Controlled Solvo-Thermal Synthesis of Novel Organic Functionalized Polyoxovanadates

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Materials and Methods

All reagents and solvents for synthesis were purchased from commercial sources and used without further purification. The C, H, and N elemental analyses were conducted on Perkin-Elmer 240C elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on Nicolet 170 SXFT/IR spectrometer. A diffuse reflectance UV-vis spectrum ($BaSO_4$ pellet) was obtained from the solid state with a Varian Cary 500 UV-vis-NIR spectrometer. The XPS spectrum was recorded on an ESAY ESCA spectrometer with an Mg–Ka achromatic X-ray source.

Synthesis

Compound **1**

A mixture of $NaVO_3$ (0.24 g, 1.53 mmol), NaN_3 (0.25 g, 3.85 mmol), p-arsanilic acid (0.17 g, 0.79 mmol), $AgNO_3$ (0.2g, 1.17 mmol), H_2O (20 mL) and DMF (10 mL) was mixed and stirred in a 70 mL beaker at 70 °C until a clear solution formed. After the addition of $N_2H_4{\cdot}H_2O$ (0.05 mL), conc. aqueous HCl (0.10 mL) was added. The dark green solution was stirred for 15 min. The solution was filtered and sealed in a 70 mL Teflon-lined stainless steel container, which was heated to 60 °C under autogenously pressure for 24 hours. Yield: 50% (based on V). CHN anal. calcd (found) for $C_{60}H_{114}N_{12}V_{16}As_8O_{72}$: C, 20.19 (20.45); H, 3.22 (3.36); N, 4.71(4.89) IR spectrum, ν (cm^{-1}) : 3412 (s), 1596(s), 1504 (s), 1484(m), 1391(m), 1310(m), 1185(m), 1092(s), 977(s), 793(s), 651(s), 519(s) cm^{-1}.

Compound **2**

The synthetic procedure for **2** was the same as for **1** except the reaction temperature was 100 °C. After slow cooling to room temperature, the resulting brown block crystals of **2** were formed. Yield: 70 % (based on V). CHN anal. calcd (found) for $C_{67}H_{149}N_{17}V_{16}As_8O_{68}$: C, 21.79 (22.01); H, 4.06 (4.16); N, 6.44 (6.56). IR spectrum, ν (cm-1): 3342(w), 2789(w), 2361(w), 1648(s), 1654(s), 1594(s), 1505(m), 1466(m), 1430(m), 1185(m), 1095(s), 986(s), 824(s),620(m), 525(m) cm^{-1}.

Compound **3**

A mixture of $NaVO_3$ (0.24 g, 1.53 mmol), NaN_3 (0.25 g, 3.85 mmol), o-arsanilic acid (0.17 g, 0.79 mmol), $AgNO_3$ (0.2g,1.17 mmol), H_2O (20 mL) and DMF (10 mL) was mixed and stirred in a 70 mL beaker at 70 °C until a clear solution formed. After the addition of $N_2H_4{\cdot}H_2O$ (0.05 mL), conc. aqueous HCl (0.10 mL) was added. The dark green solution was stirred for 15 min, The solution was filtered and sealed in a 70 mL Teflon-lined stainless steel container, which was then heated to 120 °C under autogenously pressure for 24 hours. Yield: 65% (based on V). CHN anal. calcd (found)

for C_{64} H_{122} As_8 N_{16} O_{57} V_{16}: C, 22.34 (22.51); H, 3.57 (3.36); N, 6.51(6.62) IR spectrum, ν (cm^{-1}) : 3344 (m), 3053 (m), 2788(m), 1655 (s), 1485(m), 1448(m), 1386(m), 1317(m), 1252(w), 1094(m), 988(s), 824(s),756(w), 711(w), 622(w), 521(m) cm^{-1}.

Compound **4**

The synthetic procedure for **4** was the same as for **3** except that phenylarsonic acid (0.15 g, 0.74 mmol) was used instead of o-arsanilic acid. Dark brown crystals of **4** were obtained Yield: 68% (based on V). CHN anal. calcd (found) for $C_{73}H_{150}N_{11}V_{16}As_8O_{63.5}$: C, 24.28 (24.51); H, 4.18 (4.26); N, 4.27(4.38) IR spectrum, ν (cm^{-1}) : 3310 (m), 3058 (m), 2789(m), 1658 (s), 1467(m), 1431(m), 1379(w), 1245(s), 1090(s), 987(s), 832(s),693(s), 622(s), 521(s) cm^{-1}.

Compound **5**

The synthetic procedure was the same as for **2** except the reaction temperature was 160 °C. After cooling to room temperature, the mother liquor was left to evaporate at room temperature. Block-shaped brown crystals of **5** were obtained after two months. Yield: 5% based on V).

X-ray Crystallography

Single-crystal X-ray diffraction data for compounds **1**–**4 (5)** were conducted on a Bruker-AXS CCD diffractometer equipped with a graphite-monochromated Mo Ka radiation (k = 0.71073 A °) at 150 (296) K. All absorption corrections were applied using multi-scan technique. The structures were solved by the direct method and refined through full-matrix least-squares techniques method on F^2 using the SHELXTL 97 crystallographic software package.[1,2] The hydrogen atoms of the organic ligands were refined as rigid groups. The water H atoms could not be positioned reliably. The diffraction data of compound **1-4** was treated by the ‘‘SQUEEZE’’ method as implemented in PLATON[3] to remove diffuse electron density associated with these badly disordered solvent molecules. The application of SQUEEZE had the effect of dramatically improving the agreement indices. The structure of compound **4** was found to be racemically twinned with the major twin fraction being refined to a value of 0.334(6).

Crystallographic Data for Compounds **1-5** are summarized in Table S2. The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as entries 860491-860494.

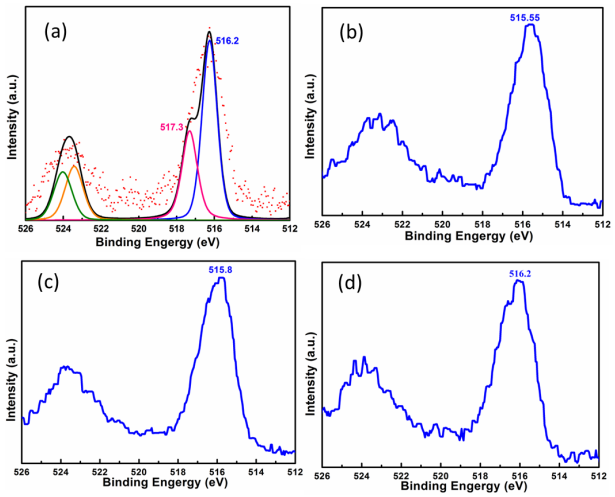

Fig. S1: The XPS spectra for V in compound **1-4**

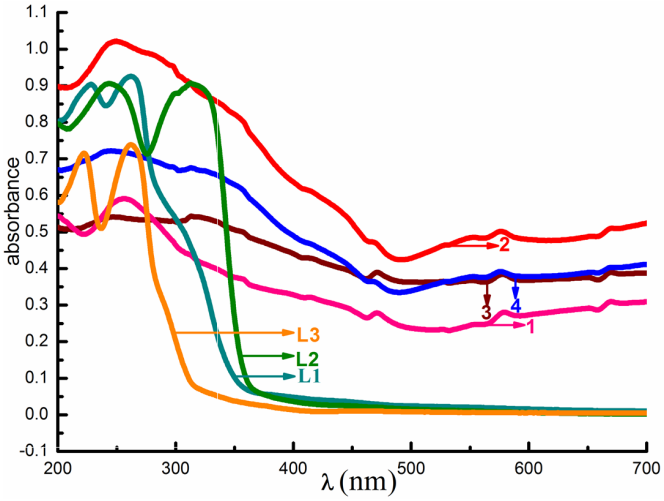

Fig. S2: The UV-vis absorption spectra of **1-4** and the ligands

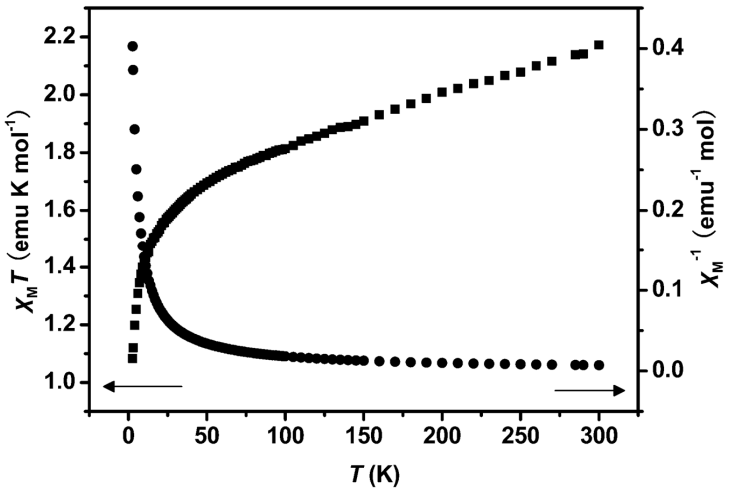

Fig. S3: Temperature dependences of $\chi_M T$ (■) andχ_M(●) of compound **2**

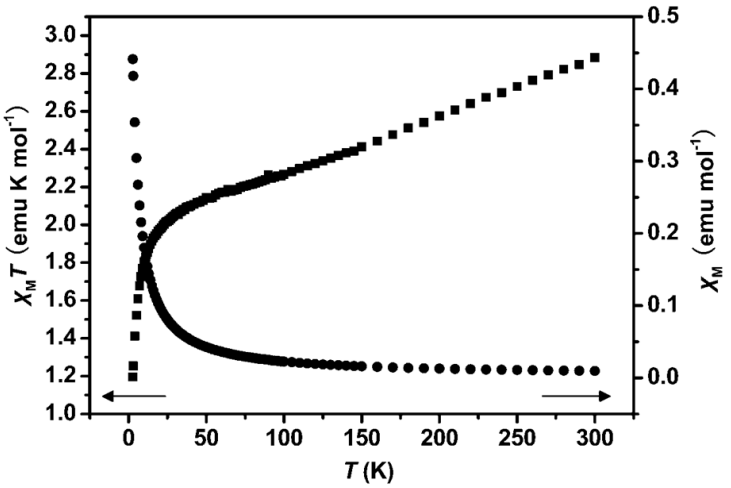

Fig. S4: Temperature dependences of $\chi_M T$ (■) and χ_M (●) of compound **3**

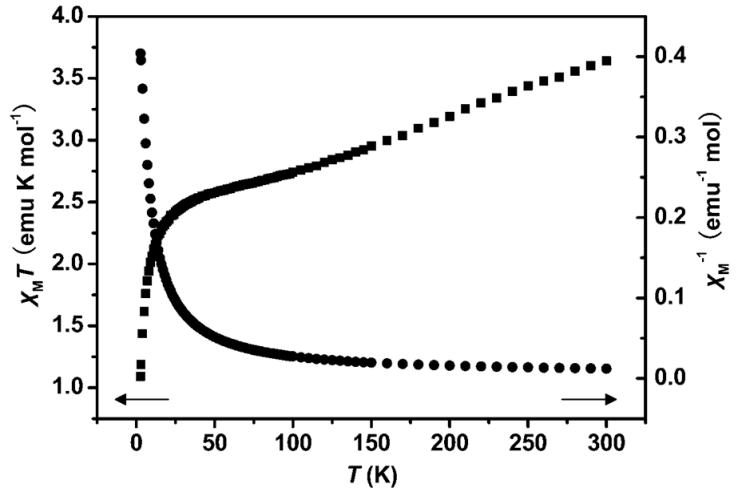

Fig. S5: Temperature dependences of $\chi_M T$ (■) and χ_M (●) of compound **4**

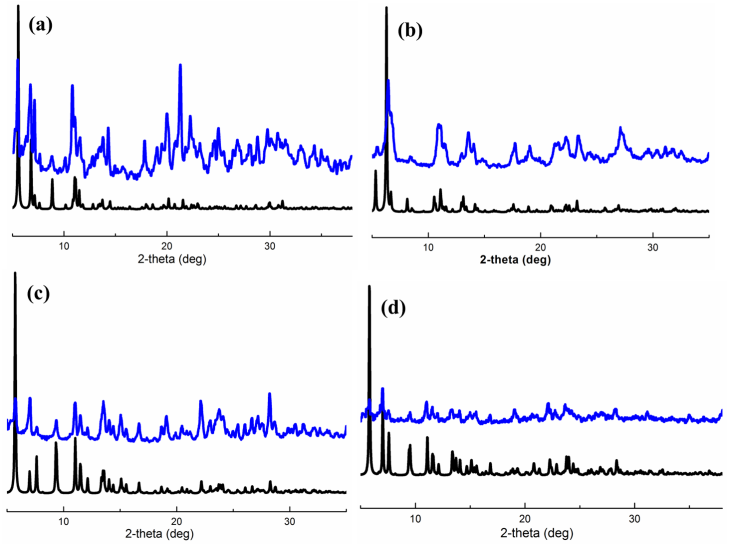

Fig. S6. The simulated (black) and experimental (blue) powder XRD pattern of Compound **1-4**. Simulation based on the single crystal X-ray diffraction data.

Three powder X-ray diffraction patterns of the bulk products **1** to **4** are in good agreement with the calculated patterns based on the results from single-crystal X-ray diffraction (**Fig. S6**), which confirm that both phases are pure.

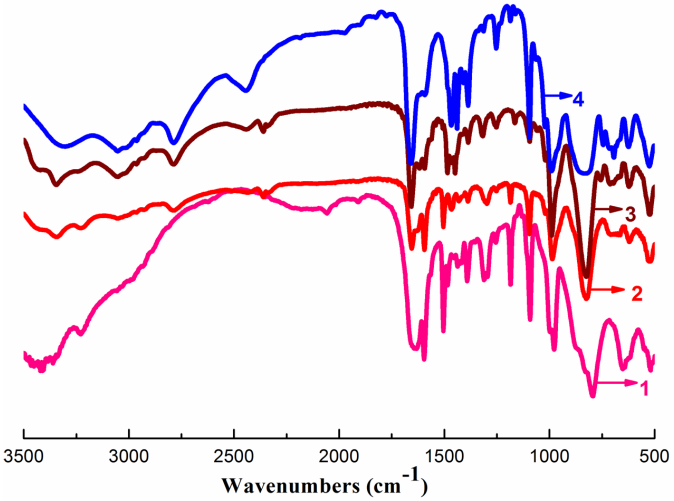

Fig. S7: The FT-IR spectra of compounds **1**-**4**

The IR spectrum of **1** exhibits a strong bands at 1091 cm^{-1}(1095, 1090, 1090 $cm^{-1}$for **2**, **3** and **4**) and 979 cm^{-1} (986, 988 and 987 cm^{-1} for **2**, **3** and **4**), associated with the {$[4(2)\text{-}NH_2\text{-}PhAsO_3]^{2-}$ and $[PhAsO_3]^{2-}$} group and the $\nu(V^{IV}=O)$ stretching vibration, respectively.

Table S1. Bond valance sum calculations for compound **1-5.**[4]

1	**V site**	V1	V2	V3	V4	V5	V6		
	BVS	4.212	5.166	4.403	4.268	4.425	4.374		
	assigned O.S.	+4	+5	+4	+4	+4	+4		
2	**V site**	V1	V2	V3	V4	V5	V6	V7	V8
	BVS	4.308	4.347	4.368	4.293	4.342	4.318	4.336	4.317
	assigned O.S.	+4	+4	+4	+4	+4	+4	+4	+4
3	**V site**	V1	V2	V3	V4	V5	V6	V7	V8
	BVS	4.413	4.430	4.412	4.423	4.432	4.444	4.433	4.423
	assigned O.S.	+4	+4	+4	+4	+4	+4	+4	+4
4	**V site**	V1	V2	V3	V4	V5	V6	V7	V8
	BVS	4.305	4.286	4.327	4.394	4.264	4.333	4.282	4.311
	assigned O.S.	+4	+4	+4	+4	+4	+4	+4	+4
	V site	V9	V10	V11	V12	V13	V14	V15	V16
	BVS	4.377	4.302	4.227	4.356	4.345	4.347	4.299	4.366
	assigned O.S.	+4	+4	+4	+4	+4	+4	+4	+4
5	**V site**	V1	V2	V3					
	BVS	5.022	4.441	4.950					
	assigned O.S.	+5	+4	+5					

Table S2 Crystallographic Data for Compounds **1-5**

Compounds	*1*	*2*	*3*	*4*	*5*
Formula	$C_{60}H_{114}As_8N_{12}O_{72}V_{16}$	$C_{67}H_{149}As_8N_{17}O_{68}V_{16}$	$C_{64}H_{122}As_8N_{16}O_{57}V_{16}$	$C_{73}H_{150}As_8N_{11}O_{63.5}V_{16}$	$AsNa_2O_{68}H_{56}V_{14}$
M_r	3570.40	3695.83	3442.57	3612.90	1978.51
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Tetragonal
Space group	C 2/m	Pbcn	C 2/c	C c	I4/mmm
Temperature	150(2) K	150(2) K	150(2) K	150(2) K	296(2)
a (Å)	24.181(4)	21.7320(18)	27.341(3)	26.9560(10)	10.8586(5)
b (Å)	26.241(4)	25.715(2)	26.566(3)	26.4805(10)	10.8586(5)
c (Å)	14.983(2)	26.451(2)	20.434(2)	20.1034(8)	21.7258(18)
α (deg)	90	90	90	90	90
β (deg)	124.473(3)	90	112.657(2)	111.0210(10)	90
γ (deg)	90	90	90	90	90
V (Å^3)	7837(2)	14782(2)	13697(3)	13395.0(9)	2561.7(3)
Z	2	4	4	1	2
$D_{calc.}$ (g cm^{-3})	1.493	1.626	1.664	1.779	2.492
F(000)	3440	7076	6784	7120	1842
$R_1[I>2\sigma(I)]$	0.0740	0.0728	0.0501	0.0371	0.0379
$wR_2[I>2\sigma(I)]$	0.2175	0.2015	0.1476	0.0976	0.1185
R_1(all data)	0.1057	0.0942	0.0653	0.0438	0.0426
wR_2(all data)	0.2425	0.2122	0.1572	0.1007	0.1364
GOOF	0.963	1.065	1.083	1.036	1.168

References:

1 G.M. Sheldrick, SHELXS-97, *Program for Crystal Structure Solution*, Göttingen University, Germany, 1997;

2 G.M. Sheldrick, SHELXL-97, *Program for Crystal Structure Refinement*, Göttingen University, Germany, 1997.

3 P. van der Sluis and A. L. Spek, Acta Crystallogr., Sect. A: Found. *Crystallogr*., 1990, **46**, 194.

4 N. E. Brese, M. O'Keeffe, *Acta Crystallogr. Sect. B,* 1991, **47**, 192.