

Electronic Supplementary Information

for

Cation-controlled capture of polyoxovanadate-based organic-inorganic 1D architectures

1. Instrumentation:	2
2. Synthetic Section	3
Synthesis of [Ba(DMSO) ₈][(C ₈ N ₄ H ₂₃)V ₁₂ O ₃₂ (NO ₃)] (1):.....	3
Synthesis of [La(DMSO) ₈][(C ₈ N ₄ H ₂₂)V ₁₂ O ₃₂ (NO ₃)] x DMSO (2):.....	3
3. Crystallographic Information	4
4. TGA Studies	5
5. Infrared Measurements.....	6
6. Energy-dispersive X-ray spectroscopy	7
7. Literature:.....	7

1. Instrumentation:

Single-crystal X-ray diffraction (sc-XRD) was measured on a Bruker APEX-II CCD Single-crystal X-ray diffractometer equipped with a graphite monochromator using Mo K α radiation (wavelength $\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$). Details on data collection, processing and refinement are given in the crystallographic section below.

Thermogravimetric analysis (TGA) was carried out on a NETZSCH TG 209F1 analyzer at a heating rate of 10.0 K min⁻¹ in a range between 30 and 600 °C under O₂ in an Al crucible.

Optical microscope: Images of single-crystals of **1** and **2** were taken using a Bresser Microscope - 5803100 - Researcher ICD LED 20x-80x equipped with a Bresser Full HD Microscope Camera USB 2.0 with built-in UV/IR Filter.

Attenuated total reflectance-Fourier-transformed infrared spectroscopy (ATR-FT-IR) was performed using a Bruker Alpha II equipped with an ATR Platinum Diamond unit. The data were recorded with 24 scans at a resolution of 4 cm⁻¹. A background correction was used for all spectra within the OPUS 8.1 software.

Energy-dispersive X-ray spectroscopy (EDX) was performed on a Zeiss Leo-1530 scanning electron microscope (equipped with an Oxford Instruments X-maxN EDX detector (operated at 10 kV).

2. Synthetic Section

General remarks: All chemicals were purchased from Sigma Aldrich, ABCR or Carl Roth and were of reagent grade. The chemicals were used without further purification unless stated otherwise. $(^n\text{Bu}_4\text{N})_4[\text{V}_4\text{O}_{12}]$ was prepared according to reference S1.

Synthesis of $[\text{Ba}(\text{DMSO})_8][(\text{C}_8\text{H}_{23}\text{N}_4)\text{V}_{12}\text{O}_{32}(\text{NO}_3)]$ (**1**):

$(^n\text{Bu}_4\text{N})_4[\text{V}_4\text{O}_{12}]$ (200 mg, 0.139 mmol, 1.0 eq.), $\text{Ba}(\text{NO}_3)_2$ (24 mg, 0.139 mmol, 0.67 eq.) and cyclen (23 mg, 0.139 mmol, 1 eq.) were dissolved in 10 mL DMSO and stirred at 80 °C. The yellowish solution was cooled to rt after 4 hours and acidified with 350 μL 3 M aqueous HNO_3 . The solution changed to orange and was stored under dark ambient conditions for several days. Dark orange-red cubic crystals of **1** were recovered by filtration, washed with DMSO and diethyl ether (3x each) and dried.

Yield: 39.2 mg, 0.0185 mmol, 39.9 % based on V).

Characteristic IR bands (in cm^{-1}): 3284 (w); 3175 (w); 3002 (w); 2913 (w); 1552 (w); 1434 (w); 1410 (w); 1400 (w); 1368 (w); 1344 (w); 1312 (w); 1025 (s); 985 (vs); 951 (s); 846 (s); 793 (s); 747 (s); 701 (s); 629 (vs); 539 (s); 510 (s)

Elemental analysis (EDX): metal ratio (at.-%): Ba:V: obs.: 1.0:11.50 (obsd); 1.0:12.0 (calcd)

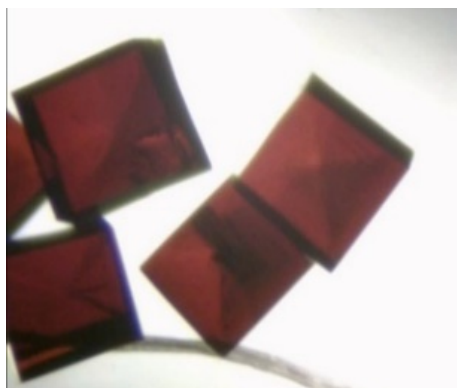


Figure S1: photograph of single-crystals of **1**.

Synthesis of $[\text{La}(\text{DMSO})_8][(\text{C}_8\text{H}_{22}\text{N}_4)\text{V}_{12}\text{O}_{32}(\text{NO}_3)] \times \text{DMSO}$ (**2**):

$(^n\text{Bu}_4\text{N})_4[\text{V}_4\text{O}_{12}]$ (200 mg, 0.139 mmol, 1.0 eq.), $\text{La}(\text{NO}_3)_3 \times 6 \text{H}_2\text{O}$ (60 mg, 0.139 mmol, 1 eq.) and Cyclen (24 mg, 0.139 mmol, 1 eq.) were dissolved in 10 mL DMSO and stirred at 80 °C. The yellowish solution was cooled to rt after 4 hours and acidified with 350 μL 3 M aqueous HNO_3 . The solution turned orange and was stored under dark ambient conditions. Over a period of a few days, dark orange red cubic crystals were obtained, recovered by filtration, washed with DMSO and diethyl ether (3x each) and dried.

Yield: 39.3 mg, 0.0178 mmol, 38.5 % based on V).

Characteristic IR bands (in cm^{-1}): 3317 (w); 3173 (w); 2996 (w); 2911 (w); 2864 (w); 1543 (w); 1398 (w); 1319 (w); 1048 (w); 1000 (w); 976 (vs); 953 (vs); 845 (s); 820 (w); 788 (w); 746 (s); 702 (s); 630 (vs); 605 (s); 539 (s); 511 (s); 456 (w)

Elemental analysis (EDX): metal ratio (at.-%): La:V: obs.: 1.0:12.05 (obsd); 1.0:12.0 (calcd)

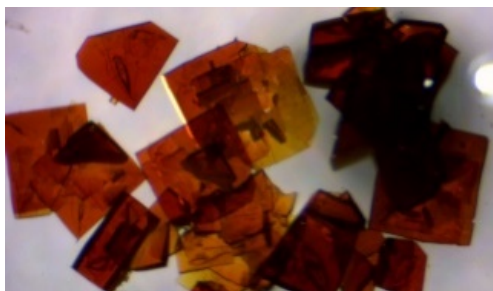


Figure S 2: photograph of single-crystals of **2**.

3. Crystallographic Information

Suitable single-crystals were mounted onto a microloop using Fomblin oil. X-ray diffraction intensity data were measured at 150 K on a Bruker D8 QUEST diffractometer ($\lambda(\text{MoK}\alpha) = 0.71073 \text{ \AA}$) equipped with a graphite monochromator. Structure solution was carried out using SHELX-2013^{S2} package through OLEX2.^{S3}. Corrections for incident and diffracted beam absorption effects were applied using empirical methods.^{S4}. Structures were solved by a combination of direct methods and difference Fourier syntheses and refined against F^2 by the full matrix least-squares technique. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added to carbon atoms using a riding model. The single crystals are twinned and were correct by the Twin Law $[010; 100; 00\bar{1}]$ and by a basf parameter. Most atoms were refined anisotropically, only disordered DMSO solvent ligands were refined isotropically to ensure stability of the crystallographic model. No constraints were used. CIF file can be obtained free of charge from the CCDC.

Table S 1: Crystallographic parameters for the samples.

Compound	1	2
CCDC no	2194286	2194313
Empirical formula	BaC ₂₄ H ₇₁ N ₅ O ₄₀ S ₈ V ₁₂	C ₃₀ H ₇₆ LaN ₅ O ₄₀ S ₉ V ₁₂
Formula weight	2074.98	2185.73
Temperature/K	150.0	150.0
Crystal system	tetragonal	tetragonal
Space group	P4/n	P4/n
a/Å	19.6114(12)	19.6892(16)
b/Å	19.6114(12)	19.6892(16)
c/Å	11.0115(9)	10.9971(13)
$\alpha/^\circ$	90	90
$\beta/^\circ$	90	90
$\gamma/^\circ$	90	90
Volume/Å ³	4235.1(6)	4263.2(8)
Z	2	2
$\rho_{\text{calc}}/\text{g/cm}^3$	1.911	1.899
μ/mm^{-1}	2.101	2.122
F(000)	2446.0	2448.0
Radiation	MoK α ($\lambda = 0.71073$)	MoK α ($\lambda = 0.71073$)
2 θ range for data collection/ $^\circ$	3.698 to 55.084	3.704 to 55.184
Index ranges	-25 \leq h \leq 25, -25 \leq k \leq 25, -14 \leq l \leq 14	-25 \leq h \leq 25, -25 \leq k \leq 25, -14 \leq l \leq 14
Reflections collected	368824	189090
Independent reflections	4893 [$R_{\text{int}} = 0.0555$, $R_{\text{sigma}} = 0.0099$]	4937 [$R_{\text{int}} = 0.0942$, $R_{\text{sigma}} = 0.0255$]
Data/restraints/parameters	4893/90/298	4937/42/298
Goodness-of-fit on F^2	1.127	1.085
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0249$, $wR_2 = 0.0693$	$R_1 = 0.0357$, $wR_2 = 0.0917$
Final R indexes [all data]	$R_1 = 0.0262$, $wR_2 = 0.0711$	$R_1 = 0.0374$, $wR_2 = 0.0928$
Largest diff. peak/hole / e Å ⁻³	1.21/-0.47	1.28/-0.79

4. TGA Studies

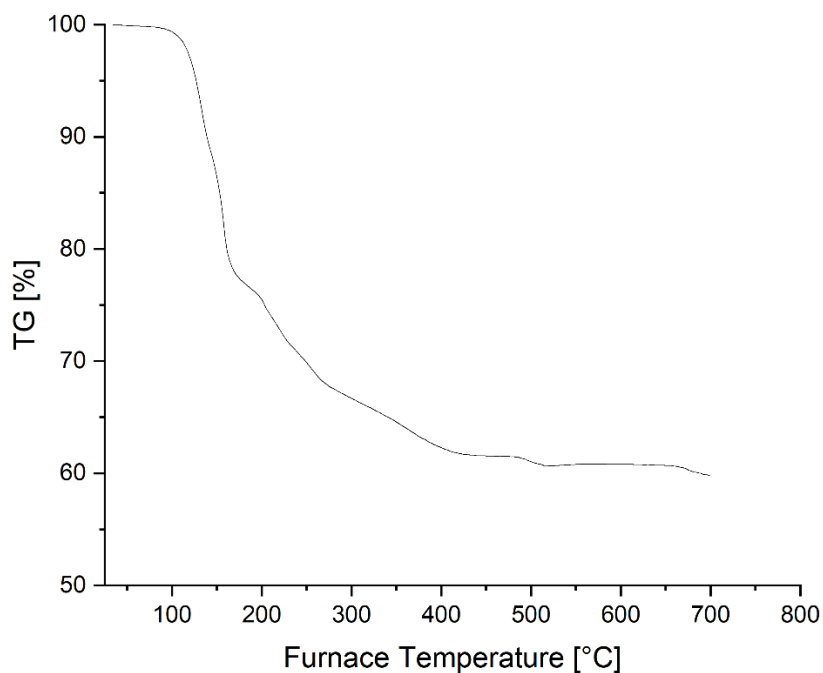


Figure S 3: Thermogravimetric analysis (under air) of compound 1. The weight loss between 25 °C and 220 °C corresponds to cyclen and five DMSO molecules (calc.: 28.3 wt.-%, obs: 28.7 wt.-%). The weight loss between 220 °C and 420 °C can be assigned to the remaining three DMSO molecules (calc.: 11.7 wt.-%, obs.: 9.7 wt.-%).

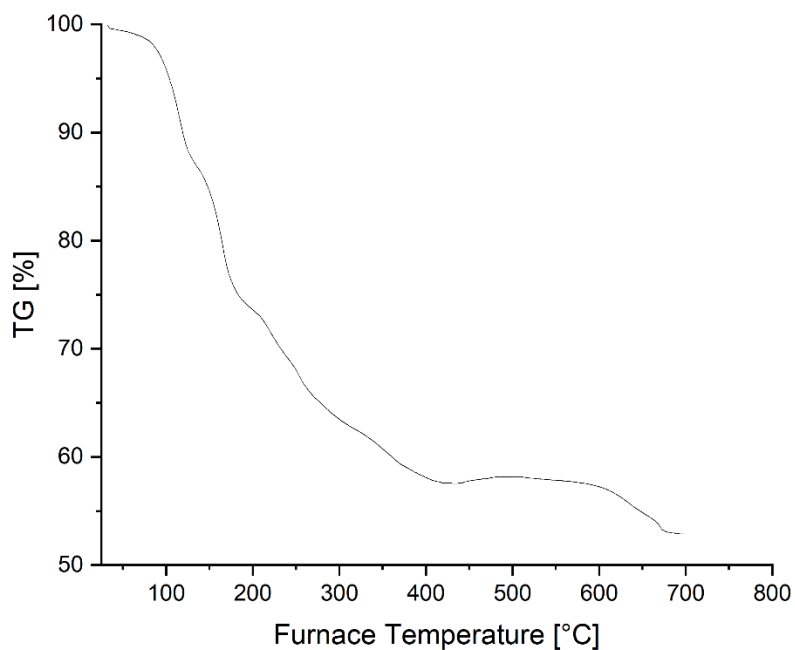


Figure S 4: Thermogravimetric analysis (under air) of compound 2. A weight loss between 25 °C and 180 °C corresponds to cyclen and three DMSO molecules (calc.: 19.8 wt.-%, obs.: 20.3 wt.-%). Further weight loss between 180 °C and 440 °C can be assigned to loss of six DMSO molecules (calc.: 22.7 wt.-%, obs.: 22.0 wt.-%).

5. Infrared Measurements

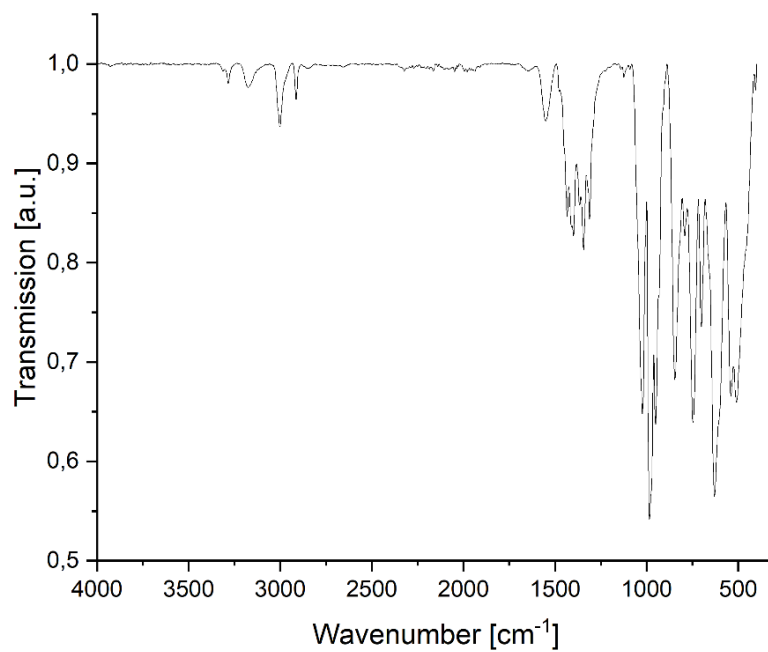


Figure S 5: ATR-FT-IR spectrum of compound 1.

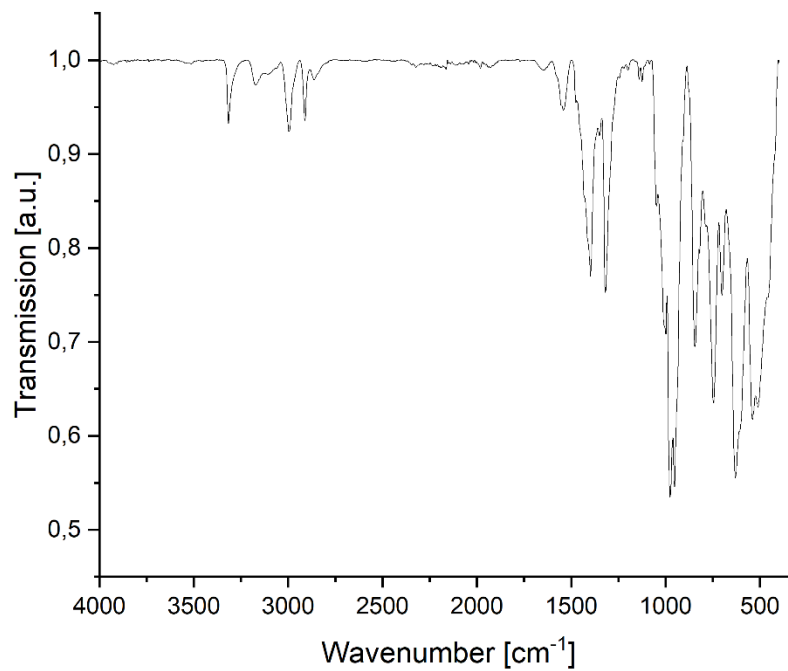


Figure S 6: ATR-FT-IR spectrum of compound 2.

6. Energy-dispersive X-ray spectroscopy

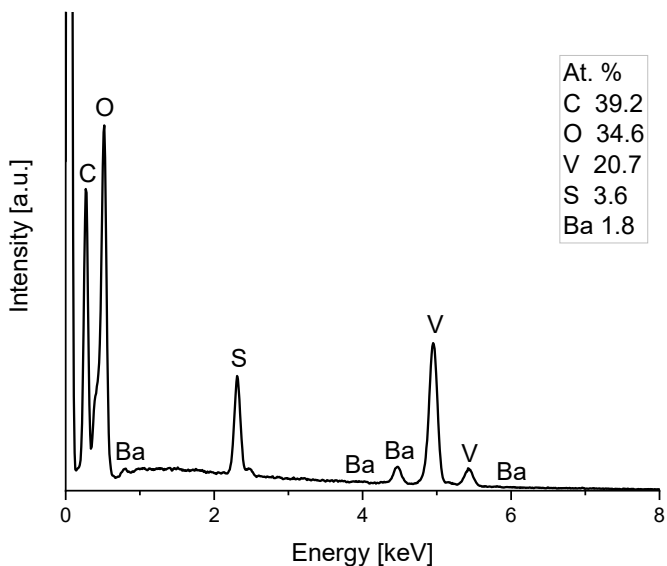


Figure S 7: EDX spectrum and elemental analysis of compound 1.

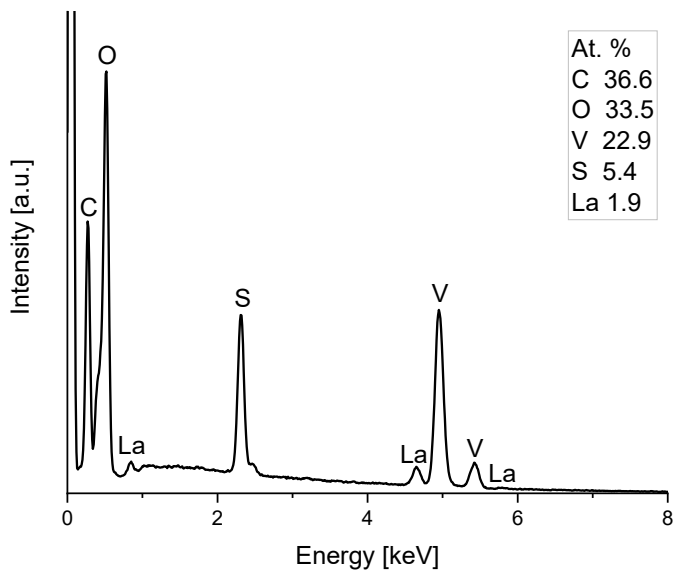


Figure S 8: EDX spectrum and elemental analysis of compound 2.

7. Literature:

S1: J. Forster, B. Rösner, M. M. Khusniyarov, C. Streb, *Chem. Commun.*, **2011**, 47, 3114-3116

S2: G. M. Sheldrick, *Acta Crystallogr. Sect. C* **2015**, 71, 3–8.

S3: O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, 42, 339–341

S4: R. H. Blessing, *Acta Crystallogr. Sect. A* **1995**, 51, 33–38.