

Supporting Information

Syntheses and post-functionalization of tri-substituted polyalkoxo hexavanadates containing tris(alkoxo) ligands

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Yongge Wei^{*a,b}

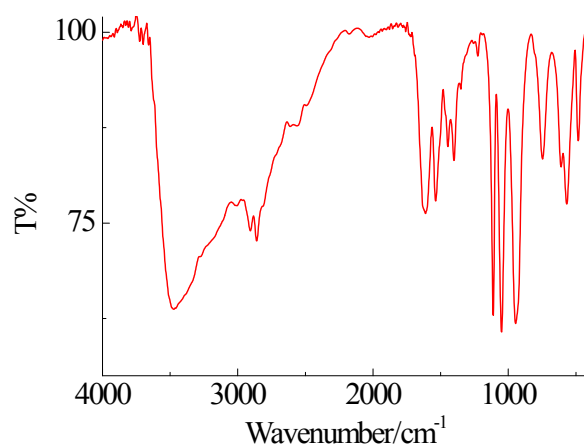


Figure S1. FT-IR spectrum measured for the solid sample of **1**.

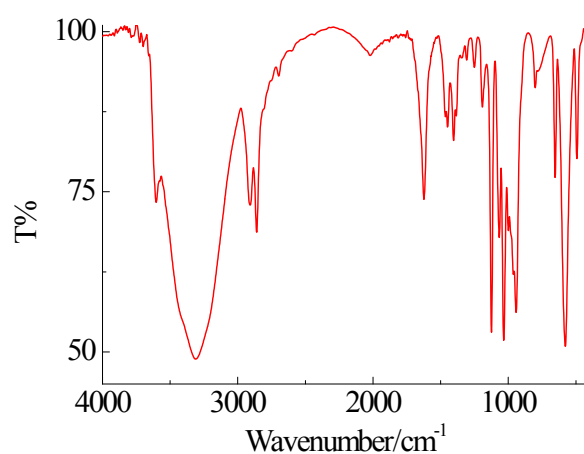


Figure S2. FT-IR spectrum measured for the solid sample of **2**.

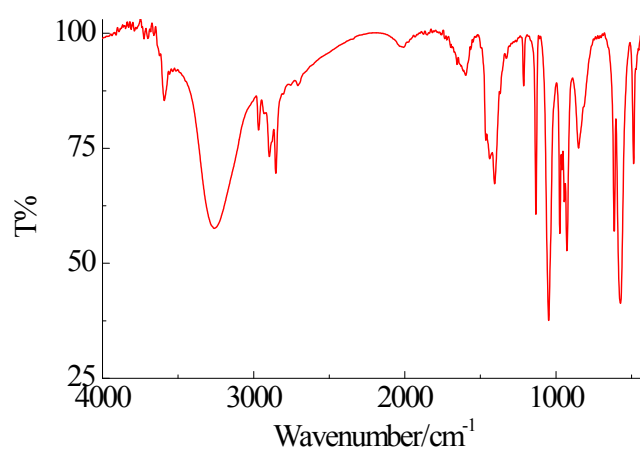


Figure S3. FT-IR spectrum measured for the solid sample of **3**.

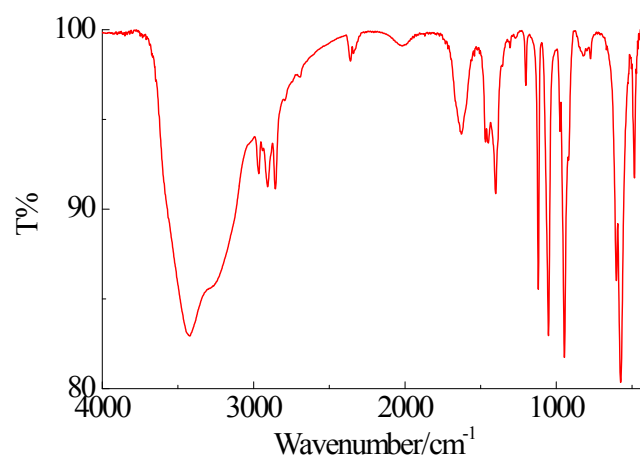


Figure S4. FT-IR spectrum measured for the solid sample of **4**.

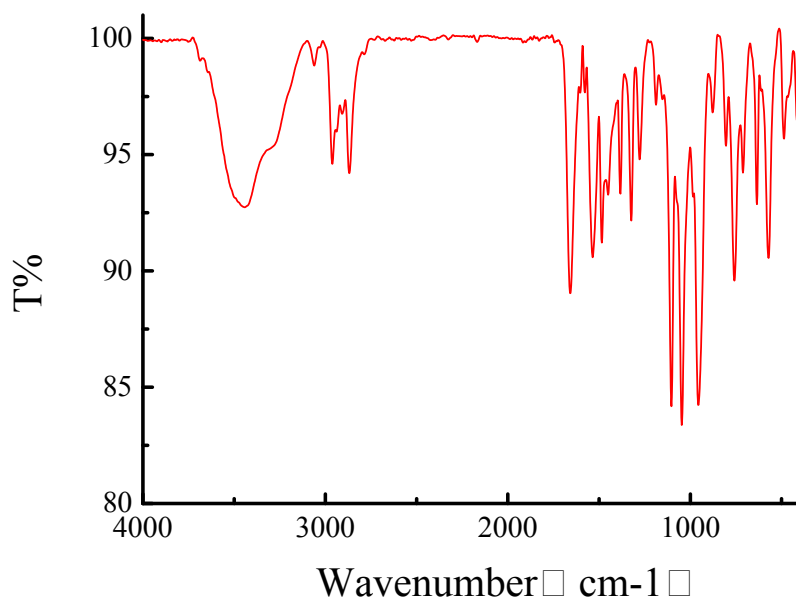
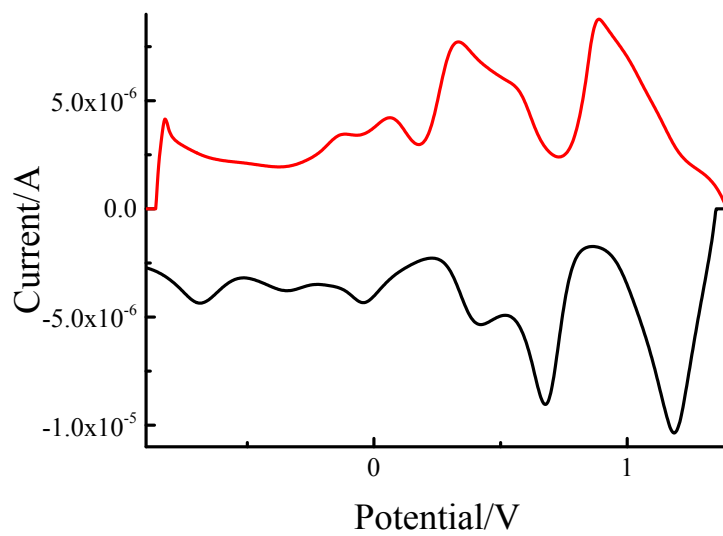


Figure S5. FT-IR spectrum measured for the solid sample of **5**.



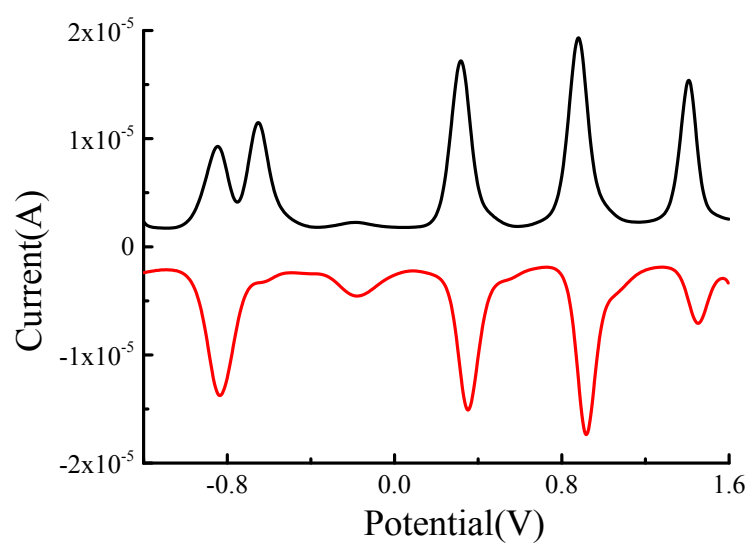
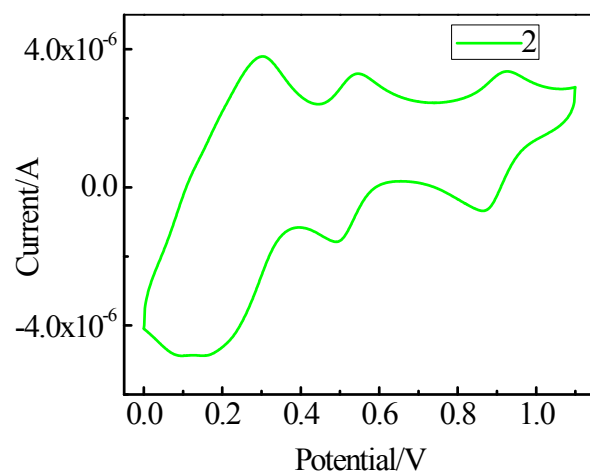


Figure S6. Differential Pulse Voltammetry spectra of **1** and **5**.



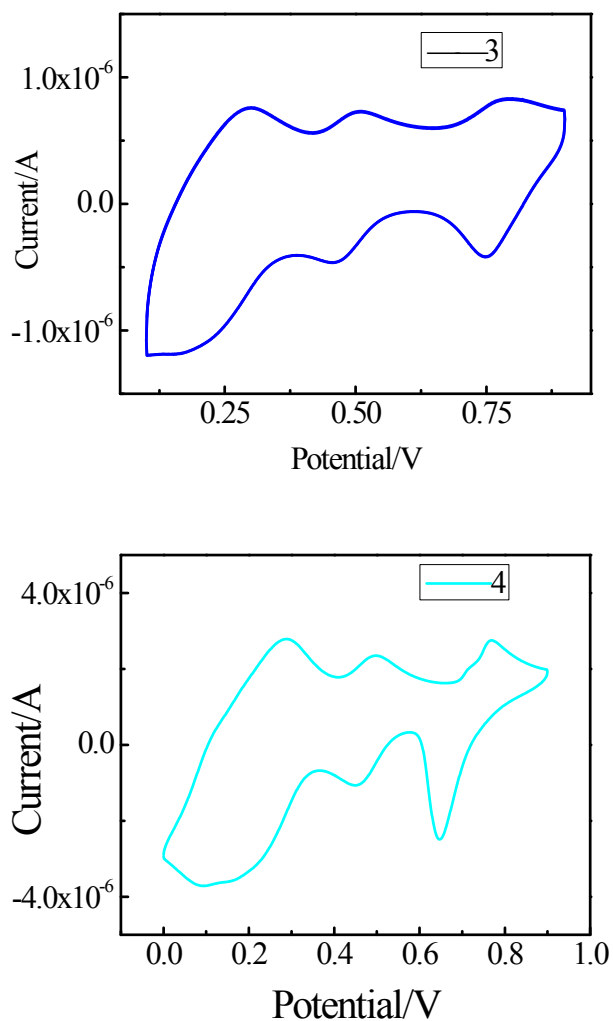


Figure S7. Cyclic voltammogram spectrum of **2,3,4**.

Table S1 Summary of BVS calculations for the vanadium atoms in **1 - 5**

1	2	3	4	5
V1 4.921	V1 4.025	V1 4.022	V1 4.03	V1 3.990 4.038
V2 4.110	V2 4.091	V2 4.036	V2 4.056	V2 4.044 4.048
	V3 4.044		V3 4.009	V3 4.141 4.055
	V4 3.977		V4 4.01	V4 4.988 4.931
			V5 4.026	V5 5.002 5.082
			V6 4.051	V6 4.981 4.973
				V7 V8 V9 V10 V11 V12

Table S2 Binding Energies (eV) for Compounds **1-5**

	1 (0.66)		2	3	4	5	
FWHE(eV)	1.85	2.10	1.96	2.20	2.14	1.79	2.05
2p3/2(eV)	515.85	517.1	515.76	515.7	515.9	515.75	516.95
FWHE(eV)	2.14	2.10	2.20	2.20	2.51	2.1	2.1
2p1/2(eV)	523.05	524.3	522.91	522.875	523	523.2	524.15

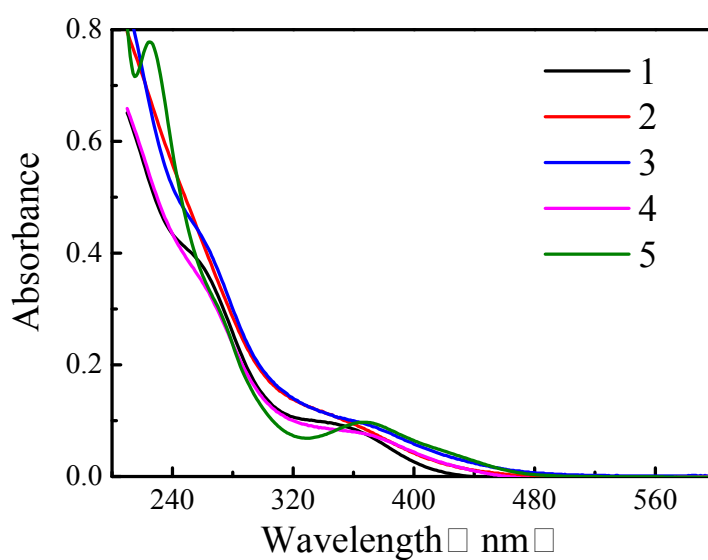


Fig. S8 UV-vis spectra in water solution (**1-4**) and in acetonitrile (**5**).

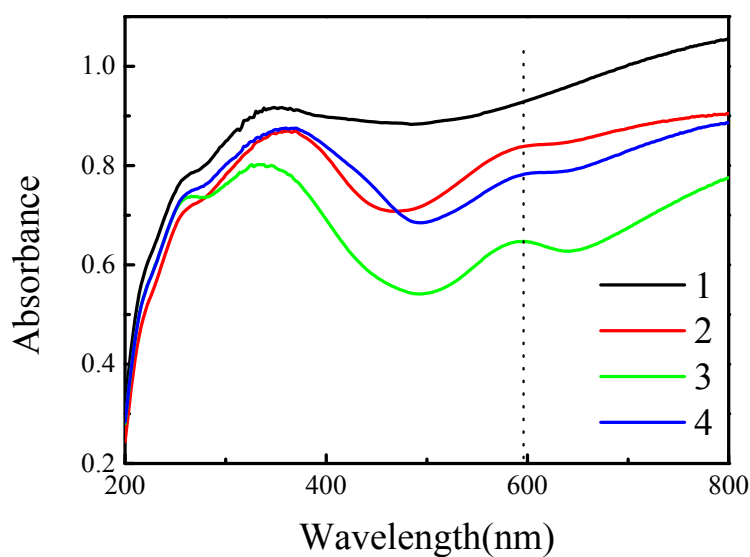


Fig. S9 UV-vis DRS spectra of compounds **1-4**.

Table S3 Details of crystal data and structure refinement for **1-5**.

Identification code	1	2	3	4	5
Empirical formula	$\text{Na}_2\text{V}_6\text{N}_3\text{O}_{28}\text{C}_{12}\text{H}_{42}$	$\text{Na}_2\text{V}_6\text{O}_{31}\text{C}_{13}\text{H}_{48}$	$\text{C}_{15}\text{H}_{30}\text{N}_3\text{O}_{19}\text{V}_6$	$\text{C}_{18}\text{H}_{52}\text{N}_2\text{O}_{23}\text{V}_6$	$\text{C}_{114}\text{H}_{180}\text{N}_9\text{NaO}_{44}\text{V}_{12}$
Formula weight	1028.09	1076.14	862.06	970.25416	3014.93
Temperature/K	293(2)	121.7	105(2)	105.6	106.6
Crystal system	cubic	orthorhombic	hexagonal	monoclinic	triclinic
Space group	<i>I</i> 23	<i>Pnmm</i>	<i>P63mc</i>	<i>P21/c</i>	<i>P-1</i>
a/Å	19.168(2)	10.2542(8)	12.9234(4)	9.9874(3)	17.3307(7)
b/Å	19.168(2)	27.096(2)	12.9234(4)	26.3528(10)	17.3855(8)
c/Å	19.168(2)	12.9530(10)	9.8515(3)	16.3613(4)	32.3235(12)
$\alpha / ^\circ$	90	90	90	90	90.823(3)
$\beta / ^\circ$	90	90	90	127.6200(10)	100.203(4)
$\gamma / ^\circ$	90	90	120	90	119.450(5)
Volume/Å ³	7042(2)	3599.0(5)	1424.91(11)	3410.86(18)	8287.9(7)
Z	8	4	2	4	2
$\rho_{\text{calc}}/\text{cm}^3$	1.724	1.955	2.009	1.86	1.208
μ/mm^{-1}	1.631	1.627	1.975	1.67	0.713
F(000)	3624.0	2108	862	1916	3132
Crystal size/mm ³	0.30 × 0.25 × 0.25	0.30 × 0.25 × 0.02	0.20 × 0.12 × 0.05	0.20 × 0.20 × 0.17	0.140 × 0.130 × 0.050
Radiation MoK α	($\lambda = 0.71073$)	($\lambda = 0.7107$)	($\lambda = 0.71073$)	($\lambda = 0.7107$)	($\lambda = 0.71073$)

2 θ range for data collection/ $^{\circ}$	3.004 to 52.544	5.9 to 52	6.3 to 52	6 to 51.98	6.272 to 52
Index ranges	-23 \leq h \leq 23, -23 \leq k \leq 23, -23 \leq l \leq 23	-8 \leq h \leq 12, -22 \leq k \leq 33, -14 \leq l \leq 15	-9 \leq h \leq 15, -15 \leq k \leq 15, -12 \leq l \leq 12	-12 \leq h \leq 12, -32 \leq k \leq 32, -20 \leq l \leq 20	-21 \leq h \leq 21, -18 \leq k \leq 21, -39 \leq l \leq 39
Reflections collected	27422	13506	6521	33983	76443
Independent reflections	2403 [R _{int} = 0.1000, R _{sigma} = 0.0442]	3697 [R _{int} = 0.0892, R _{sigma} = 0.0907]	1064 [R _{int} = 0.0426, R _{sigma} = 0.0276]	6697 [R _{int} = 0.0420, R _{sigma} = 0.0312]	32532 [R _{int} = 0.0891, R _{sigma} = 0.1677]
Data/restraints/parameters	2403/2/136	3697/0/294	1064/1/83	6697/0/446	32532/71/1676
Goodness-of-fit on F ²	1.075	1.082	1.083	1.051	0.910
Final R indexes [I > 2 σ (I)]	R ₁ = 0.0386, wR ₂ = 0.0967	R ₁ = 0.0895, wR ₂ = 0.2013	R ₁ = 0.0268, wR ₂ = 0.0724	R ₁ = 0.0353, wR ₂ = 0.0895	R ₁ = 0.0735, wR ₂ = 0.1682
Final R indexes [all data]	R ₁ = 0.0549, wR ₂ = 0.1061	R ₁ = 0.1208, wR ₂ = 0.2191	R ₁ = 0.0284, wR ₂ = 0.0734	R ₁ = 0.0387, wR ₂ = 0.0918	R ₁ = 0.1375, wR ₂ = 0.1935
Largest diff. peak/hole / e \AA^{-3}	0.46/-0.32	1.42/-1.19	0.61/-0.30	0.70/-0.56	1.46/-0.49

1#395-460 RT: 0.92-1.07 AV: 66 SB: 67 0.27-0.34, 0.27-0.34 NL: 6.22E7
T: FTMS - p ESI/Full.ms [133.40-2000.00]

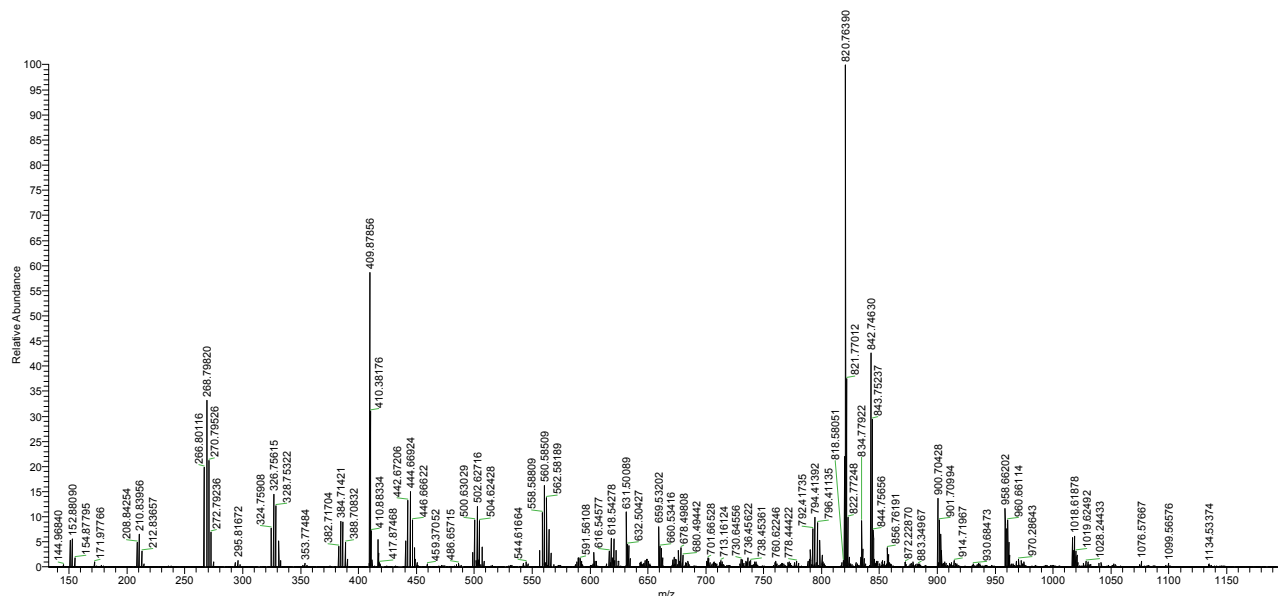


Fig. S10 ESI mass spectrum of compound 1.

5 #403-582 RT: 0.94-1.35 AV: 180 SB: 68 0.20-0.28 , 0.20-0.27 NL: 5.65E8
T: FTMS - p ESI Full ms [133.40-2000.00]

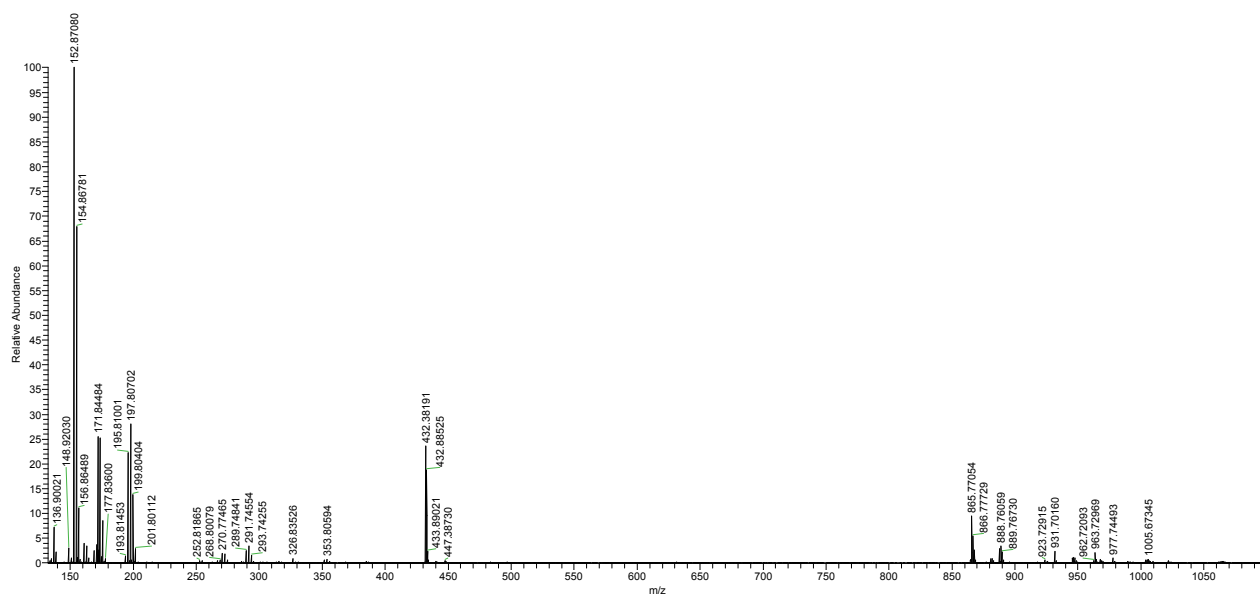


Fig. S11 ESI mass spectrum of compound 2.

3 #657-724 RT: 1.53-1.68 AV: 68 SB: 148 0.22-0.39 , 0.22-0.39 NL: 4.48E7
T: FTMS - p ESI Full ms [133.40-2000.00]

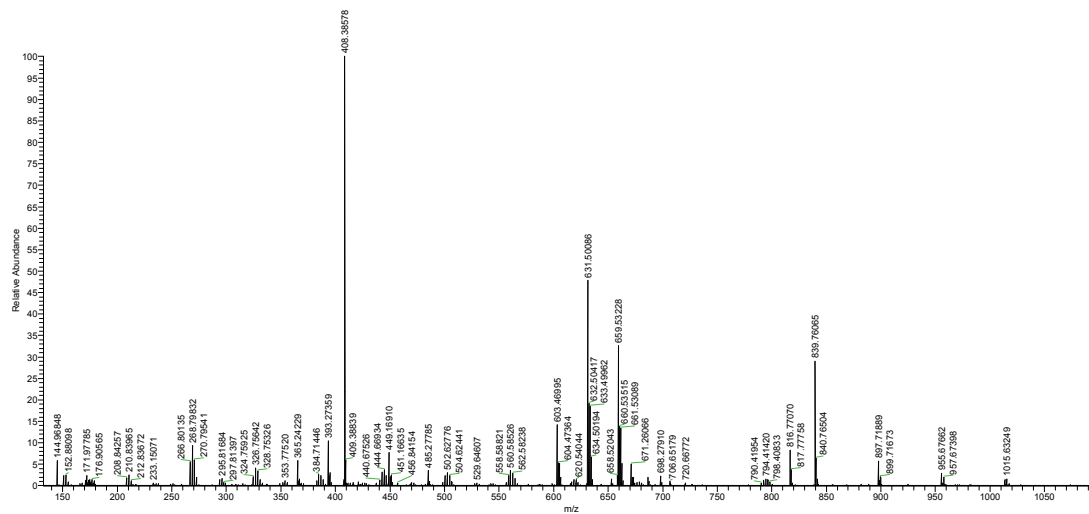


Fig. S12 ESI mass spectrum of compound 3.

4 #581-656 RT: 1.35-1.53 AV: 76 SB: 126 0.23-0.38, 0.23-0.37 NL: 1.86E8
T: FTMS - p ESI Full ms [133.40-2000.00]

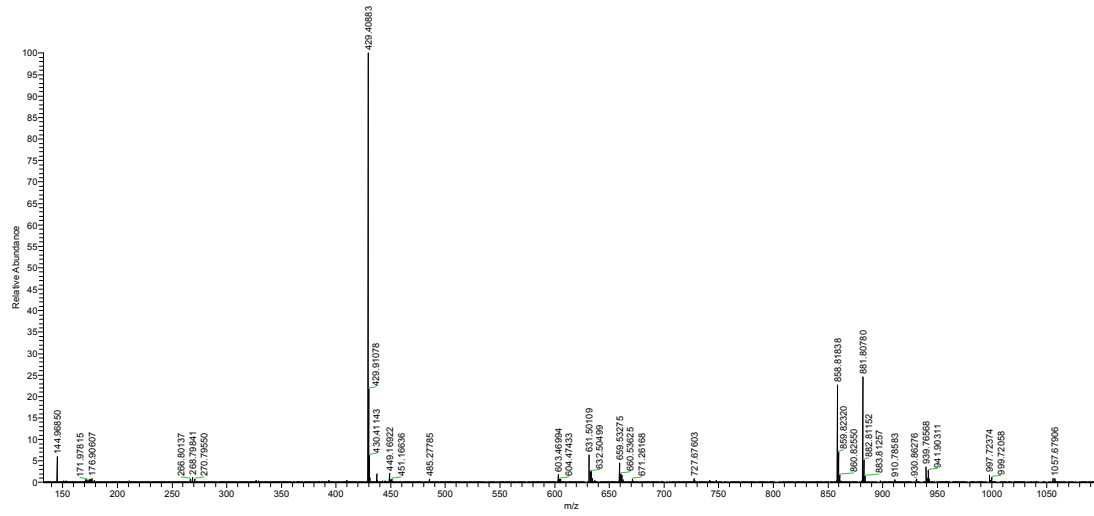


Fig. S13 ESI mass spectrum of compound 4.

1 #434-480 RT: 1.01-1.12 AV: 47 SB: 72 0.21-0.29, 0.20-0.28 NL: 1.86E8
T: FTMS - p ESI Full ms [133.40-2000.00]

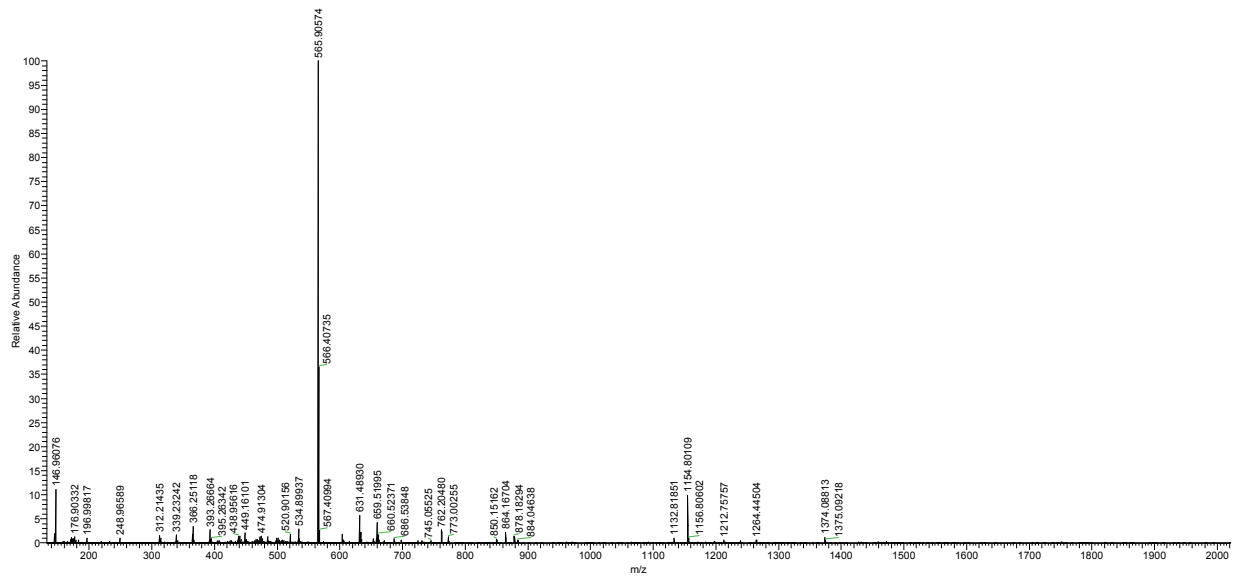


Fig. S14 ESI mass spectrum of compound 5.

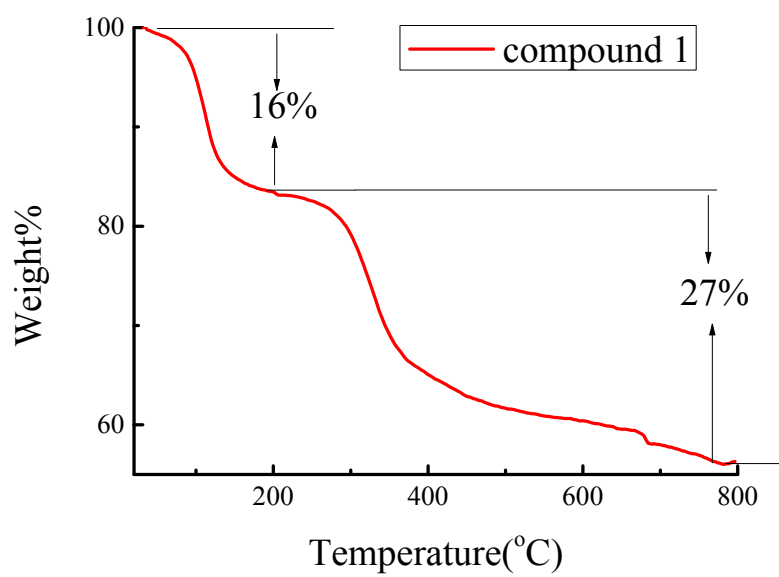


Fig. S15 TGA curve of compound 1.

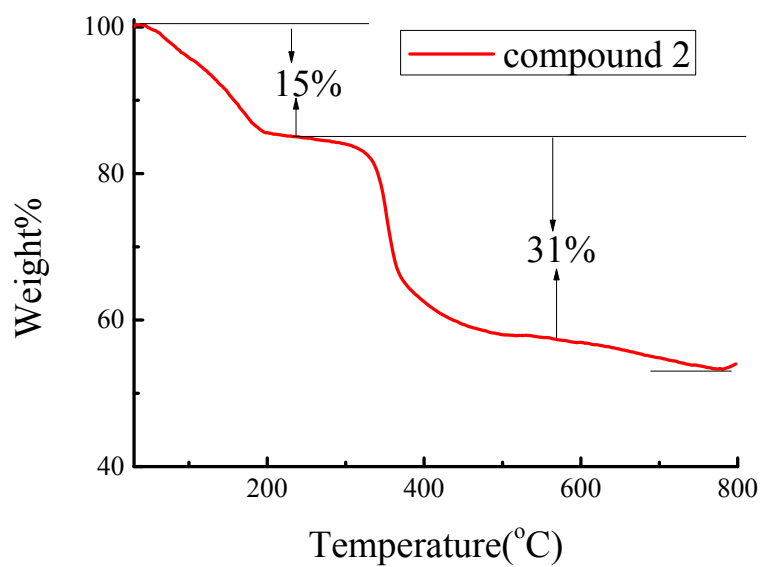


Fig. S16 TGA curve of compound 2.

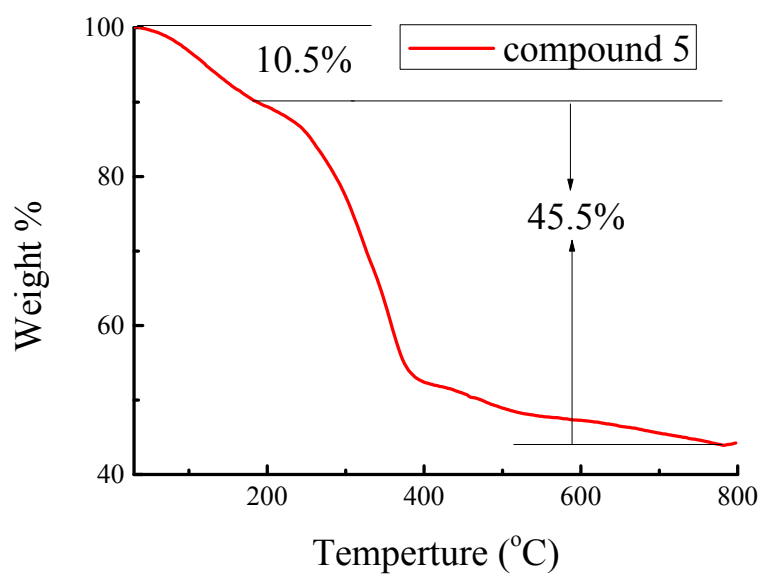


Fig. S17 TGA curve of compound 5.

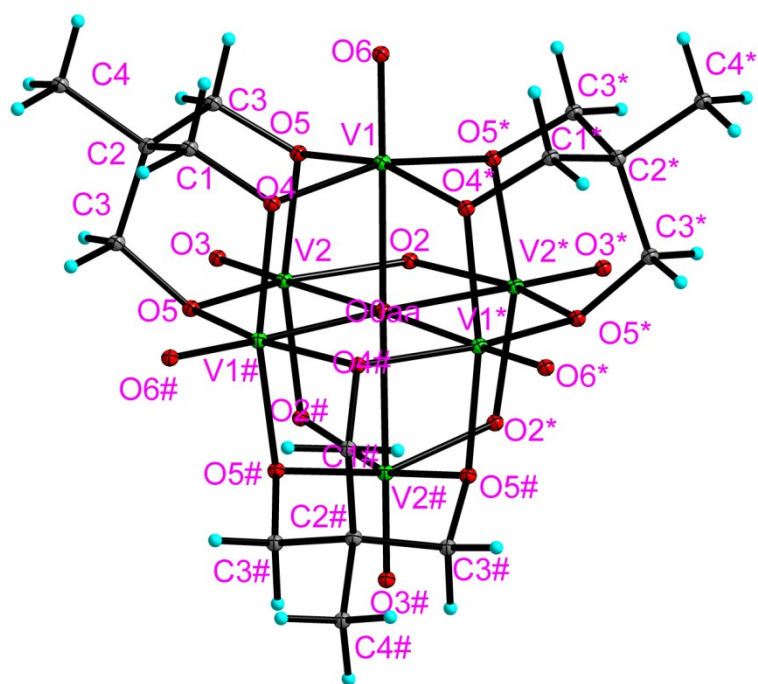


Fig. S18 ORTEP drawing of the cluster anions of 1

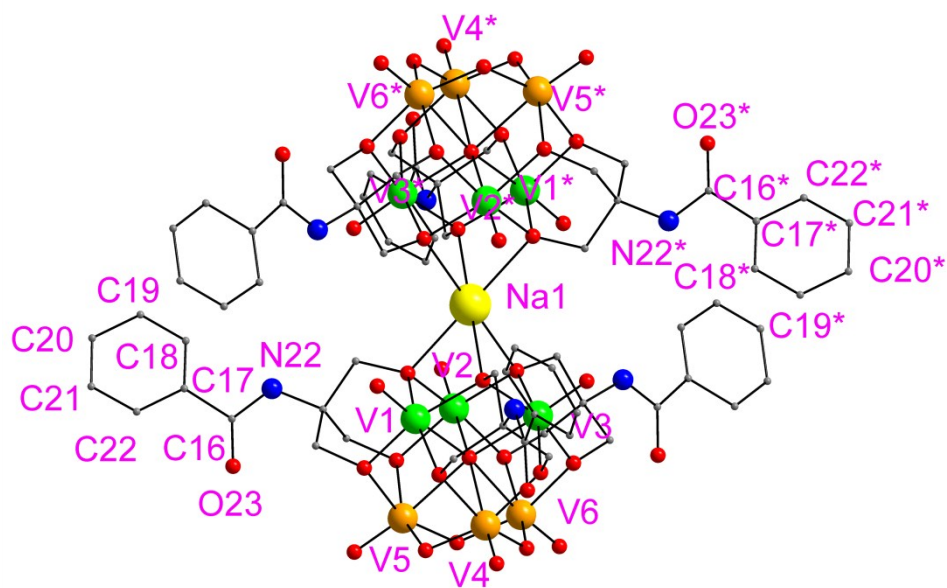


Fig.S19 Center symmetrical structure through sodium ions of **5**.

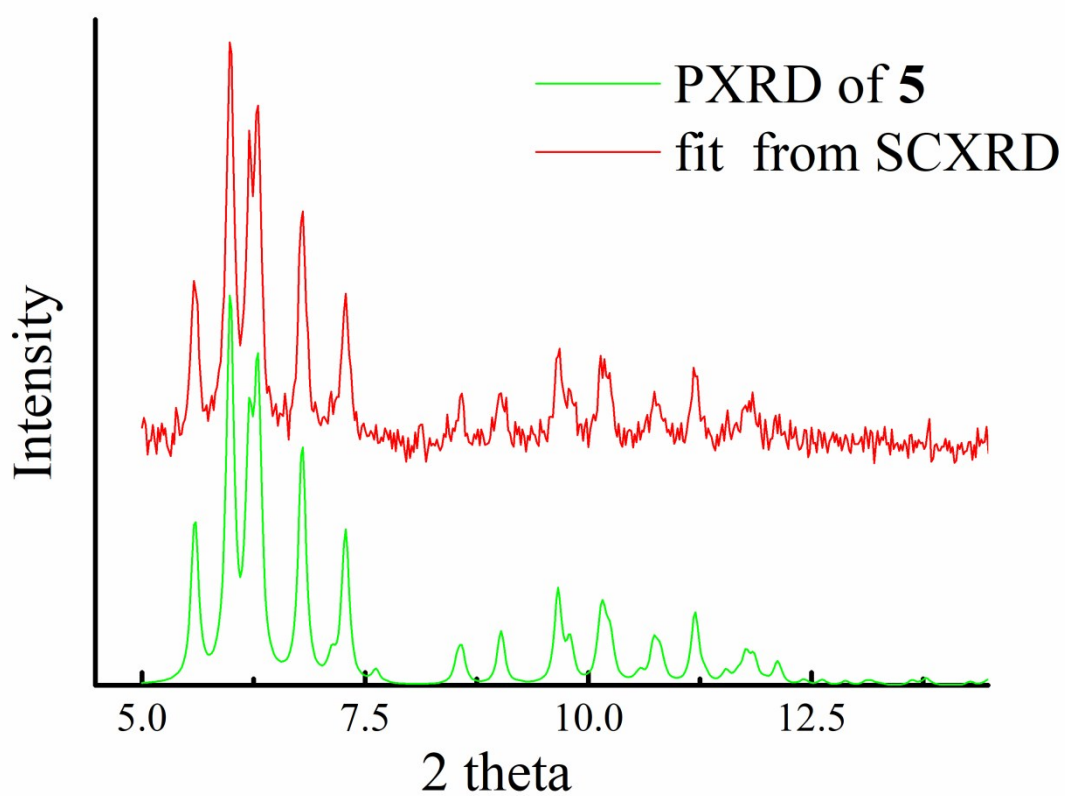


Fig.S20 PXR and SCXRD analysis of **5**.