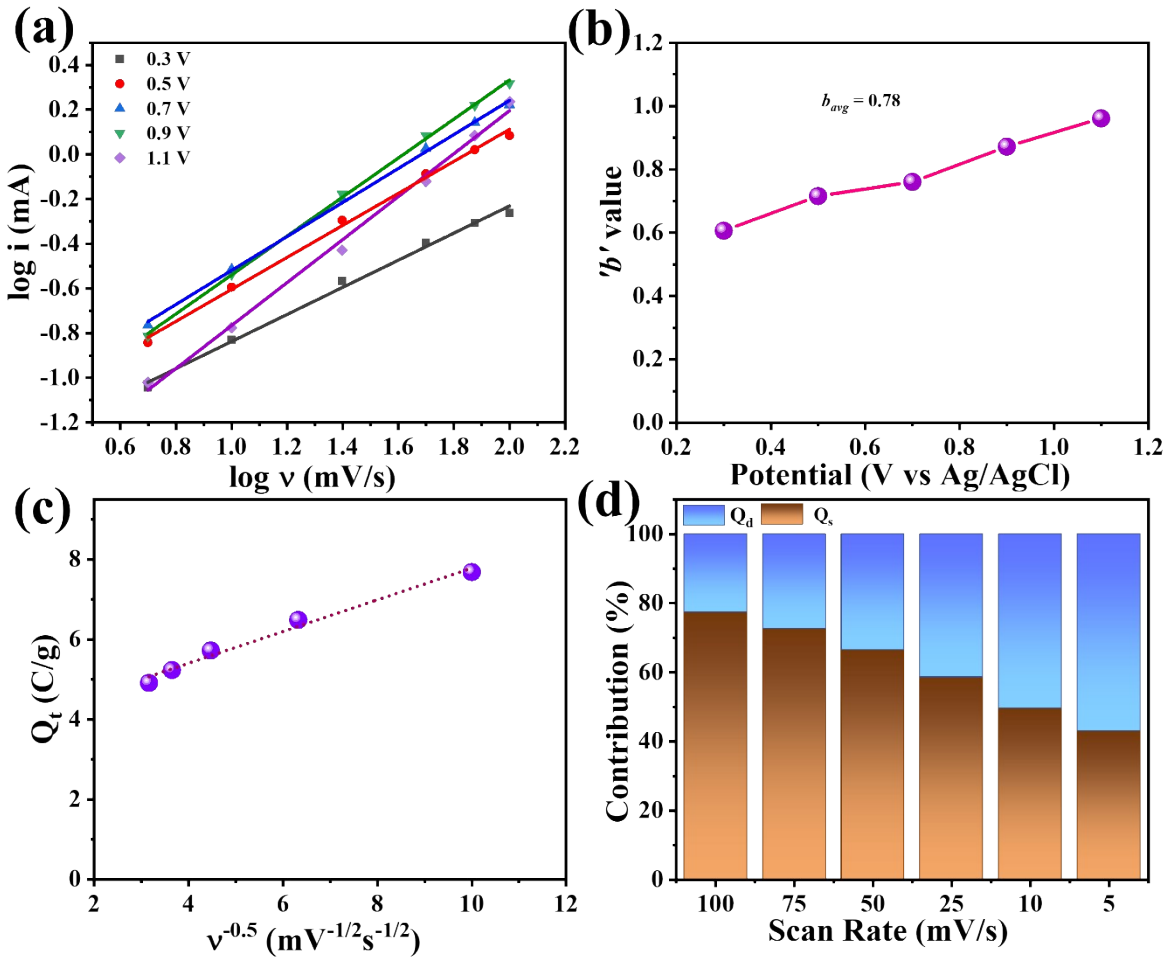


Figure S21. Supercapacitor performance of prepared electrode **1-MWCNT@SS** in a 0.5 M $NaClO_4$ electrolyte solution. **(a)** $log(i)\ vs.\ log(v)$ plot, **(b)** $b-value$ at various potentials, **(c)** $Q_t\ vs.\ v^{-0.5}$ plot, and **(d)** Capacitive contribution at different scan rates.

Table S3. Bond Valence Sum Calculations for compound **1**.

Bond	Bond Length (Å)	Bond Valence	Bond Valence Sum
V1-O1V1	1.606	1.6178	∑(V1) = 4.0958
V1-O123	1.995	0.5653	
V1-O124	2.015	0.5356	
V1-O134	2.357	0.2125	
V1-O1P1	2.001	0.5562	
V1-O2P3	1.968	0.6081	

Bond	Bond Length (Å)	Bond Valence	Bond Valence Sum
V2-O1V2	1.586	1.7076	∑(V2) = 4.1396
V2-O123	2.004	0.5517	
V2-O124	2.031	0.5129	
V2-O234	2.32	0.2348	
V2-O2P2	1.997	0.5623	
V2-O2P4	1.992	0.5699	

Bond	Bond Length (Å)	Bond Valence	Bond Valence Sum
V3-O1V3	1.599	1.6487	∑(V3) = 4.0504
V3-O123	2.317	0.2367	
V3-O134	2.028	0.5171	
V3-O234	2.043	0.5060	
V3-O1P2	1.984	0.5824	
V3-O2P1	1.999	0.5592	

Bond	Bond Length (Å)	Bond Valence	Bond Valence Sum
V4-O1V4	1.592	1.6802	∑(V4) = 4.1150
V4-O124	2.27	0.2688	
V4-O134	2.025	0.5213	
V4-O234	2.065	0.4679	
V4-O1P3	1.968	0.6081	
V4-O3P4	1.993	0.5684	

Table S4. Hydrogen-bonding parameters for compound **1a**

Donor-H····Acceptor	D-H (Å)	H····A (Å)	D····A (Å)
N1C-H1C1····O10$^{\#1}$	0.91	1.95	2.84
N1C-H1C2····O6$^{\#2}$	0.91	1.99	2.85
C9-H9····O6	0.95	2.52	2.94
C20-H2O3····O14	0.98	2.42	3.17
C30-H3O3····O23$^{\#3}$	0.98	2.54	3.48
C24-H24····O20	0.95	2.58	2.97
C24-H24····O12$^{\#4}$	0.95	2.53	3.42

Symmetry transformations used to generate equivalent atoms:

$^{\#1}$: ½+x, ½-y, 1-z

$^{\#2}$: ½+y, ½-x, z

$^{\#3}$: -1/2+x, ½-y, 1-z

$^{\#4}$: -x, -y, z

Optimised coordinates of $[V^{IV}_4O_4(O_3P\text{-}Me)_2]^{4-}$ (1a′)

Complex **1a′** in B3LYP-D3(BJ)/def2-SVP level of theory

Quintet State (**S = 2**)

Energy = −5590.8611429 hf

23	-1.454647000	1.259302000	-0.979559000
23	1.458908000	1.258601000	-0.977956000
23	-0.002118000	-1.023809000	1.088838000
23	0.003022000	1.757870000	1.498283000
15	-2.753020000	-1.701920000	-0.458596000
15	2.749416000	-1.705591000	-0.458557000
8	-2.503942000	2.348669000	-1.551154000
8	2.508166000	2.348222000	-1.549097000
8	-0.001276000	-1.432897000	2.629645000
8	-0.003903000	2.827786000	2.748028000
8	0.002881000	0.707814000	-1.973474000
8	0.001449000	2.462360000	-0.200927000
8	-1.310639000	0.558235000	0.953740000
8	1.314265000	0.557324000	0.956503000
8	-2.566369000	-0.422433000	-1.337661000
8	1.379494000	-2.108668000	0.229576000
8	-1.387008000	-2.109165000	0.235156000
8	2.571426000	-0.422527000	-1.334357000
8	-3.469478000	-2.862510000	-1.135552000
8	3.462853000	-2.867222000	-1.136877000
6	3.824800000	-1.172024000	0.966479000
1	3.976424000	-2.019589000	1.660051000
1	4.809415000	-0.844068000	0.584270000
1	3.317517000	-0.343546000	1.482567000
6	-3.830033000	-1.159654000	0.961897000

1	-3.987894000	-2.005038000	1.656740000
1	-3.320190000	-0.332593000	1.477738000
1	-4.811947000	-0.827542000	0.576307000

Triplet state (**S = 1**)

Energy = −5590.864829 hf

23	1.478073000	-1.214869000	-0.982781000
23	-1.478867000	-1.214929000	-0.982661000
23	0.000178000	0.992023000	1.110052000
23	-0.000374000	-1.869854000	1.399695000
15	2.747615000	1.714792000	-0.438615000
15	-2.746778000	1.715479000	-0.439103000
8	2.537665000	-2.310910000	-1.522319000
8	-2.537979000	-2.311317000	-1.522400000
8	-0.000932000	1.404633000	2.650272000
8	-0.000699000	-2.665498000	2.840274000
8	-0.000540000	-0.691774000	-1.957120000
8	-0.000365000	-2.568671000	-0.227062000
8	1.284894000	-0.561196000	0.915972000
8	-1.285155000	-0.560892000	0.915929000
8	2.565139000	0.445255000	-1.345068000
8	-1.380770000	2.109998000	0.246626000
8	1.383525000	2.110350000	0.250149000
8	-2.567983000	0.444335000	-1.343954000
8	3.475574000	2.874416000	-1.104955000
8	-3.474094000	2.875292000	-1.105780000
6	-3.819277000	1.142887000	0.972212000
1	-3.976002000	1.974743000	1.683223000
1	-4.801723000	0.815340000	0.584001000
1	-3.305661000	0.308016000	1.471698000

6	3.821820000	1.138495000	0.969929000
1	3.981275000	1.969128000	1.681779000
1	3.307804000	0.303795000	1.469276000
1	4.803004000	0.809918000	0.579425000

Singlet state (**S = 0**)

Energy = −5590.8637221 hf

23	1.477769000	-1.208665000	-0.979975000
23	-1.478271000	-1.208693000	-0.980301000
23	0.000081000	1.013697000	1.101309000
23	-0.000422000	-1.903779000	1.381502000
15	2.757067000	1.716629000	-0.432121000
15	-2.756263000	1.717328000	-0.432641000
8	2.542165000	-2.302185000	-1.515358000
8	-2.541760000	-2.302574000	-1.516729000
8	-0.001077000	1.415496000	2.644403000
8	-0.001759000	-2.704073000	2.821193000
8	-0.000360000	-0.676140000	-1.950319000
8	-0.000426000	-2.583569000	-0.248745000
8	1.264528000	-0.563686000	0.917182000
8	-1.264681000	-0.563326000	0.916905000
8	2.570700000	0.449065000	-1.339626000
8	-1.387126000	2.121912000	0.242095000
8	1.390145000	2.122419000	0.246243000
8	-2.574193000	0.447945000	-1.338447000
8	3.497786000	2.871261000	-1.092864000
8	-3.496337000	2.872256000	-1.093571000
6	-3.810356000	1.135559000	0.987981000
1	-3.966270000	1.964855000	1.702110000
1	-4.793833000	0.800802000	0.608870000

1	-3.284869000	0.303928000	1.480733000
6	3.813159000	1.131062000	0.985392000
1	3.971899000	1.959190000	1.700260000
1	3.287387000	0.299600000	1.478132000
1	4.795359000	0.795252000	0.603877000