SUPPORTING INFORMATION

An enantioenriched vanadium phosphonate generated *via* asymmetric chiral amplification of crystallization from achiral sources showing a single-crystal-to-single-crystal dehydration process

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Experimental Section.

The reagents and solvents employed were commercially available and used without further purification. The 2-carboxyphenylphosphonic acid (2-cppH_3) was synthesized by the Arbuzov reaction.[1] Elemental analyses for C, H were performed on an Elementar Vario MICRO elemental analyzer. The infrared spectra were recorded on a Bruker VECTOR 22 IR spectrometer with pressed KBr pellets in the 400–4000 cm^{-1} region. Thermogravimetric analyses were performed with a METTLER TOLEDO TGA/DSC 1 instrument in the range of 30-800 ^{o}C under a nitrogen flow at a heating rate of 10^{o}C min^{-1}. Powder X-ray diffraction patterns were recorded on a SHIMADZU XRD-6000 instrument using Cu-Kα radiation. The magnetic susceptibility data were obtained on polycrystalline samples using a Quantum Design MPMSXL7 SQUID magnetometer. The data were corrected for the diamagnetic contributions of both the sample holder and the compound obtained from Pascal's constants.[2]

Synthesis of $(VO)_3(2\text{-cpp})_2(H_2O)_6\cdot H_2O$ (1)

NH_4VO_3 (0.0232 g, 0.2 mmol) and 2-cppH_3 (0.0404 g, 0.2 mmol) were added to 8 mL 1:1 mixed solution of H_2O / ethanol, the pH value was adjusted to 0.9 with 1 M HNO_3. Then the mixture was transferred to a Teflon-lined autoclave and kept at 120 ◦C for 48 h. After slow cooling to room temperature, blue plate-like crystals were obtained as a monophasic material based on the powder XRD measurement. The crystals were washed with distilled water and dried in air, then used for physical measurements. Yield: 0.0300 g (62% based on V). Elemental anal. calcd. for $C_{14}H_{22}O_{20}P_2V_3$: C, 23.17; H, 3.03. Found: C, 22.94; H, 3.12 %. IR (KBr, cm^{-1}): 3228.9(br,s), 1578.1(s), 1546.8(vs), 1471.5(m), 1447.3(m), 1396.7(s), 1264.0(w), 1153.4(s), 1127.1(vs), 1091.2(s), 1053.8(vs), 1023.5(s), 1004.1(s), 872.8(w), 803.1(w), 756.4(m), 720.3(w), 664.1(w), 620.1(m), 561.3(w), 483.8(m).

Single-Crystal Structure Determination.

Single crystals were selected for indexing and intensity data collection on a Bruker SMART APEX CCD diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) at room temperature. A hemisphere of data were collected in the θ range 2.15–25.00° for **1**, 2.66-25.00° for **1a**, using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 5 s/frame. The data were integrated using the Siemens SAINT program,[3] with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector face plate. Absorption corrections were applied. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares using SHELXTL.[4] All the non-hydrogen atoms were located from the Fourier maps, and were refined anisotropically. All H atoms were allowed for as riding atoms with isotropic vibration parameters related to the non-hydrogen atoms to which they are bonded. The selected bond lengths and angles for the two compounds are listed in Tables S2 and S3.

References

1 I. P. Beletskaya and M. A. Kazankova, *Russian J. Org. Chem.,* 2002, **38**, 1391-1430.
2 O. Kahn, *Molecular Magnetism*, VCH Publishers, Inc., New York, **1993**.
3 *SAINT, Program for Data Extraction and Reduction*, Siemens Analytical. X-ray Instruments, Madison, WI, 1994–1996.
4 *SHELXTL (version 5.0), Reference Manual*, Siemens Industrial Automation. Analytical Instruments, Madison, WI, 1995.

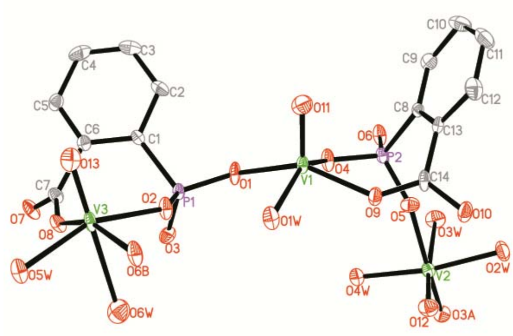

Fig. S1. The building unit of **1** in ORTEP view (50% thermal ellipsoids). All H atoms and lattice water molecules are omitted for clarity. Symmetry transformations used to generate equivalent atoms: (A) -x+1, y-1/2, -z+2; (B) x+1, y, z.

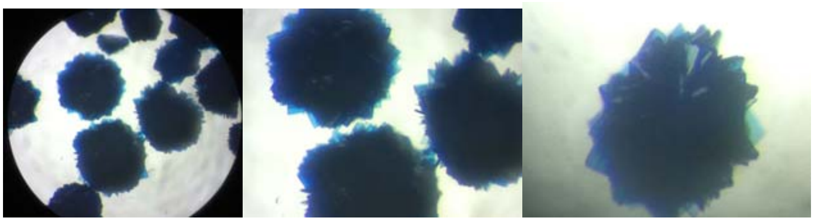

Fig. S2. Photographs of crystals of **1** in the form of cluster.

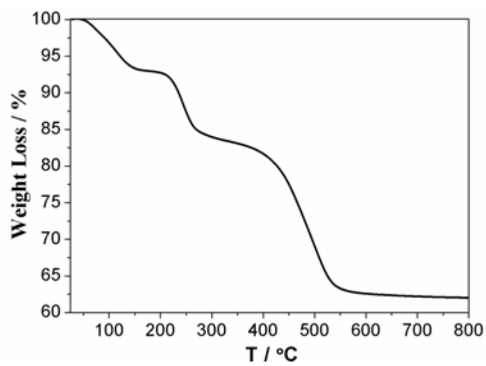

Fig. S3. TG curve of compound **1**

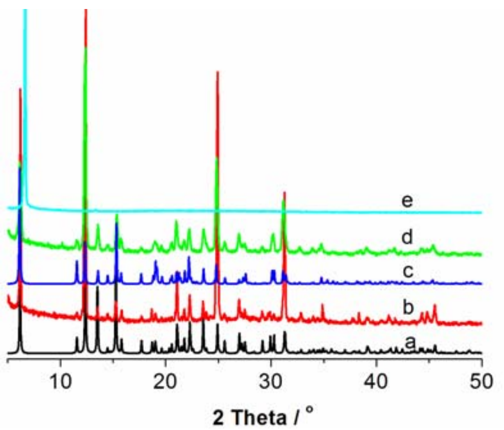

Fig. S4. Powder X-ray diffraction patterns for **1**, **1a** and **1b**: (a) calculated from single-crystal data for **1**, (b) bulk sample of **1**, (c) calculated from single-crystal data for **1a**, (d) bulk sample of **1a** obtained by heating **1** at 160 °C for 2 h, (e) bulk sample of **1b** by heating **1** at 270 °C for 2 h.

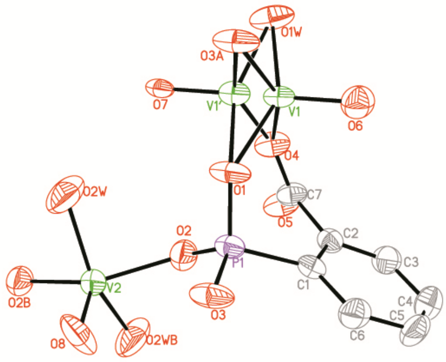

Fig. S5. The building unit of **1a** in ORTEP view (50% thermal ellipsoids). All H atoms are omitted for clarity. Symmetry transformations used to generate equivalent atoms: (A) x, -y+5/2, z+1/2; (B) -x+1, -y+2, -z.

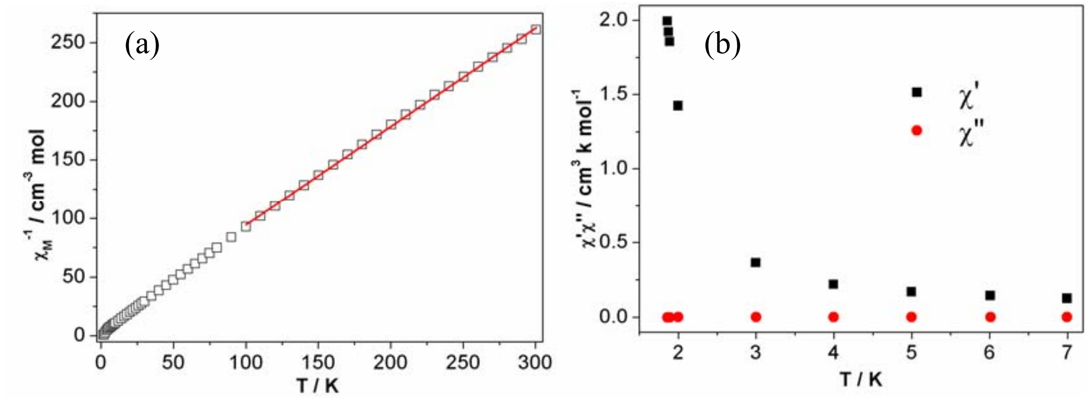

Fig. S6. (a) χ_M^{-1} vs. T plot and (b) temperature dependent *ac* magnetic susceptibility for **1.**

Table S1. Selected bond lengths [Å] and angles [deg] for compound **1**.

V1-O1	1.961(4)	V3-O6B	1.976(4)
V1-O4	1.959(4)	V3-O13	1.570(4)
V1-O9	1.993(4)	V3-O8	2.005(4)
V1-O11	1.570(4)	V3-O5W	2.043(4)
V1-O1W	2.030(4)	V3-O6W	2.407(5)
V2-O3A	1.956(3)	P1-O1	1.499(4)
V2-O5	1.967(4)	P1-O3	1.508(4)
V2-O12	1.578(4)	P1-O2	1.533(4)
V2-O2W	2.033(4)	P2-O5	1.501(4)
V2-O3W	2.272(4)	P2-O6	1.522(4)
V2-O4W	2.046(5)	P2-O4	1.527(4)
V3-O2	1.973(4)		
O11-V1-O4	108.9(2)	O12-V2-O3W	174.7(2)
O11-V1-O1	106.4(2)	O5-V2-O3W	79.52(16)
O4-V1-O1	82.32(17)	O2W-V2-O3W	78.8(2)
O11-V1-O9	104.6(2)	O4W-V2-O3W	85.90(19)
O4-V1-O9	88.68(17)	O13-V3-O2	103.5(2)
O1-V1-O9	148.95(17)	O13-V3-O8	101.0(2)
O11-V1-O1W	106.7(2)	O2-V3-O8	91.33(16)
O4-V1-O1W	144.32(19)	O13-V3-O5W	100.0(2)
O1-V1-O1W	85.96(18)	O2-V3-O5W	156.23(18)
O9-V1-O1W	84.26(17)	O8-V3-O5W	87.47(16)
O12-V2-O5	100.38(19)	O13-V3-O6W	177.6(2)
O12-V2-O2W	95.9(2)	O2-V3-O6W	75.88(17)
O5-V2-O2W	89.18(18)	O8-V3-O6W	76.73(17)
O12-V2-O4W	99.4(2)	O5W-V3-O6W	80.75(17)
O5-V2-O4W	88.95(18)	O6B-V3-O6W	79.34(18)
O3A-V2-O5	156.57(18)	O6B-V3-O5W	87.63(16)
O3A-V2-O2W	91.20(18)	O6B-V3-O8	156.04(17)
O3A-V2-O4W	84.55(18)	O2-V3-O6B	83.88(16)
O3A-V2-O3W	77.57(16)	O13-V3-O6B	102.9(2)
O2W-V2-O4W	164.7(2)		

Symmetry transformations used to generate equivalent atoms: (A) -x+1, y-1/2, -z+2; (B) x+1, y, z; (C) -x+1, y+1/2, -z+2; (D) x-1, y, z.

Table S2. Selected bond lengths [A] and angles [deg] for **1a**.

V1-O6	1.576(5)	V1'-O1W	1.932(9)
V1-O3A	1.947(4)	V1'-O1	1.944(8)
V1-O1	1.959(4)	V1'-O3A	1.984(8)
V1-O4	1.982(4)	V2-O8	1.508(9)
V1-O1W	1.997(4)	V2-O2	1.940(5)
V1'-O7	1.653(17)	V2-O2W	1.941(5)
V1'-O4	1.928(8)		
O6-V1-O3A	105.5(2)	O1W-V1'-O1	156.1(5)
O6-V1-O1	107.9(2)	O7-V1'-O3A	107.9(9)
O3A-V1-O1	82.40(18)	O4-V1'-O3A	152.9(5)
O6-V1-O4	103.6(2)	O1W-V1'-O3A	87.1(3)
O3A-V1-O4	150.9(2)	O1-V1'-O3A	81.8(3)
O1-V1-O4	88.39(19)	O8-V2-O2	106.0(4)
O6-V1-O1W	105.2(2)	O8-V2-O2W	113.2(5)
O3A-V1-O1W	86.30(17)	O2-V2-O2W	88.9(2)
O1-V1-O1W	146.8(2)	O8-V2-O2B	107.0(4)
O4-V1-O1W	86.53(18)	O2-V2-O2B	146.29(13)
O7-V1'-O4	99.2(9)	O2W-V2-O2B	84.3(2)
O7-V1'-O1W	99.5(9)	O8-V2-O2WB	99.8(5)
O4-V1'-O1W	89.9(4)	O2-V2-O2WB	82.4(2)
O7-V1'-O1	104.0(9)	O2W-V2-O2WB	147.03(14)
O4-V1'-O1	90.4(3)	O2B-V2-O2WB	85.7(2)

Symmetry transformations used to generate equivalent atoms: (A) x,-y+5/2,z+1/2; (B) -x+1,-y+2,-z; (C) x,-y+5/2,z-1/2.

Table S3. Valence sum calculations for the crystallographically independent vanadium atoms in compound **1**.

	bond-valence sums		
	V(1)	V(2)	V(3)
V^{III}	3.836	3.645	3.842
V^{IV}	**4.286**	**4.072**	**4.293**
V^{V}	4.511	4.287	4.520

Table S5. A summary of structure determinations of 6 randomly selected crystals of compound **1** from the same cluster

Crystals	**Cluster 1**					
	1-a	**1-b**	**1-c**	**1-d**	**1-e**	**1-f**
a	9.543(3)	9.530(3)	9.5238(8)	9.550(2)	9.555(1)	9.438(4)
b	8.970(3)	9,056(3)	9.0820(8)	9.006(2)	8.988(1)	8.911(4)
c	14.288(5)	14.429(5)	14.392(1)	14.342(3)	14.317(2)	14.144(6)
β	95.920(6)	96.100(7)	96.135(2)	95.901(5)	95.980(2)	95.783(7)
V	1216.5(7)	1238.3(7)	1237.7(2)	1226.9(5)	1223.0(2)	1183.4(9)
R_1	0.0473	0.0869	0.1417	0.0585	0.0369	0.078
wR_2	0.1166	0.2361	0.3732	0.1432	0.1044	0.2007
Flack parameter	**0.29(3)**	**0.35(7)**	**0.02(8)**	**0.44(8)**	**-0.02(2)**	**0.53(8)**
Residue peak	1.128	3.281	5.665	1.437	1.084	1.501