Supporting Information

High-nuclear polyoxovanadates assembly from pentagonal building block

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1. Material and methods.

All the reagents and chemicals were obtained from commercial sources and used without further purification.

reagents / chemicals	commercial sources	purity
$VOSO_4 \cdot xH_2O$	aladdin	99.9%
$Na_2WO_4 \cdot 2H_2O$	aladdin	99%
phenylphosphonic acid	aladdin	98%
$Gd(NO_3)_3 \cdot 6H_2O$	aladdin	99.9%
1,3,5-Benzenetricarboxylic acid	macklin	98%
Methyl phenyl sulfide	aladdin	99%
Ethyl Phenyl Sulfide	aladdin	98%
4-Methoxythioanisole	aladdin	98%
4-Chlorothioanisole	aladdin	98%
Diphenyl sulfide	aladdin	98%
Dibenzothiophene	aladdin	98%
4,6-Dimethyl dibenzothiophene	aladdin	97%
H_2O_2	aladdin	AR
N,N′-dimethyl formamide	Tianjin Fuyu Fine Chemical Co., Ltd	AR
N,N′-dimethyl acetamide	Tianjin Fuyu Fine Chemical Co., Ltd	AR
CH_3OH	Tianjin Fuyu Fine Chemical Co., Ltd	AR

Powder X-ray diffraction (PXRD) measurement were recorded ranging from 5 to 50° at room temperature on a Siemens D5005 diffractometer with Cu-*Kα* radiation (λ = 1.5418 Å). The FT-IR spectra were performed in the range 4000−400 cm^{-1} using KBr pellets on an Alpha Centaurt FT/IR spectrophotometer. Thermogravimetric analysis (TGA) of the samples was performed using a PerkinElmer TG-7 analyzer heated from 50 to 800 °C under nitrogen at the heating rate of 10 °C·min^{-1}. The C, H, and N elemental analyses were conducted on a Perkin-Elmer 2400CHN elemental analyzer. HPLC equipment was applied to determine catalytic oxidation products.

2. **Synthesis and Characterization**

(1) Synthesis of compound **1**

$VOSO_4 \cdot xH_2O$ (20 mg, 0.12 mmol), $Na_2WO_4 \cdot 2H_2O$ (15 mg, 0.05 mmol), and phenylphosphonic acid (10 mg, 0.06 mmol) were dissolved in 2 mL DMA (N,N′-dimethyl acetamide) and 2 mL CH_3OH (methanol). The mixture was transferred to a Teflon-lined stainless steel vessel and heated to 160 °C for three days, and gradually cooled to room

temperature. The green crystals were obtained by filtration, washed with CH_3OH, and dried in air. Yield: 68% based on phenylphosphonic acid. Elemental analysis (%) cacld: C, 29.57; H, 3.28; N, 2.24. Found: C, 29.78; H, 3.49; N, 2.36. IR spectrum (KBr, cm^{-1}): 3457 (*w*), 3041 (*w*), 1629 (*w*), 1492 (*w*), 1435 (*w*), 1128 (*s*), 1077 (*s*), 997 (*s*), 761 (*m*), 694 (*s*), 562 (*s*), 534 (*s*), 421 (*s*).

(2) Synthesis of compound **2**

$VOSO_4$ (20 mg, 0.12 mmol), $Na_2WO_4{\cdot}2H_2O$ (15 mg, 0.05 mmol), phenylphosphonic acid (10 mg, 0.06 mmol), $Gd(NO_3)_3{\cdot}6H_2O$ (10 mg, 0.02 mmol) and 1,3,5-Benzenetricarboxylic acid (10 mg, 0.05 mmol) were dissolved in 2 mL DMF (N,N′-dimethyl formamide) and 2 mL CH_3OH. The mixture was transferred to a Teflon-lined stainless steel vessel and heated to 160 °C for three days, and gradually cooled to room temperature. The green crystals were obtained by filtration, washed with CH_3OH, and dried in air. Yield: 59% based on phenylphosphonic acid. Elemental analysis (%) cacld: C, 26.50; H, 3.47; N, 3.04. Found: C, 26.82; H, 3.68; N, 332. IR spectrum (KBr, cm^{-1}): 3225 (*w*), 2914 (*w*), 1644 (*s*), 1587 (*m*), 1558 (*s*), 1492 (*s*), 1379 (*s*), 1356 (*s*), 1247 (*m*), 1100 (*m*), 1006 (*m*), 860 (*m*), 794 (*m*), 756 (*s*), 708 (*s*), 633 (*m*), 586 (*s*), 505 (*m*), 468 (*s*).

(3) Synthesis of compound **3**

$VOSO_4$ (20 mg, 0.12 mmol), $Na_2WO_4{\cdot}2H_2O$ (15 mg, 0.05 mmol), phenylphosphonic acid (10 mg, 0.06 mmol) and $Gd(NO_3)_3{\cdot}6H_2O$ (10 mg, 0.02 mmol) were dissolved in 2 mL DMF, 2 mL CH_3OH. The mixture was transferred to a Teflon-lined stainless steel vessel and heated to 160 °C for three days, and gradually cooled to room temperature. The green crystals were obtained by filtration, washed with CH_3OH, and dried in air. Yield: 41% based on phenylphosphonic acid. Elemental analysis (%) cacld: C, 23.82; H, 3.35; N, 3.22. Found: C, 24.07; H, 3.51; N, 3.44. IR spectrum (KBr, cm^{-1}): 3438 (*w*), 3051 (*w*), 2928 (*w*), 2876 (*w*), 2777 (*w*), 1714 (*s*), 1667 (*s*), 1478 (*w*), 1426 (*w*), 1393 (*w*), 1265 (*w*), 1096 (*m*), 1044 (*s*), 982 (*s*), 907 (*m*), 789 (*s*), 694 (*s*), 543 (*s*), 487(*s*).

3. Single-crystal X-ray Crystallography

The crystallographic data for compounds **1-3** are given in Table S1. The crystallographic diffraction data were collected at 173K on Bruker D8 VENTURE with Cu Kα radiation (λ = 1.5418 Å). The data frames were collected using the program APEX 3 and processed using

the program SAINT routine in APEX 3. The structures were solved by direct methods and refined by the full1matrix least-squares on F^2 using the SHELXL-2014 program. The hydrogen atoms of organic ligand were generated geometrically (C-H = 0.96 Å). As the dimethylamine counter anions and solvents cannot be defined clearly and no distinguishable electron-density peaks were observed, so the SQUEEZE routines in PLATON were applied to model the diffuse electron density caused by disordered dimethylamine molecules and solvents. The total solvent-accessible surface area of compounds **1**, **2**, and **3** is about 25.8%, 39.5%, and 32.4%, respectively, which were occupied by dimethylamine molecules and solvents. The restrained DFIX, SIMU, SADI, RIGU, ISOR, DELU instructions were used to make the structures more reasonable. The formula unit was obtained through a combination of elemental analyses and thermogravimetric characterization. (CCDC number: 2195409 for **1**; 2195410 for **2**; 2195411 for **3**)

Table S1. Crystallographic data for **1-3**

Compound	**1**	**2**	**3**
Empirical formula	$C_{154}H_{204}Na_{10}N_{10}O_{110}P_{20}S_2V_{20}W_2$	$C_{132}H_{206}Na_7N_{13}O_{110}P_{14}V_{18}W_4$	$C_{155}H_{260}Na_{10}N_{18}O_{143}P_{16}V_{26}W_6$
Formula weight	6255.18	5981.92	7816.75
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	*C2/c*	*Pnma*	$P2_1/c$
Temperature (K)	173.02	173.02	173.02
a (Å)	38.1926(13)	37.4678(17)	16.2280(7)
b (Å)	19.4384(7)	28.5413(10)	23.1623(9)
c (Å)	33.8946(18)	20.4155(8)	36.2890(14)
α (°)	90	90	90
β (°)	115.4190(10)	90	92.039(2)
γ (°)	90	90	90
Volume/Å^3	22727.5(17)	21831.9(15)	13631.6(10)
Z	4	4	2
$D_{calc.}$ (g/cm^3)	1.828	1.820	1.904
Reflections collected	117735	100373	101039
Independent reflections	22368	18209	22295
GOF on F^2	1.038	1.046	1.035
R(int)	0.0628	0.0964	0.0792
Final *R* indices [$I > 2\text{sigma}(I)$]	$R_1 = 0.0691$ $wR_2 = 0.1885$	$R_1 = 0.0988$ $wR_2 = 0.2526$	$R_1 = 0.0713$ $wR_2 = 0.1757$

Table S2. BVS results for the vanadium and tungsten cations in **1**

Atom	BVS calc. for V (IV)
V1	4.426
V2	4.432
V3	4.389
V4	4.505
V5	4.428
V6	4.303
V7	4.394
V8	4.372
V9	4.373
V10	4.385

Atom	BVS calc. for W (VI)
W1	6.015

Table S3. BVS results for the vanadium and tungsten cations in **2**

Atom	BVS calc. for V (IV)
V1	4.202
V2	4.310
V3	4.398
V4	3.678
V5	4.426
V6	4.301
V7	4.338
V8	4.396
V9	3.920
V10	4.466

Atom	BVS calc. for W (VI)
W1	5.909
W2	6.340
W3	5.866

Table S4. BVS results for the vanadium and tungsten cations in **3**

Atom	BVS calc. for V (IV)
V1	4.352
V2	4.336

V3	4.459
V4	4.139
V5	4.339
V6	4.405
V7	4.530
V8	4.301
V9	4.362
V10	4.396
V11	4.332
V12	4.456
V13	4.374

Atom	BVS calc. for W (VI)
W1	6.130
W2	5.965
W3	5.922

Table S5. Selected bond distances (Å) for compound **1**

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
W1	O1	1.999(4)	V10	O24	1.972(5)
W1	O5	2.276(5)	V10	O37	1.576(5)
W1	O12	2.019(5)	V10	O51[1]	1.986(5)
W1	O20	2.025(4)	Na1	O4	2.958(6)
W1	O33	1.692(5)	Na1	O21	3.004(6)
W1	O44	2.029(5)	Na1	O23	2.334(13)
W1	O48	2.009(4)	Na1	O26	2.230(14)
V1	O12	1.924(4)	Na1	O29[1]	2.381(6)
V1	O20	1.929(5)	Na1	O32[1]	2.444(6)
V1	O30	1.598(4)	Na1	O35	2.426(5)
V1	O34	1.976(5)	Na1	O39	2.399(5)
V1	O43	1.979(5)	Na2	O18	2.548(8)
V2	O11	1.942(5)	Na2	O21	2.428(7)
V2	O21	2.007(5)	Na2	O25	2.568(8)
V2	O25	1.959(5)	Na2	O28	2.575(7)
V2	O29[1]	1.965(5)	Na2	O31	2.469(7)
V2	O41	1.581(6)	Na2	O45	2.726(8)
V3	O1	1.921(5)	Na2	O49	2.383(14)
V3	O8	1.962(5)	Na3	O4	2.837(8)
V3	O10	1.969(5)	Na3	O8	2.383(7)

V3	O44	1.945(5)	Na3	O9[1]	2.497(6)
V3	O47	1.605(5)	Na3	O10	2.357(7)
V4	O4[1]	2.009(5)	Na3	O24[1]	2.420(6)
V4	O7	1.573(5)	Na3	O51	2.908(7)
V4	O9	1.960(5)	Na4	O6	2.251(14)
V4	O32	1.958(5)	Na4	O15	2.778(6)
V4	O53	1.946(5)	Na4	O34	2.463(6)
V5	O17	1.587(5)	Na4	O40	2.422(6)
V5	O18	1.951(5)	Na4	O43	2.472(5)
V5	O28	2.001(4)	Na4	O46	2.445(6)
V5	O36	1.957(5)	Na4	O49	2.461(13)
V5	O46	1.971(5)	Na4	O50	2.603(13)
V6	O35	1.983(5)	Na5	O4	2.788(9)
V6	O39	1.978(5)	Na5	O8	2.485(10)
V6	O42	1.603(4)	Na5	O9[1]	2.674(9)
V6	O44	1.932(5)	Na5	O10	2.546(9)
V6	O48	1.933(4)	Na5	O13	2.914(16)
V7	O20	1.926(4)	Na5	O24[1]	2.507(9)
V7	O31	1.980(5)	Na5	O26	2.754(18)
V7	O45	1.980(5)	Na5	O51	2.696(10)
V7	O48	1.939(4)	Na6	O18	2.476(7)
V7	O52	1.609(4)	Na6	O21	2.614(8)
V8	O2	1.568(5)	Na6	O25	2.468(7)
V8	O15	2.001(5)	Na6	O28	2.733(8)
V8	O16[1]	1.962(5)	Na6	O31	2.389(7)
V8	O19	1.932(6)	Na6	O45	2.582(8)
V8	O40	1.938(6)	Na7	O13	2.053(13)
V9	O1	1.942(5)	Na7	O14	2.394(6)
V9	O12	1.936(4)	Na7	O15	2.549(7)
V9	O14	1.979(5)	Na7	O16[1]	2.475(6)
V9	O27	1.979(5)	Na7	O22[1]	2.428(6)
V9	O38	1.599(5)	Na7	O27	2.571(6)
V10	O3	1.946(5)	Na7	O50	2.445(13)
V10	O22	1.971(5)	Na7	O51	2.877(6)

Symmetry code: 3/2-X,1/2-Y,1-Z

Table S6. Selected bond distances (Å) for compound **2**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
W1	O10	1.779(15)	V7	O27	2.407(10)
W1	O32[1]	1.791(9)	V7	O36	1.998(6)
W1	O32	1.791(9)	V7	O41	2.005(11)
W1	O44	1.720(13)	V7	O43	1.647(8)
W2	O5	1.800(10)	V8	O13	1.951(12)
W2	O51	1.800(10)	V8	O19	1.601(11)
W2	O10	2.113(15)	V8	O20	1.907(12)
W2	O31	2.118(10)	V8	O28	1.966(10)
W2	O31[1]	2.118(10)	V8	O38	1.992(10)
W2	O33	1.687(15)	V9	O14[1]	2.040(9)
W3	O11	1.707(10)	V9	O14	2.040(9)
W3	O18	2.448(10)	V9	O251	1.914(10)
W3	O20	2.036(9)	V9	O25	1.913(10)
W3	O28	1.969(12)	V9	O39	1.898(12)
W3	O40	2.014(10)	V9	O42	1.874(11)
W3	O46	2.051(11)	V10	O20	1.963(11)
W3	O52	1.998(11)	V10	O24	1.992(11)
V1	O1	2.020(10)	V10	O34	1.973(11)
V1	O8	1.999(6)	V10	O37	1.647(9)
V1	O12	2.007(10)	V10	O52	1.936(10)
V1	O15	1.673(8)	P1	O1	1.544(10)
V1	O32	2.218(9)	P1	O1[1]	1.544(10)
V1	O50	1.999(11)	P1	O4	1.537(14)
V2	O2	2.012(12)	P1	C1	1.818(12)
V2	O40	1.976(12)	P2	O13	1.541(11)
V2	O46	1.930(10)	P2	O29	1.502(12)
V2	O47	1.661(9)	P2	O48	1.506(12)
V2	O49	2.013(12)	P2	C7	1.802(10)
V3	O3	1.966(12)	P3	O21[1]	1.540(13)
V3	O9	1.990(11)	P3	O21	1.540(13)
V3	O23	1.677(9)	P3	O39	1.666(13)
V3	O46	1.942(11)	P3	C13	1.775(14)
V3	O52	1.915(11)	P4	O12	1.480(10)
V4	O4	2.062(13)	P4	O34	1.517(12)
V4	O16	2.032(10)	P4	O38	1.506(11)
V4	O16[1]	2.032(10)	P4	C19	1.807(8)

V4	O221	1.962(10)	P5	O2	1.529(13)
V4	O22	1.962(10)	P5	O17	1.517(12)
V4	O42	1.918(13)	P5	O41	1.488(12)
V5	O17	1.978(11)	P5	C24	1.800(7)
V5	O28	1.918(10)	P6	O6	1.519(10)
V5	O29	1.972(13)	P6	O31	1.519(11)
V5	O40	1.939(13)	P6	O50	1.507(11)
V5	O45	1.595(10)	P6	C30	1.810(8)
V6	Na2	3.527(6)	P7	O3	1.520(13)
V6	O5	2.025(10)	P7	O25	1.625(12)
V6	O6	1.990(10)	P7	O49	1.506(13)
V6	O26	2.023(10)	P7	C36	1.826(10)
V6	O30	2.328(11)	P8	O9	1.519(11)
V6	O35	1.592(12)	P8	O22	1.540(11)
V6	O48	1.982(11)	P8	O24	1.550(12)
V7	O7	2.036(12)	P8	C42	1.807(9)
V7	O21	1.981(13)			

Symmetry code: +X,3/2-Y,+Z

Table S7. Selected bond distances (Å) for compound **3**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
W1	O39	1.786(7)	V10	O34	1.935(6)
W1	O45	1.779(7)	V10	O44	1.999(7)
W1	O53	1.724(7)	V10	O49	1.605(8)
W1	O59	1.748(7)	V10	O52	1.923(7)
W2	O2	2.038(8)	V11	O19	1.977(7)
W2	O15	1.711(7)	V11	O27	1.600(8)
W2	O21	2.034(7)	V11	O46	1.954(8)
W2	O32	2.035(6)	V11	O54	1.929(7)
W2	O45	2.220(7)	V11	O64	1.924(8)
W2	O54	1.991(8)	V12	O5	1.585(8)
W2	O64	2.032(7)	V12	O10	1.997(7)
W3	O30	1.982(6)	V12	O18	1.989(7)
W3	O34	2.041(6)	V12	O32	1.961(7)
W3	O39	2.262(7)	V12	O54	1.912(7)
W3	O40	2.016(7)	V13	O2	1.928(7)
W3	O43	1.709(8)	V13	O16	1.972(7)
W3	O52	2.020(7)	V13	O17	1.992(8)

W3	O58	2.028(7)	V13	O32	1.904(7)
V1	O6	1.983(7)	V13	O41	1.582(7)
V1	O8	1.981(7)	Na1	O3[1]	2.470(9)
V1	O20	1.608(6)	Na1	O4	2.404(7)
V1	O24	2.022(7)	Na1	O20	2.327(7)
V1	O36	2.029(7)	Na1	O22	2.876(7)
V1	O50	2.200(7)	Na1	O23[1]	2.652(9)
V2	O9	1.970(8)	Na1	O28	2.414(7)
V2	O13	1.591(8)	Na1	O59	2.530(8)
V2	O25	1.977(8)	Na2	O1	2.337(7)
V2	O42	1.946(7)	Na2	O3[1]	2.196(9)
V2	O60	1.967(7)	Na2	O22	2.466(7)
V3	O11	1.968(9)	Na2	O31[1]	2.341(11)
V3	O21	1.927(8)	Na2	O36	2.382(8)
V3	O35	1.974(9)	Na3	O10	2.389(8)
V3	O57	1.613(9)	Na3	O18	2.597(8)
V3	O64	1.922(8)	Na3	O20	2.978(8)
V4	O1	2.025(6)	Na3	O23[1]	2.242(9)
V4	O22	1.986(6)	Na3	O24	2.435(8)
V4	O30	1.923(6)	Na3	O31	2.375(10)
V4	O34	1.921(6)	Na4	O6	2.655(8)
V4	O62	1.598(7)	Na4	O14	2.430(8)
V5	O33	1.955(9)	Na4	O16	2.436(8)
V5	O40	1.931(7)	Na4	O17	2.484(8)
V5	O51	2.011(8)	Na4	O29	2.467(16)
V5	O55	1.610(9)	Na4	O63	2.408(12)
V5	O58	1.933(7)	Na5	O9	2.569(9)
V6	O12	1.981(7)	Na5	O11	2.503(10)
V6	O26	1.990(7)	Na5	O25	2.652(11)
V6	O30	1.924(6)	Na5	O33	2.522(9)
V6	O40	1.936(7)	Na5	O35	2.649(10)
V6	O56	1.583(7)	Na5	O51	2.663(11)
V7	O7	1.590(7)	Na5	O53	2.364(8)
V7	O37	2.064(8)	Na5	O61	2.334(12)
V7	O38	2.037(7)	Na4	O17	2.484(8)
V7	O52	1.912(7)	Na4	O29	2.467(16)
V7	O58	1.909(7)	Na4	O63	2.408(12)
V8	O4	2.006(7)	Na5	O9	2.569(9)
V8	O28	2.022(7)	Na5	O11	2.503(10)
V8	O42	1.982(7)	Na5	O25	2.652(11)

V8	O48	1.587(7)	Na5	O33	2.522(9)
V8	O60	2.003(7)	Na5	O35	2.649(10)
V9	O2	1.930(7)	Na5	O51	2.663(11)
V9	O21	1.924(9)	Na5	O53	2.364(8)
V9	O37	2.033(8)	Na5	O61	2.334(12)
V9	O38	2.031(8)	Na5	O61	2.334(12)
V9	O47	1.567(7)	Na5	O61	2.334(12)
V10	O14	1.974(7)	Na5	O61	2.334(12)

Symmetry code: 1-X,1-Y,1-Z

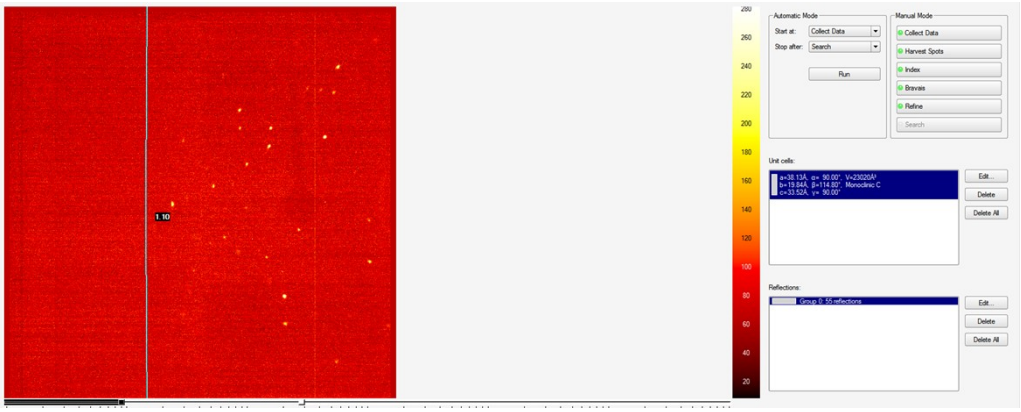

Fig. S1. Single-crystal diffraction pattern for **1** that has been in the air for more than one year.

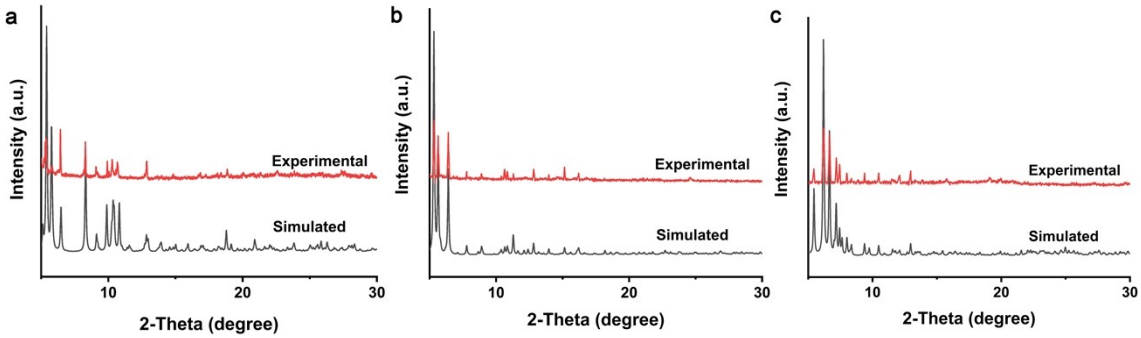

Fig. S2. The experimental (red) and simulated (black) PXRD patterns for **1-3.**

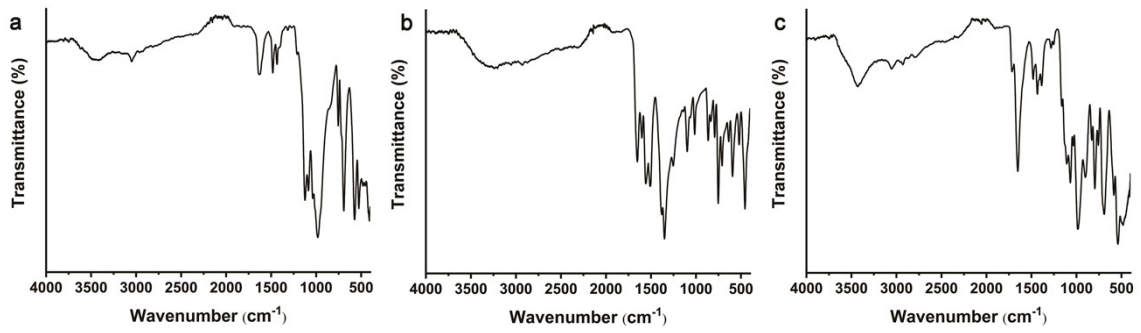

Fig. S3. IR spectra of **1-3.**

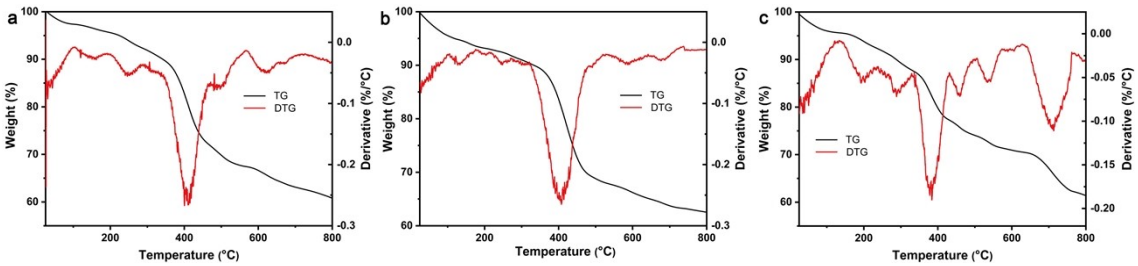

Fig. S4. TGA curves of **1-3**.

There are three essential steps in weight loss. For **1**, the first weight loss is 2.55% in the range of 25-100 °C, which can be attributed to the loss of CH_3OH (**2** is 4.48% matching with 25-100 °C, **3** is 4.32% matching with 25-130 °C). Following is the second decline, corresponding to the removal of dimethylamine counter cations and solvent DMF molecules, the weight loss is 14.72% during 100-400 °C (**2** is 12.11% in the range of 100-400°C, **3** is 12.88% in the range of 130-380°C). Last of all, as the temperature increases, the frameworks of compounds start to decompose, remaining the final weight of 21.91% (**2** is 20.90%, **3** is 21.33%) occupied by V_2O_5.

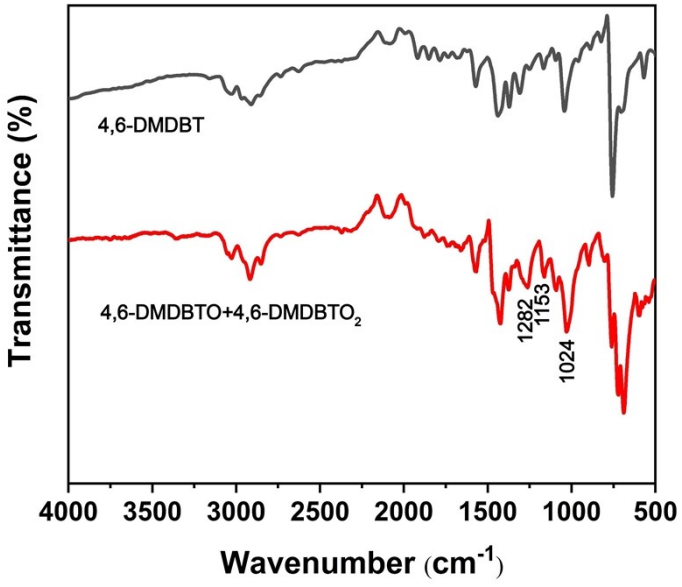

Fig. S5. FT-IR spectra of the 4,6-DMDBT (black) and the corresponding catalytic oxidation products of the 4,6-DMDBTO and 4,6-DMDBTO$_2$ (red). The characteristic frequencies at ν_{as} (O=S=O) = 1282 cm $^{-1}$, ν_{as} (O=S=O) = 1153 cm $^{-1}$ and ν (S=O) = 1024 cm $^{-1}$ suggest the appearance of the sulfoxides and sulfones.

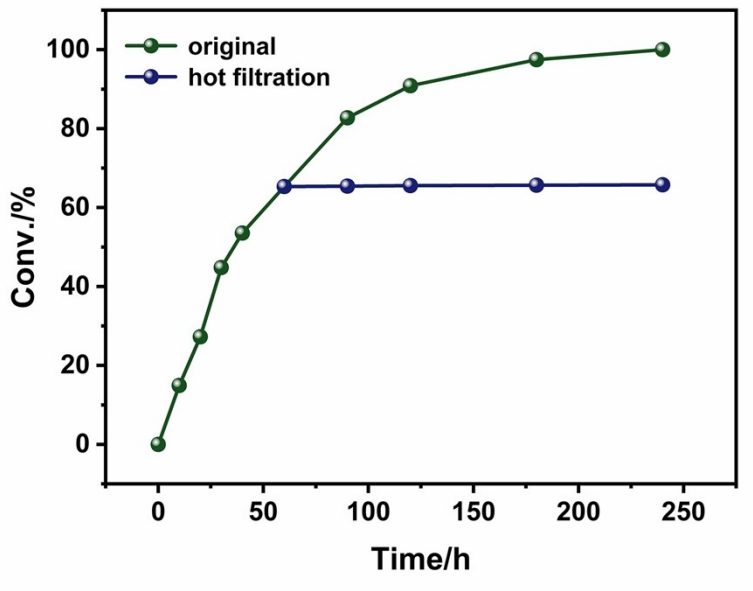

Fig. S6. Time profile for phenyl sulfide oxidation with compound **1** as catalyst (green) and heat filter out the catalyst during the reaction (blue). Reaction conditions: substrate (0.4 mmol), **1** (0.002 mmol), H_2O_2 (1 mmol), and MeOH (5 mL), 25 °C.

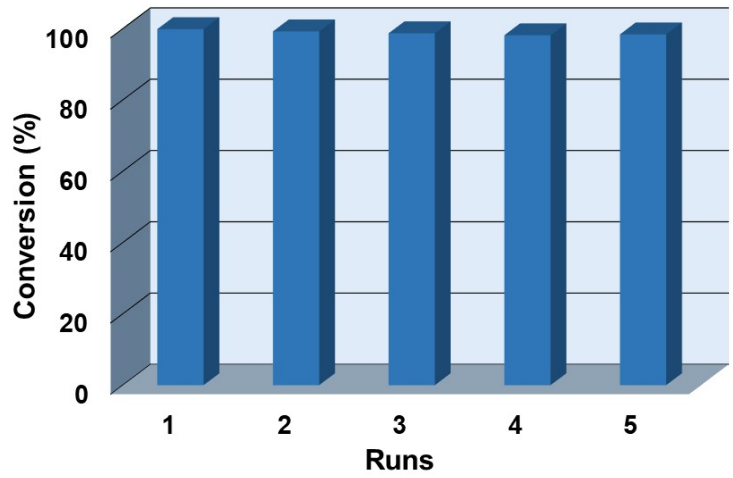

Fig. S7. Circular experimental diagram of methyl phenyl sulfide catalyzed by compound **1**.

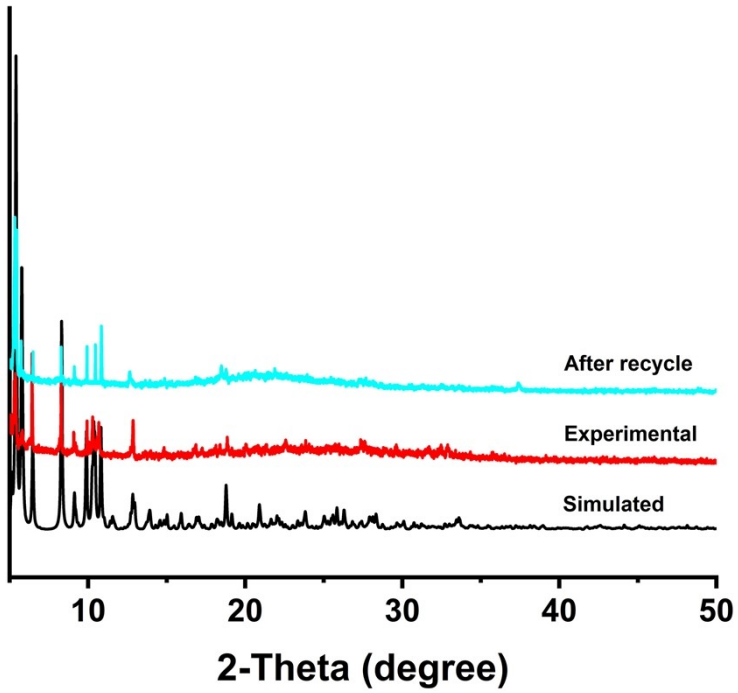

Fig. S8. The PXRD patterns for **1**: Simulated (black), Experimental (red), After recycle (light blue).