Electronic supporting Information

A vanadium(IV) pyrazolate metal organic polyhedron with permanent porosity and adsorption selectivity

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Experimental Section

Materials and methods

All materials including solvents were obtained from commercial sources, were of reagent grade and were used without further purification. **Infrared (IR)** spectra were acquired in transmission mode on a ATR unit (Diamond) spectrometer. **Elemental analyses** were carried out on a METTLER M-3Analyzer. **EPR** spectra were acquired in Bruker ELEXSYS E500 CW-EPR spectrometer. Microwaves frequencies: X-band (about 9.5 GHz with Frequency counter E 41 FC). **Thermogravimetric analyses (TGA)** were performed, under either nitrogen or a reactive air atmosphere, on a Shimadzu-TGA-50H equipment, at a heating rate of 20 °C min^{-1}. **X-ray Powder Diffraction Structural Analysis (XRPD):** except for the structural analysis, all the X-ray powder diffraction data were acquired on a D2 PHASER Bruker AXS diffractometer using CuKα radiation (λ = 1.5418 Å). **X-ray Crystallography:** the crystal structure of **1** was measured at room temperature on a Bruker Apex instrument using λMoKα = 0.71073 Å radiation, for details see Table S1. **Gas Adsorption Measurements** conventional adsorption isotherms were measured using a Micromeritics Tristar 3000 volumetric instrument under continuous adsorption conditions. Brunauer–Emmet–Teller (BET) and Langmuir analyses were carried out to determine the total specific surface areas for the N_2 isotherms at 77 K. In addition, CO_2 isotherms at 273 K were measured to evaluate the micropore region by means of the Dubinin–Radushkevich equation (Table 2). Prior to measurement, powdered samples were heated at 453 K for 12 h and outgassed to 10–6 Torr. **Dynamic Gas Adsorption experiments:** A 15 cm long glass tube with an inner diameter of 5 mm was packed with 0.35 g of **1** and subsequently was activated under a pure He flow (20 mL min^{-1}) at 423 K for 24 h and then used for evaluating the CO_2/N_2 separation performances of the materials. The desired gas mixture (10 mL min^{-1}) was prepared via mass flow controllers. For instance, CO_2/N_2 (0.14:0.86) mixtures were prepared

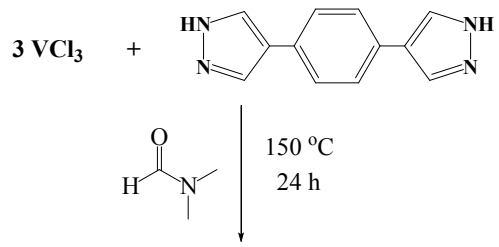
to simulate the emission of flue gas from a power plant employing 1.4 mL min^{-1} of CO_2 and 8.6 mL min^{-1} of N_2 flows, and the breakthrough experiments were carried out at 273, K by step changes from He to CO_2/N_2 flow mixtures. In the case of cyclohexane/benzene separation a mixture of cyclohexane (2 μL)/benzene (2 μL)/methane (0.1 mL) was injected into a pure He flow (20 mL min^{-1}) and the mixture elution was analyzed by means of a Mass Spectrometer (Omnistar). The interaction of methane was considered negligible and taken as reference.

Synthesis of ligand

The 1,4-bis(1*H*-pyrazol-4-yl)benzene ligand (H_2BDP) was prepared as described in the literature.[1]

Synthesis of $[V_3(\mu^3\text{-}O)O(OH)_2(BPD)_{1,5}(HCOO)_3]$ 1

A mixture of VCl_3 (200 mg, 1.27 mmol) and 1,4-bi(1Hpyrazol-4-yl)benzene (134 mg, 0.64 mmol) in DMF (10 mL) was placed in a teflon line (20 mL), heated to 150 °C and held at this temperature for 24 h as shown in Scheme S1. The reaction mixture was slowly cooled to obtain a brown crystalline solid. The product was filtered, washed with DMF (2 × 5 mL), and dried in air to yield **1** (190 mg, 44 %). Calc. for $V_3O_2(OH)_2(C_{12}H_8N_4)_{1.5}(HCOO)_3(H_2O)_2(C_3NH_7O)_{1.5}$ **C 37.72, H 3.91, N 12.93**; found **C 37.72, H 3.78, N 12.97**. FT-IR (ATR): 1647 (s), 1596 (vs), 1577 (vs), 1488 (w), 1429 (w), 1361 (vs), 1242 (m), 1173 (w), 1115 (m) , 1038 (s), 1003 (w), 952 (m), 838 (s), 761 (m), 694 (m), 645 (m) , 602 (m), 539 (m), 510 (vs), 423 (s) cm^{-1}.



$[V_3(\mu^3\text{-}O)O(OH)_2(BPD)_{1,5}(HCOO)_3]$

Scheme S1.

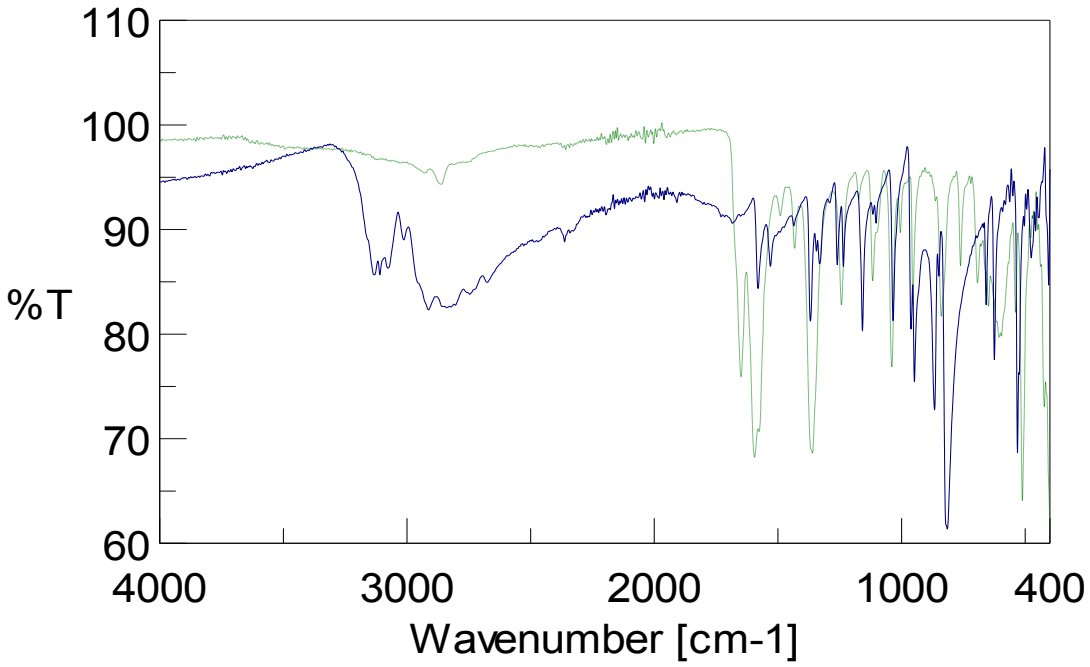


Fig. S1. IR-ATR spectra of H_2BDP spacer (doted line) and of as synthetized **1** (solid line).

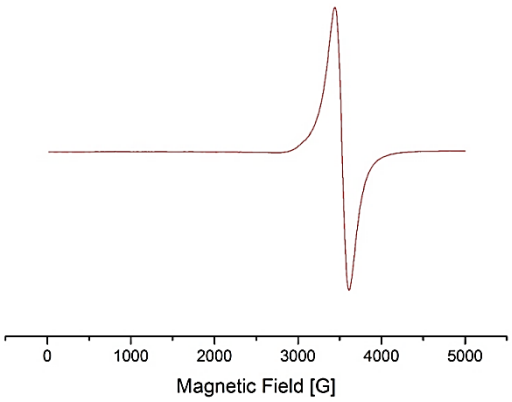


Fig. S2. X-band EPR spectrum of solid sample of **1** at 295 K.

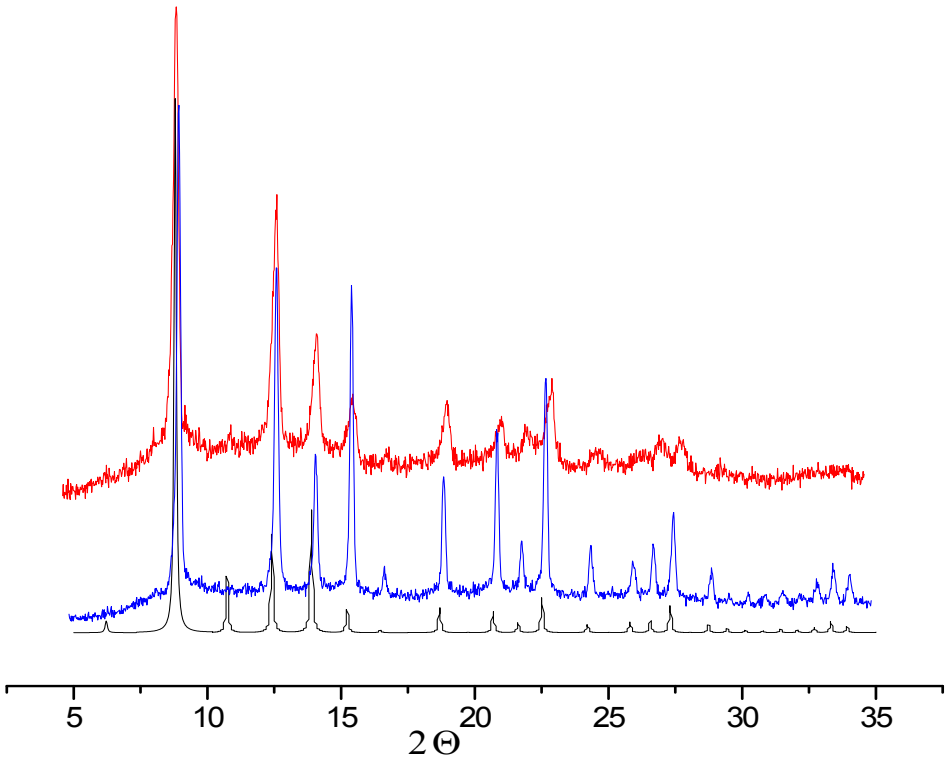


Fig. S3. X-ray powder patterns of **1**: simulated from single crystal analysis (**black**), as-synthesized (**blue**) and after activation **(red**)

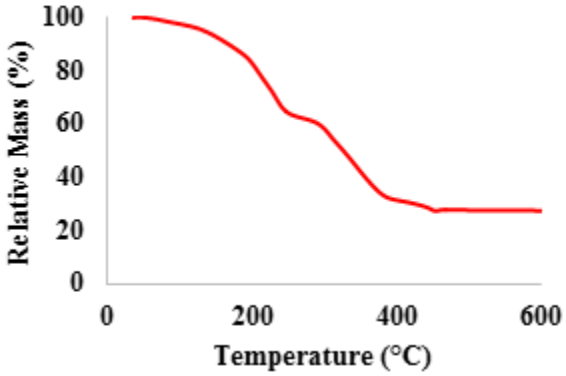


Fig. S4. TG analysis of as-synthesized **1** in air.

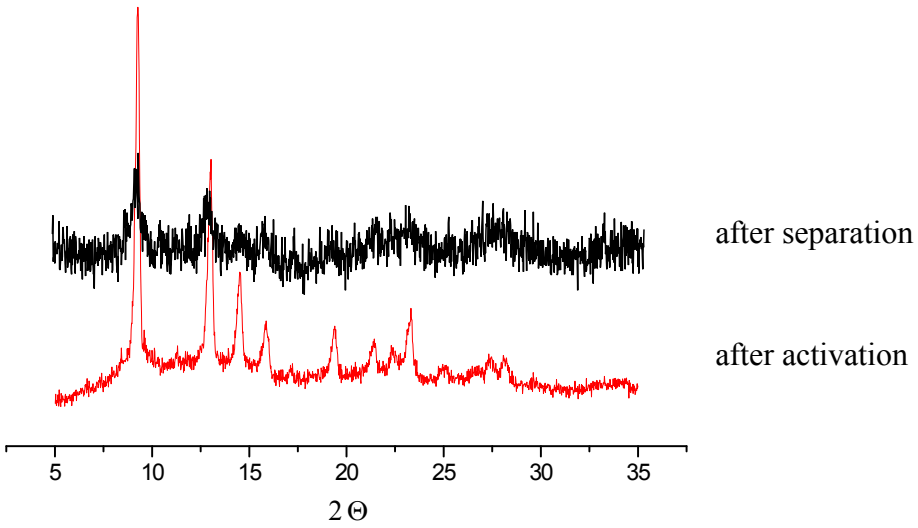


Fig. S5. XPRD after activation and after separation

Table S1. Summary of crystal data, data collection and structural refinement parameters for **1**

Parameters	$[V_3(\mu^3\text{-}O)O(OH)_2(BPD)_{1,5}(HCOO)_3]$
Empirical formula	$C_{84}H_{68}N_{24}O_{40}V_{12}$
Formula weight (M)	2664.87
Temperature, *T* (K)	100(2)
Wavelength, Mo Kα (Å)	0.71069
Crystal sys tem	Cubic
Space group	*I-43m*
a (Å)	20.084(5)
b (Å)	20.084(5)
c (Å)	20.084(5)
α (°)	90.000(5)
β (°)	90.000(5)
γ (°)	90.000(5)
Volume, *V* (Å^3)	8101(3)
Z	2
Calculated density, *ρ* (mg m^{-3})	1.084
Absorption coefficient, *μ* (mm^{-1})	0.720
F(000)	2632
Crystal size (mm^3)	0.1 x 0.1 x 0.1
Index ranges	$-16 \le h \le 16, -16 \le k \le 15, -16 \le l \le 16$
Independent reflections	9445
Data/restraints/parameters	497/0/68
Goodness-of-fit on F^2	1.250
Final *R* indices [$I > 2\sigma(I)$]	0.0683
R indices (all data)	0.0744
Largest diff. peak and hole (e Å^{-3})	0.257/-0.300

Table S2. Bond length (Å) and bond angles (°) for **1**

Bond lengths	**(Å)**	**Bond angles**	**(°)**
V(1) – N(1)	2.08(1)	O(1) –V(1) – O(3)	91.1(4)
V(1) – O(3)	2.041(8)	O(1) –V(1) –O(3)	91.1(4)
V(1) – O(1)	1.93(1)	O(3) –V(1) –O(3)	88.3(5)
V(1) – O(2)	2.11(1)	O(1) –V(1) –N(1)	87.5(5)
V(1) – N(1)	2.08(1)	O(3) –V(1) –N(1)	176.7(4)
V(1) – O(3)	2.041(8)	O(3) –V(1) –N(1)	88.7(3)
C(2) – C(3)	1.51(2)	O(1) –V(1) –N(1)	87.5(5)
C(2) – C(1)	1.34(2)	O(3) –V(1) –N(1)	88.7(3)
C(2) – C(1)	1.34(2)	O(3) –V(1) –N(1)	176.7(4)
C(3) – C(4)	1.33(2)	N(1) –V(1) –N(1)	94.1(5)
C(3) – C(4)	1.33(2)	O(1) –V(1) –O(2)	176.5(6)
C(4) – H(3)	0.93	O(3) –V(1) –O(2)	91.4(3)
C(4) – C(4)	1.41(2)	O(3) –V(1) –O(2)	91.4(3)
N(1) – C(1)	1.35(2)	N(1) –V(1) –O(2)	90.1(4)
N(1) – N(1)	1.39(1)	N(1) –V(1) –O(2)	90.1(4)
C(1) – H(1)	0.93	C(1) –C(2) –C(1)	105.7(17)
C(5) – O(3)	1.26(2)	C(1) –C(2) –C(3)	127.1(9)
C(5) – O(3)	1.26(2)	C(1) –C(2) –C(3)	127.1(9)
O(1) – V(1)	1.93(1)	C(4) –C(3) –C(4)	115.7(17)
O(1) – V(1)	1.93(1)	C(4) –C(3) –C(2)	122.1(8)
C(4) – H(3)	0.93	C(4) –C(3) –C(2)	122.1(8)
C(4) – C(4)	1.41(2)	C(3) –C(4) –C(4)	122.1(8)
N(1) – C(1)	1.35(2)	C(1) –N(1) –N(1)	106.1(7)

N(1) – V(1)	2.08(1)	C(1) –N(1) –V(1)	136.0(9)
C(1) – H(1)	0.93	N(1) –N(1) –V(1)	117.8(3)
C(2) – C(3)	1.51(2)	C(2) –C(1) –N(1)	111.0(13)
C(2) – C(1)	1.34(2)	O(3) –C(5) –O(3)	124.5(18)
C(2) – C(1)	1.34(2)	C(5) –O(3) –V(1)	133.1(11)
C(3) – C(4)	1.33(2)	V(1) –O(1) –V(1)	118.88(18)
C(3) – C(4)	1.33(2)	V(1) –O(1) –V(1)	118.88(18)
C(4) – H(3)	0.93	V(1) –O(1)–V(1)	118.88(18)
N(1) – C(1)	1.35(2)	O(1) –V(1) – O(3)	91.1(4)
N(1) – N(1)	1.39(1)	O(1) –V(1) –O(3)	91.1(4)
N(1) – V(1)	2.08(1)	O(3) –V(1) –O(3)	88.3(5)
C(1) – H(1)	0.93	O(1) –V(1) –N(1)	87.5(5)
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N(1) – C(1)	1.35(2)	O(3) –V(1) –N(1)	88.7(3)
N(1) – V(1)	2.08(1)	O(1) –V(1) –N(1)	87.5(5)
C(1) – H(1)	0.93	O(3) –V(1) –N(1)	88.7(3)
O(3) – V(1)	2.041(8)	O(3) –V(1) –N(1)	176.7(4)
V(1) – O(3)	2.041(8)	N(1) –V(1) –N(1)	94.1(5)
V(1) – O(1)	1.93(1)	O(1) –V(1) –O(2)	176.5(6)
V(1) – O(2)	2.11(1)	O(3) –V(1) –O(2)	91.4(3)
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C(4) – H(3)	0.93	V(1) –O(1) –V(1)	118.88(18)
C(4) – C(4)	1.41(2)	V(1) –O(1) –V(1)	118.88(18)
N(1) – C(1)	1.35(2)	V(1) –O(1)–V(1)	118.88(18)
N(1) – N(1)	1.39(1)	O(1) –V(1) – O(3)	91.1(4)
C(1) – H(1)	0.93	O(1) –V(1) –O(3)	91.1(4)
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N(1) – N(1)	1.39(1)	C(1) –C(2) –C(1)	105.7(17)
N(1) – V(1)	2.08(1)	C(1) –C(2) –C(3)	127.1(9)

C(1) – H(1)	0.93	C(1) –C(2) –C(3)	127.1(9)
C(4) – H(3)	0.93	C(4) –C(3) –C(4)	115.7(17)
N(1) – C(1)	1.35(2)	C(4) –C(3) –C(2)	122.1(8)
N(1) – V(1)	2.08(1)	C(4) –C(3) –C(2)	122.1(8)
C(1) – H(1)	0.93	C(3) –C(4) –C(4)	122.1(8)
O(3) – V(1)	2.041(8)	C(1) –N(1) –N(1)	106.1(7)
V(1) – N(1)	2.08(1)	C(1) –N(1) –V(1)	136.0(9)
V(1) – O(3)	2.041(8)	N(1) –N(1) –V(1)	117.8(3)
V(1) – O(2)	2.11(1)	C(2) –C(1) –N(1)	111.0(13)
C(2) – C(3)	1.51(2)	O(3) –C(5) –O(3)	124.5(18)
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C(3) – C(4)	1.33(2)	V(1) –O(1)–V(1)	118.88(18)
C(4) – H(3)	0.93	O(1) –V(1) – O(3)	91.1(4)
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C(1) – H(1)	0.93		
C(4) – H(3)	0.93		
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V(1) – O(2)	2.11(1)		
V(1) – N(1)	2.08(1)		
V(1) – O(3)	2.041(8)		
C(5) – O(3)	1.26(2)		
C(5) – O(3)	1.26(2)		
O(1) – V(1)	1.93(1)		
O(1) – V(1)	1.93(1)		
O(3) – V(1)	2.041(8)		
V(1) – N(1)	2.08(1)		
V(1) – O(3)	2.041(8)		
V(1) – O(2)	2.11(1)		
C(2) – C(3)	1.51(2)		
C(2) – C(1)	1.34(2)		
C(2) – C(1)	1.34(2)		
C(3) – C(4)	1.33(2)		
C(3) – C(4)	1.33(2)		
C(4) – H(3)	0.93		
C(4) – C(4)	1.41(2)		
N(1) – C(1)	1.35(2)		
N(1) – N(1)	1.39(1)		
C(1) – H(1)	0.93		
C(5) – O(3)	1.26(2)		
C(5) – O(3)	1.26(2)		
C(4) – H(3)	0.93		
C(4) – C(4)	1.41(2)		
N(1) – C(1)	1.35(2)		

C(1) – H(1)	0.93		
C(2) – C(3)	1.51(2)		
C(2) – C(1)	1.34(2)		
C(2) – C(1)	1.34(2)		
C(3) – C(4)	1.33(2)		
C(3) – C(4)	1.33(2)		
C(4) – H(3)	0.93		
N(1) – C(1)	1.35(2)		
N(1) – N(1)	1.39(1)		
C(1) – H(1)	0.93		
C(4) – H(3)	0.93		
N(1) – C(1)	1.35(2)		
N(1) – V(1)	2.08(1)		
C(1) – H(1)	0.93		
V(1) – O(3)	2.041(8)		
V(1) – O(2)	2.11(1)		
V(1) – O(3)	2.041(8)		
C(5) – O(3)	1.26(2)		
C(5) – O(3)	1.26(2)		
V(1) – O(3)	2.041(8)		
V(1) – O(2)	2.11(1)		
V(1) – N(1)	2.08(1)		
C(5) – O(3)	1.26(2)		
C(5) – O(3)	1.26(2)		
O(3) – V(1)	2.041(8)		
V(1) – O(2)	2.11(1)		
V(1) – O(3)	2.041(8)		
V(1) – N(1)	2.08(1)		

C(5) – O(3)	1.26(2)		
C(5) – O(3)	1.26(2)		
O(3) – V(1)	2.041(8)		
C(5) – O(3)	1.26(2)		
C(5) – O(3)	1.26(2)		
V(1) – O(2)	2.11(1)		
V(1) – N(1)	2.08(1)		
C(2) – C(3)	1.51(2)		
C(2) – C(1)	1.34(2)		
C(2) – C(1)	1.34(2)		
C(3) – C(4)	1.33(2)		
C(3) – C(4)	1.33(2)		
C(4) – H(3)	0.93		
C(4) – C(4)	1.41(2)		
N(1) – C(1)	1.35(2)		
N(1) – N(1)	1.39(1)		
C(1) – H(1)	0.93		
C(4) – H(3)	0.93		
C(4) – C(4)	1.41(2)		
N(1) – C(1)	1.35(2)		
C(1) – H(1)	0.93		
C(2) – C(3)	1.51(2)		
C(2) – C(1)	1.34(2)		
C(2) – C(1)	1.34(2)		
C(3) – C(4)	1.33(2)		
C(3) – C(4)	1.33(2)		
C(4) – H(3)	0.93		
N(1) – C(1)	1.35(2)		

N(1) – N(1)	1.39(1)		
C(1) – H(1)	0.93		
C(4) – H(3)	0.93		
N(1) – C(1)	1.35(2)		
C(1) – H(1)	0.93		

References

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