

Electronic Supplementary Information (ESI)

W^{VI}-OH Functionality on polyoxometalates for water reduction to molecular hydrogen

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Section S1. Physical characterizations

S1.1 Single-crystal X-ray diffraction (SC-XRD) analysis

A suitable single-crystal of compound **1** was selected from the mother liquor and mounted using glass fiber-tip on the X-ray diffractometer, using an Araldite resin mask, for X-ray diffraction data collection (at 293 K). The Bruker D8 Quest CCD diffractometer is equipped with a Mo-K α ($\lambda = 0.71073$ Å) graphite monochromatic X-ray beam source. A 40 mm crystal-to-detector distance was maintained during the data collection. The ω scans were recorded with a width of 0.3° . Data reduction was performed by SAINT PLUS,¹ and empirical absorption corrections were done using equivalent reflections performed by the SADABS.² Structure solutions and full-matrix least-squares refinement have done by the standard crystallographic software Olex2-1.3-ac4 embedded with SHELX 2018/1 package for compound **1**.³⁻⁵ All the non-hydrogen atoms were refined anisotropically. Fig. S1 shows the single crystal structure asymmetric unit of compound **1**. The asymmetric unit has 5 tungsten, 0.5 cobalt, 0.5 bismuth, 1.5 sodium, 19 cluster framework oxygens, one hydrogen of W-OH center, and 2 oxygens of lattice water. The W_6 center has occupancy disorder and the disordered tungsten (W_6) electron density occupancy has been found as W_{6A} (10.42879) and W_{6B} (10.07110). A very minute 0.07110 electron density of the W_6 in its asymmetric unit has been identified at the cobalt (Co_1) center and refined as W_{6B} through the Fourier electron density map.³⁻⁵ This occupancy disorder is a quite commonly observed phenomenon in similar type POM molecules.^{6,7} The EADP command has been employed for following oxygen (O_{15} and O_{16}), Na_1 , and W_{6B} atoms due to the atomic displacement parameter disorder.⁴ Attempts towards the hydrogen atom location on terminal oxo-groups of the tungsten $\{-W(OH)_2\}$ centers were made successful through the Fourier electron density map. The crystallographic details, such as structure refinement parameters and bond lengths, bond angles for compound **1** are listed in Tables S1 and S2. CSD 2033177 contains the supplementary crystallographic data for compound **1** and the crystal structure details of compound **2** such as the deposited CIF file and its CCDC number are available in the reported literature.⁸

Table S1. Compound **1** single-crystal data and its structure refinement parameters

Compound name	Compound 1
Empirical formula	$Bi_2Co_2H_{32}Na_6O_{84}W_{20}$
Formula weight	5726.77
T(K)/ λ (Å)	293(2) K/0.71073
Crystal system	Monoclinic
Space group	$C2/m$
Unit cell dimensions	$a = 17.7208(7)$ Å $b = 18.7141(7)$ Å $c = 14.1533(6)$ Å $\alpha = 90^\circ$ $\beta = 112.7410^\circ$ $\gamma = 90^\circ$
Volume	$4328.8(3)$ Å ³
Z	2
ρ(caled)	4.372 Mg/m ³
M	31.004 mm ⁻¹
$F(000)$	4884
Theta range for data collection	2.375 to 24.999°
Independent reflections	3944 [$R_{(int)} = 0.0933$]
Completeness to theta = 24.999°	99.9 %
Refinement method	Full-matrix least-squares on F^2

Goodness-of-fit on F^2	1.175
R1/ wR2 [$I > 2\sigma(I)$]	0.0421/0.1012
R1/ wR2 (all data)	0.0455/0.1029
Largest diff. peak and hole	3.344 and -2.612 e.Å ⁻³
Note: the required number of hydrogens for lattice water molecules were added to the molecular formula, to satisfy the water oxygen coordination.	

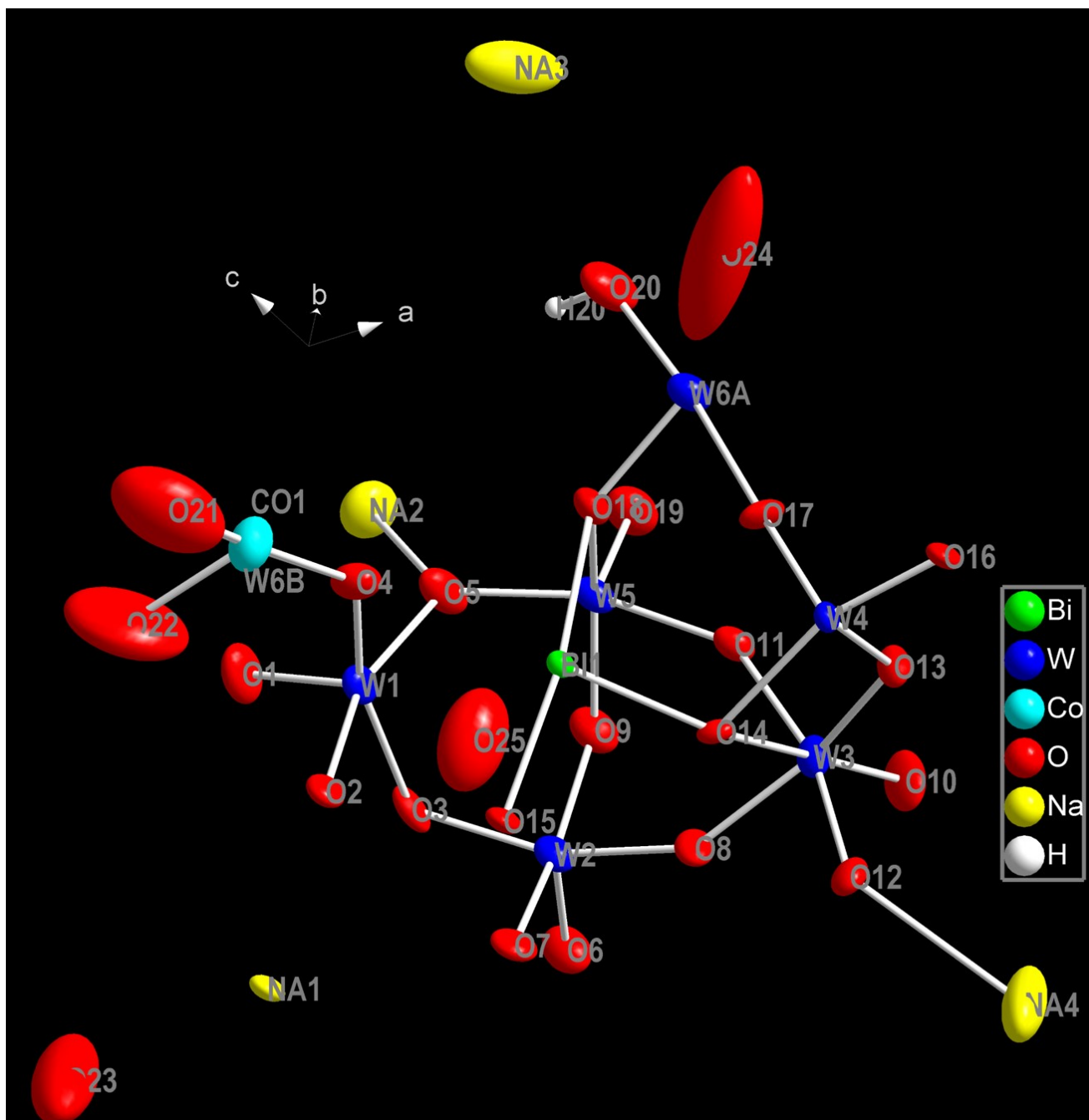


Fig. S1. Single-crystal structure asymmetric unit of compound **1** represented in thermal-ellipsoidal mode.

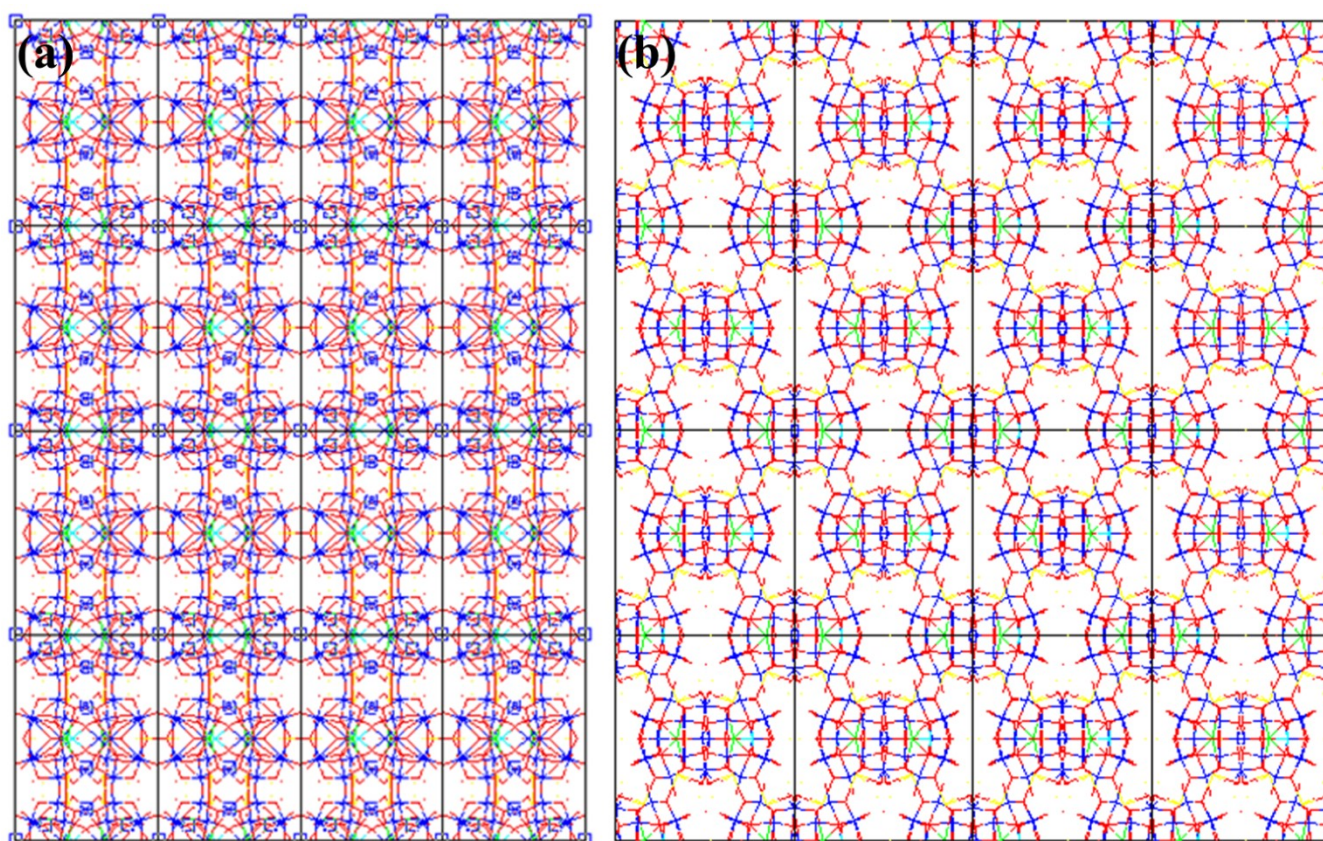


Fig. S2. $4 \times 4 \times 4$ super cell (packing diagrams) in the crystal structure of compound **1**: (a) looking down to the crystallographic a axis and (b) looking down to the crystallographic c axis.

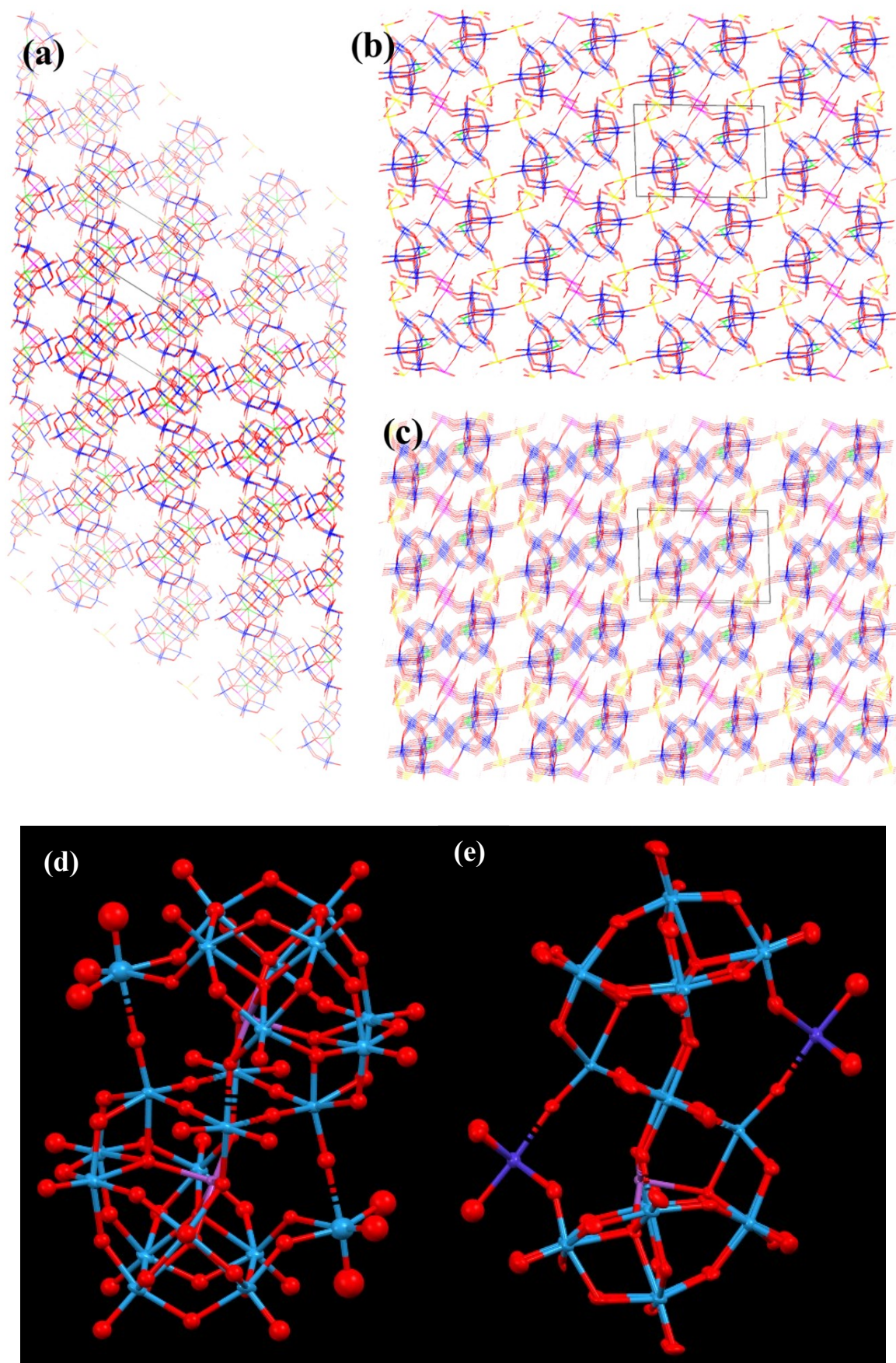


Fig. S3. 4×4×4 supercell (packing diagrams) in the crystal structure of compound 2: (a) looking down to the crystallographic *b* axis, (b and c) looking side-on view to the crystallographic *c* axis, (c and d) single-crystal structures of compounds 3 and 4 (generated from the respective published cif files).

Table S2. Bond distances (Å) and angles (°) of compound **1**

Bi(1)-O(14)	2.136(15)	W(6A)-O(17)	2.124(10)
Bi(1)-O(15)#1	2.154(10)	W(6A)-O(17)#2	2.124(10)
Bi(1)-O(15)	2.154(10)	Co(1)-O(22)	1.99(5)
W(4)-O(16)	1.760(15)	Co(1)-O(4)	2.161(18)
W(4)-O(17)#1	1.778(10)	Co(1)-O(4)#1	2.161(18)
W(4)-O(17)	1.778(10)	Co(1)-O(21)#1	2.17(4)
W(4)-O(13)	2.055(11)	Co(1)-O(21)	2.17(4)
W(4)-O(13)#1	2.055(11)	Co(1)-O(16)#3	2.23(2)
W(4)-O(14)	2.212(15)	O(2)-Na(1)	2.95(3)
W(5)-O(19)	1.715(13)	O(12)-Na(4)	2.78(3)
W(5)-O(18)	1.874(12)	O(5)-Na(2)	2.809(19)
W(5)-O(5)	1.912(13)	O(4)-W(6B)	2.17(3)
W(5)-O(11)	1.956(11)	O(4)-Na(2)#4	2.95(2)
W(5)-O(9)	1.961(12)	O(20)-Na(2)#4	2.86(2)
W(5)-O(15)#1	2.235(11)	O(20)-Na(3)	3.00(3)
W(2)-O(6)	1.716(12)	Na(1)-O(23)	2.93(4)
W(2)-O(8)	1.890(12)	Na(1)-Na(3)#4	4.16(2)
W(2)-O(3)	1.900(12)	Na(1)-Na(3)#5	4.16(2)
W(2)-O(7)	1.915(4)	Na(2)-O(21)#6	2.91(4)
W(2)-O(9)	1.954(13)	Na(2)-Na(3)#4	3.92(3)
W(2)-O(15)#1	2.288(10)	Na(4)-Na(4)#7	3.98(7)
W(1)-O(1)	1.709(12)	W(6B)-O(22)	1.95(5)
W(1)-O(4)	1.787(12)	W(6B)-O(21)#1	2.17(4)
W(1)-O(2)	1.929(5)	W(6B)-O(21)	2.17(4)
W(1)-O(5)	1.986(13)		
W(1)-O(3)	2.027(12)	O(14)-Bi(1)-O(15)#1	88.1(4)
W(1)-O(15)#1	2.194(11)	O(14)-Bi(1)-O(15)	88.1(4)
W(3)-O(10)	1.720(12)	O(15)#1-Bi(1)-O(15)	85.2(6)
W(3)-O(13)	1.862(11)	O(16)-W(4)-O(17)#1	103.6(5)
W(3)-O(11)	1.892(11)	O(16)-W(4)-O(17)	103.6(5)
W(3)-O(12)	1.941(8)	O(17)#1-W(4)-O(17)	95.8(8)
W(3)-O(8)	1.976(11)	O(16)-W(4)-O(13)	94.4(5)
W(3)-O(14)	2.299(10)	O(17)#1-W(4)-O(13)	160.0(5)
W(6A)-O(20)#2	1.821(16)	O(17)-W(4)-O(13)	88.0(5)
W(6A)-O(20)	1.821(16)	O(16)-W(4)-O(13)#1	94.4(5)
W(6A)-O(18)	1.995(11)	O(17)#1-W(4)-O(13)#1	88.0(5)
W(6A)-O(18)#2	1.995(11)	O(17)-W(4)-O(13)#1	160.0(5)

O(13)-W(4)-O(13)#1	82.1(7)	O(4)-W(1)-O(5)	90.3(6)
O(16)-W(4)-O(14)	162.3(6)	O(2)-W(1)-O(5)	161.1(6)
O(17)#1-W(4)-O(14)	88.1(4)	O(1)-W(1)-O(3)	94.0(6)
O(17)-W(4)-O(14)	88.1(4)	O(4)-W(1)-O(3)	161.3(5)
O(13)-W(4)-O(14)	72.4(4)	O(2)-W(1)-O(3)	85.1(6)
O(13)#1-W(4)-O(14)	72.4(4)	O(5)-W(1)-O(3)	87.3(5)
O(19)-W(5)-O(18)	103.3(6)	O(1)-W(1)-O(15)#1	163.6(6)
O(19)-W(5)-O(5)	99.3(6)	O(4)-W(1)-O(15)#1	88.9(5)
O(18)-W(5)-O(5)	93.7(5)	O(2)-W(1)-O(15)#1	87.4(6)
O(19)-W(5)-O(11)	100.4(6)	O(5)-W(1)-O(15)#1	73.9(5)
O(18)-W(5)-O(11)	87.4(5)	O(3)-W(1)-O(15)#1	72.6(4)
O(5)-W(5)-O(11)	159.5(5)	O(10)-W(3)-O(13)	99.8(6)
O(19)-W(5)-O(9)	99.4(6)	O(10)-W(3)-O(11)	101.1(6)
O(18)-W(5)-O(9)	156.7(5)	O(13)-W(3)-O(11)	93.7(5)
O(5)-W(5)-O(9)	87.6(6)	O(10)-W(3)-O(12)	97.7(7)
O(11)-W(5)-O(9)	83.4(5)	O(13)-W(3)-O(12)	90.4(6)
O(19)-W(5)-O(15)#1	172.3(5)	O(11)-W(3)-O(12)	159.7(5)
O(18)-W(5)-O(15)#1	81.6(4)	O(10)-W(3)-O(8)	100.8(6)
O(5)-W(5)-O(15)#1	74.3(5)	O(13)-W(3)-O(8)	159.3(5)
O(11)-W(5)-O(15)#1	85.7(4)	O(11)-W(3)-O(8)	85.0(5)
O(9)-W(5)-O(15)#1	76.4(5)	O(12)-W(3)-O(8)	84.2(6)
O(6)-W(2)-O(8)	101.9(6)	O(10)-W(3)-O(14)	170.0(6)
O(6)-W(2)-O(3)	101.7(6)	O(13)-W(3)-O(14)	73.8(5)
O(8)-W(2)-O(3)	156.0(5)	O(11)-W(3)-O(14)	87.1(4)
O(6)-W(2)-O(7)	98.1(7)	O(12)-W(3)-O(14)	75.0(5)
O(8)-W(2)-O(7)	89.8(7)	O(8)-W(3)-O(14)	85.4(5)
O(3)-W(2)-O(7)	91.0(6)	O(20)#2-W(6A)-O(20)	100.5(11)
O(6)-W(2)-O(9)	98.3(6)	O(20)#2-W(6A)-O(18)	95.6(6)
O(8)-W(2)-O(9)	86.1(6)	O(20)-W(6A)-O(18)	92.7(5)
O(3)-W(2)-O(9)	86.4(5)	O(20)#2-W(6A)-O(18)#2	92.7(5)
O(7)-W(2)-O(9)	163.5(6)	O(20)-W(6A)-O(18)#2	95.6(6)
O(6)-W(2)-O(15)#1	171.6(6)	O(18)-W(6A)-O(18)#2	167.0(7)
O(8)-W(2)-O(15)#1	83.3(4)	O(20)#2-W(6A)-O(17)	90.1(6)
O(3)-W(2)-O(15)#1	72.8(4)	O(20)-W(6A)-O(17)	169.4(7)
O(7)-W(2)-O(15)#1	88.4(5)	O(18)-W(6A)-O(17)	85.8(5)
O(9)-W(2)-O(15)#1	75.3(5)	O(18)#2-W(6A)-O(17)	84.1(5)
O(1)-W(1)-O(4)	104.7(7)	O(20)#2-W(6A)-O(17)#2	169.4(6)
O(1)-W(1)-O(2)	101.3(7)	O(20)-W(6A)-O(17)#2	90.1(6)
O(4)-W(1)-O(2)	91.4(6)	O(18)-W(6A)-O(17)#2	84.1(5)
O(1)-W(1)-O(5)	96.4(6)	O(18)#2-W(6A)-O(17)#2	85.8(5)

O(17)-W(6A)-O(17)#2	79.3(7)	W(5)-O(5)-W(1)	115.6(6)
O(22)-Co(1)-O(4)	95.4(14)	W(5)-O(5)-Na(2)	116.7(7)
O(22)-Co(1)-O(4)#1	95.4(14)	W(1)-O(5)-Na(2)	124.7(6)
O(4)-Co(1)-O(4)#1	78.0(9)	W(2)-O(8)-W(3)	146.8(7)
O(22)-Co(1)-O(21)#1	92.1(15)	W(2)-O(9)-W(5)	114.4(6)
O(4)-Co(1)-O(21)#1	95.6(10)	W(1)-O(4)-Co(1)	134.2(8)
O(4)#1-Co(1)-O(21)#1	170.5(13)	W(1)-O(4)-W(6B)	133.3(8)
O(22)-Co(1)-O(21)	92.1(15)	Co(1)-O(4)-W(6B)	1.0(10)
O(4)-Co(1)-O(21)	170.5(13)	W(1)-O(4)-Na(2)#4	123.8(7)
O(4)#1-Co(1)-O(21)	95.6(10)	Co(1)-O(4)-Na(2)#4	92.3(6)
O(21)#1-Co(1)-O(21)	89.8(19)	W(6B)-O(4)-Na(2)#4	92.7(7)
O(22)-Co(1)-O(16)#3	177.7(19)	W(4)-O(16)-Co(1)#3	172.6(10)
O(4)-Co(1)-O(16)#3	86.4(7)	W(6A)-O(20)-Na(2)#4	106.7(7)
O(4)#1-Co(1)-O(16)#3	86.4(7)	W(6A)-O(20)-Na(3)	152.5(8)
O(21)#1-Co(1)-O(16)#3	86.2(10)	Na(2)#4-O(20)-Na(3)	83.8(8)
O(21)-Co(1)-O(16)#3	86.2(10)	O(23)-Na(1)-O(2)	134.0(11)
Bi(1)-O(15)-W(1)#1	110.8(5)	O(23)-Na(1)-Na(3)#4	85.3(5)
Bi(1)-O(15)-W(5)#1	111.8(4)	O(2)-Na(1)-Na(3)#4	85.4(4)
W(1)#1-O(15)-W(5)#1	96.3(4)	O(23)-Na(1)-Na(3)#5	85.3(5)
Bi(1)-O(15)-W(2)#1	139.2(6)	O(2)-Na(1)-Na(3)#5	85.4(4)
W(1)#1-O(15)-W(2)#1	97.0(4)	Na(3)#4-Na(1)-Na(3)#5	156.0(11)
W(5)#1-O(15)-W(2)#1	93.3(4)	O(5)-Na(2)-O(20)#4	99.0(7)
W(5)-O(18)-W(6A)	132.8(6)	O(5)-Na(2)-O(21)#6	101.7(8)
W(3)-O(11)-W(5)	146.5(6)	O(20)#4-Na(2)-O(21)#6	153.9(9)
W(1)-O(2)-W(1)#1	143.6(8)	O(5)-Na(2)-O(4)#4	118.6(7)
W(1)-O(2)-Na(1)	108.0(4)	O(20)#4-Na(2)-O(4)#4	116.4(7)
W(1)#1-O(2)-Na(1)	108.0(4)	O(21)#6-Na(2)-O(4)#4	66.4(8)
W(2)-O(3)-W(1)	117.5(5)	O(5)-Na(2)-Na(3)#4	75.9(5)
W(2)#1-O(7)-W(2)	152.7(9)	O(20)#4-Na(2)-Na(3)#4	49.7(6)
W(4)-O(17)-W(6A)	177.5(7)	O(21)#6-Na(2)-Na(3)#4	121.2(10)
W(3)-O(13)-W(4)	117.6(6)	O(4)#4-Na(2)-Na(3)#4	163.3(7)
W(3)#1-O(12)-W(3)	117.5(8)	O(20)-Na(3)-Na(2)#4	46.6(5)
W(3)#1-O(12)-Na(4)	120.2(4)	O(20)-Na(3)-Na(1)#4	123.7(10)
W(3)-O(12)-Na(4)	120.2(4)	Na(2)#4-Na(3)-Na(1)#4	123.0(6)
Bi(1)-O(14)-W(4)	105.9(6)	O(12)-Na(4)-Na(4)#7	67.2(10)
Bi(1)-O(14)-W(3)	129.0(4)	O(22)-W(6B)-O(21)#1	93.4(17)
W(4)-O(14)-W(3)	96.0(5)	O(22)-W(6B)-O(21)	93.4(17)
Bi(1)-O(14)-W(3)#1	129.0(4)	O(21)#1-W(6B)-O(21)	90(2)
W(4)-O(14)-W(3)#1	96.0(5)	O(22)-W(6B)-O(4)	96.2(15)
W(3)-O(14)-W(3)#1	92.4(5)	O(21)#1-W(6B)-O(4)	95.4(10)

O(21)-W(6B)-O(4)	168.6(16)	O(21)-W(6B)-O(16)#3	85.4(11)
O(22)-W(6B)-O(4)#1	96.2(15)	O(4)-W(6B)-O(16)#3	85.1(10)
O(21)#1-W(6B)-O(4)#1	168.6(16)	O(4)#1-W(6B)-O(16)#3	85.1(10)
O(21)-W(6B)-O(4)#1	95.4(10)	W(6B)-O(21)-Co(1)	1.1(10)
O(4)-W(6B)-O(4)#1	77.5(11)	W(6B)-O(21)-Na(2)#5	94.0(16)
O(22)-W(6B)-O(16)#3	178(2)	Co(1)-O(21)-Na(2)#5	93.2(15)
O(21)#1-W(6B)-O(16)#3	85.4(11)	W(6B)-O(22)-Co(1)	0.3(13)

Symmetry transformations used to generate equivalent atoms: #1 x,-y+1,z #2 -x+1,y,-z+1 #3 -x+1,-y+1,-z+1 #4 -x+1/2,-y+3/2,-z+1 #5 -x+1/2,y-1/2,-z+1 #6 -x+1/2,y+1/2,-z+1 #7 -x+1,-y+1,-z

S1.2 Bond valence sum (BVS) calculations

Bond valence calculation. Numbers in brackets after atom symbols are at. no., r and c - see O"Keeffe and Brese, J.A.C.S. 1991, 113, 3226

.....01 of W-OH for [Compound 1]

O (8, .63, 3.15)		Rij	Dij	Vij
	-W (74, 1.38, 1.40)	1.93	1.84	1.29

Bond valence sum for O 1.29

.....02 of W-OH for [Compound 1]

O (8, .63, 3.15)		Rij	Dij	Vij
	-W (74, 1.38, 1.40)	1.93	1.84	1.29

Bond valence sum for O 1.29

.....01 of W-OH for [BWCN]

O (8, .63, 3.15)		Rij	Dij	Vij
	-W (74, 1.38, 1.40)	1.93	1.85	1.26

Bond valence sum for O 1.26

.....02 of W-OH for [BWCN]

O (8, .63, 3.15)		Rij	Dij	Vij
	-W (74, 1.38, 1.40)	1.93	1.89	1.11

Bond valence sum for O 1.11

.....01 of W-OH for [Compound 2]

O (8, .63, 3.15)		Rij	Dij	Vij
	-W (74, 1.38, 1.40)	1.93	1.86	1.23

Bond valence sum for O 1.23

.....02 of W-OH for [Compound 2]

O (8, .63, 3.15)		Rij	Dij	Vij
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-W (74, 1.38, 1.40) 1.93 1.84 1.30

Bond valence sum for O 1.30

For Compound 1:

.....Bi1

Bi (83, 1.54, 1.67)		Rij	Dij	Vij
-O (8, .63, 3.15)		2.12	2.15	.91
-O (8, .63, 3.15)		2.12	2.15	.91
-O (8, .63, 3.15)		2.12	2.13	.97

Bond valence sum for Bi 2.79

.....Bi1

Bi (83, 1.54, 1.67)		Rij	Dij	Vij
-O (8, .63, 3.15)		2.12	2.15	.91
-O (8, .63, 3.15)		2.12	2.15	.91
-O (8, .63, 3.15)		2.12	2.13	.97

Bond valence sum for Bi 2.79

.....Co1

Co (27, 1.09, 1.70)		Rij	Dij	Vij
-O (8, .63, 3.15)		1.68	2.26	.21
-O (8, .63, 3.15)		1.68	2.16	.27
-O (8, .63, 3.15)		1.68	2.16	.27
-O (8, .63, 3.15)		1.68	2.14	.29
-O (8, .63, 3.15)		1.68	2.14	.29
-O (8, .63, 3.15)		1.68	2.98	.03

Bond valence sum for Co 1.35

.....Co2

Co (27, 1.09, 1.70)		Rij	Dij	Vij
-O (8, .63, 3.15)		1.68	2.26	.21
-O (8, .63, 3.15)		1.68	2.16	.27
-O (8, .63, 3.15)		1.68	2.16	.27
-O (8, .63, 3.15)		1.68	2.14	.29
-O (8, .63, 3.15)		1.68	2.14	.29
-O (8, .63, 3.15)		1.68	2.98	.03

Bond valence sum for Co 1.35

.....W1

W (74, 1.38, 1.40)		Rij	Dij	Vij
-O (8, .63, 3.15)		1.93	1.72	1.79
-O (8, .63, 3.15)		1.93	2.29	.38

-0	(8, .63, 3.15)	1.93	1.96	.94
-0	(8, .63, 3.15)	1.93	1.91	1.05
-0	(8, .63, 3.15)	1.93	1.90	1.10
-0	(8, .63, 3.15)	1.93	1.88	1.14

Bond valence sum for W 6.41

.....W1

W (74, 1.38, 1.40)		Rij	Dij	Vij
-0	(8, .63, 3.15)	1.93	1.72	1.79
-0	(8, .63, 3.15)	1.93	2.29	.38
-0	(8, .63, 3.15)	1.93	1.96	.94
-0	(8, .63, 3.15)	1.93	1.91	1.05
-0	(8, .63, 3.15)	1.93	1.90	1.10
-0	(8, .63, 3.15)	1.93	1.88	1.14

Bond valence sum for W 6.41

.....W1

W (74, 1.38, 1.40)		Rij	Dij	Vij
-0	(8, .63, 3.15)	1.93	1.72	1.79
-0	(8, .63, 3.15)	1.93	2.29	.38
-0	(8, .63, 3.15)	1.93	1.96	.94
-0	(8, .63, 3.15)	1.93	1.91	1.05
-0	(8, .63, 3.15)	1.93	1.90	1.10
-0	(8, .63, 3.15)	1.93	1.88	1.14

Bond valence sum for W 6.41

.....W1

W (74, 1.38, 1.40)		Rij	Dij	Vij
-0	(8, .63, 3.15)	1.93	1.72	1.79
-0	(8, .63, 3.15)	1.93	2.29	.38
-0	(8, .63, 3.15)	1.93	1.96	.94
-0	(8, .63, 3.15)	1.93	1.91	1.05
-0	(8, .63, 3.15)	1.93	1.90	1.10
-0	(8, .63, 3.15)	1.93	1.88	1.14

Bond valence sum for W 6.41

.....W2

W (74, 1.38, 1.40)		Rij	Dij	Vij
-0	(8, .63, 3.15)	1.93	1.72	1.77
-0	(8, .63, 3.15)	1.93	2.30	.37
-0	(8, .63, 3.15)	1.93	1.86	1.21
-0	(8, .63, 3.15)	1.93	1.98	.87
-0	(8, .63, 3.15)	1.93	1.94	.97
-0	(8, .63, 3.15)	1.93	1.89	1.11

Bond valence sum for W 6.29

.....W2

W (74, 1.38, 1.40)		Rij	Dij	Vij
-0 (8, .63, 3.15)	1.93	1.72	1.77	
-0 (8, .63, 3.15)	1.93	2.30	.37	
-0 (8, .63, 3.15)	1.93	1.86	1.21	
-0 (8, .63, 3.15)	1.93	1.98	.87	
-0 (8, .63, 3.15)	1.93	1.94	.97	
-0 (8, .63, 3.15)	1.93	1.89	1.11	

Bond valence sum for W 6.29

.....W2

W (74, 1.38, 1.40)		Rij	Dij	Vij
-0 (8, .63, 3.15)	1.93	1.72	1.77	
-0 (8, .63, 3.15)	1.93	2.30	.37	
-0 (8, .63, 3.15)	1.93	1.86	1.21	
-0 (8, .63, 3.15)	1.93	1.98	.87	
-0 (8, .63, 3.15)	1.93	1.94	.97	
-0 (8, .63, 3.15)	1.93	1.89	1.11	

Bond valence sum for W 6.29

.....W2

W (74, 1.38, 1.40)		Rij	Dij	Vij
-0 (8, .63, 3.15)	1.93	1.72	1.77	
-0 (8, .63, 3.15)	1.93	2.30	.37	
-0 (8, .63, 3.15)	1.93	1.86	1.21	
-0 (8, .63, 3.15)	1.93	1.98	.87	
-0 (8, .63, 3.15)	1.93	1.94	.97	
-0 (8, .63, 3.15)	1.93	1.89	1.11	

Bond valence sum for W 6.29

.....W3

W (74, 1.38, 1.40)		Rij	Dij	Vij
-0 (8, .63, 3.15)	1.93	1.75	1.65	
-0 (8, .63, 3.15)	1.93	1.78	1.51	
-0 (8, .63, 3.15)	1.93	1.78	1.51	
-0 (8, .63, 3.15)	1.93	2.21	.47	
-0 (8, .63, 3.15)	1.93	2.06	.71	
-0 (8, .63, 3.15)	1.93	2.06	.71	

Bond valence sum for W 6.56

.....W3

W (74, 1.38, 1.40)		Rij	Dij	Vij
-0 (8, .63, 3.15)	1.93	1.75	1.65	
-0 (8, .63, 3.15)	1.93	1.78	1.51	
-0 (8, .63, 3.15)	1.93	1.78	1.51	
-0 (8, .63, 3.15)	1.93	2.21	.47	
-0 (8, .63, 3.15)	1.93	2.06	.71	
-0 (8, .63, 3.15)	1.93	2.06	.71	

Bond valence sum for W 6.56

.....W4

W (74, 1.38, 1.40)		Rij	Dij	Vij
-0 (8, .63, 3.15)		1.93	1.72	1.80
-0 (8, .63, 3.15)		1.93	1.87	1.18
-0 (8, .63, 3.15)		1.93	1.97	.92
-0 (8, .63, 3.15)		1.93	1.95	.94
-0 (8, .63, 3.15)		1.93	2.24	.44
-0 (8, .63, 3.15)		1.93	1.92	1.04

Bond valence sum for W 6.32

.....W4

W (74, 1.38, 1.40)		Rij	Dij	Vij
-0 (8, .63, 3.15)		1.93	1.72	1.80
-0 (8, .63, 3.15)		1.93	1.87	1.18
-0 (8, .63, 3.15)		1.93	1.97	.92
-0 (8, .63, 3.15)		1.93	1.95	.94
-0 (8, .63, 3.15)		1.93	2.24	.44
-0 (8, .63, 3.15)		1.93	1.92	1.04

Bond valence sum for W 6.32

.....W4

W (74, 1.38, 1.40)		Rij	Dij	Vij
-0 (8, .63, 3.15)		1.93	1.72	1.80
-0 (8, .63, 3.15)		1.93	1.87	1.18
-0 (8, .63, 3.15)		1.93	1.97	.92
-0 (8, .63, 3.15)		1.93	1.95	.94
-0 (8, .63, 3.15)		1.93	2.24	.44
-0 (8, .63, 3.15)		1.93	1.92	1.04

Bond valence sum for W 6.32

.....W4

W (74, 1.38, 1.40)		Rij	Dij	Vij
-0 (8, .63, 3.15)		1.93	1.72	1.80
-0 (8, .63, 3.15)		1.93	1.87	1.18
-0 (8, .63, 3.15)		1.93	1.97	.92
-0 (8, .63, 3.15)		1.93	1.95	.94
-0 (8, .63, 3.15)		1.93	2.24	.44
-0 (8, .63, 3.15)		1.93	1.92	1.04

Bond valence sum for W 6.32

.....W5

W (74, 1.38, 1.40)		Rij	Dij	Vij
-0 (8, .63, 3.15)		1.93	1.71	1.82
-0 (8, .63, 3.15)		1.93	2.19	.49

-0	(8, .63, 3.15)	1.93	1.79	1.48
-0	(8, .63, 3.15)	1.93	2.03	.77
-0	(8, .63, 3.15)	1.93	1.99	.85
-0	(8, .63, 3.15)	1.93	1.93	1.01

Bond valence sum for W 6.43

.....W5

W (74, 1.38, 1.40)		Rij	Dij	Vij
-0	(8, .63, 3.15)	1.93	1.71	1.82
-0	(8, .63, 3.15)	1.93	2.19	.49
-0	(8, .63, 3.15)	1.93	1.79	1.48
-0	(8, .63, 3.15)	1.93	2.03	.77
-0	(8, .63, 3.15)	1.93	1.99	.85
-0	(8, .63, 3.15)	1.93	1.93	1.01

Bond valence sum for W 6.43

.....W5

W (74, 1.38, 1.40)		Rij	Dij	Vij
-0	(8, .63, 3.15)	1.93	1.71	1.82
-0	(8, .63, 3.15)	1.93	2.19	.49
-0	(8, .63, 3.15)	1.93	1.79	1.48
-0	(8, .63, 3.15)	1.93	2.03	.77
-0	(8, .63, 3.15)	1.93	1.99	.85
-0	(8, .63, 3.15)	1.93	1.93	1.01

Bond valence sum for W 6.43

.....W5

W (74, 1.38, 1.40)		Rij	Dij	Vij
-0	(8, .63, 3.15)	1.93	1.71	1.82
-0	(8, .63, 3.15)	1.93	2.19	.49
-0	(8, .63, 3.15)	1.93	1.79	1.48
-0	(8, .63, 3.15)	1.93	2.03	.77
-0	(8, .63, 3.15)	1.93	1.99	.85
-0	(8, .63, 3.15)	1.93	1.93	1.01

Bond valence sum for W 6.43

.....W6

W (74, 1.38, 1.40)		Rij	Dij	Vij
-0	(8, .63, 3.15)	1.93	1.84	1.29
-0	(8, .63, 3.15)	1.93	1.84	1.29
-0	(8, .63, 3.15)	1.93	1.99	.86
-0	(8, .63, 3.15)	1.93	1.99	.86
-0	(8, .63, 3.15)	1.93	2.12	.61
-0	(8, .63, 3.15)	1.93	2.12	.61

Bond valence sum for W 5.51

.....W6

W	(74, 1.38, 1.40)	R _{ij}	D _{ij}	V _{ij}
-0	(8, .63, 3.15)	1.93	1.84	1.29
-0	(8, .63, 3.15)	1.93	1.84	1.29
-0	(8, .63, 3.15)	1.93	1.99	.86
-0	(8, .63, 3.15)	1.93	1.99	.86
-0	(8, .63, 3.15)	1.93	2.12	.61
-0	(8, .63, 3.15)	1.93	2.12	.61

Bond valence sum for W 5.51

S1.3 X-ray photoelectron spectroscopy

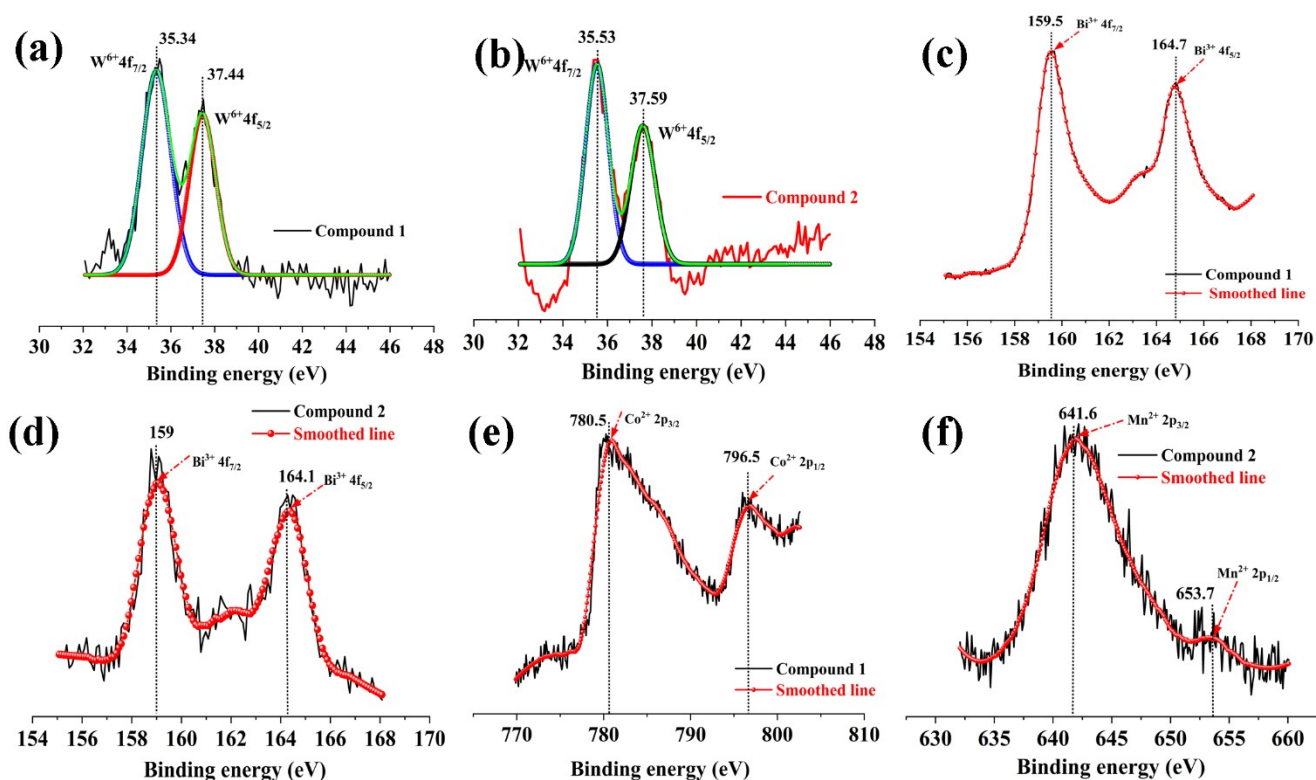


Fig. S4. (a and b) W4f core level XPS spectra of compounds 1 and 2, (c and d) Bi4f core level XPS spectra of compounds 1 and 2, (e) Co2p core level XPS spectra of compound 1, (f) Mn2p core level XPS spectra of compound 2.

S1.4 Powder X-ray diffraction analyses

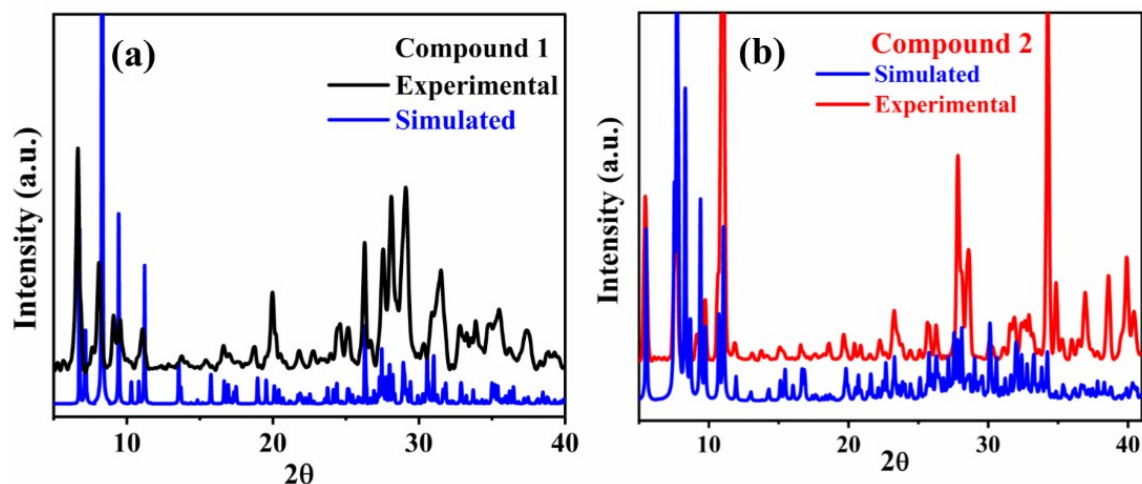


Fig. S5. (a and b) Powder X-ray diffraction patterns for compounds 1 and 2.

Section S2. Electrochemical analysis

All the electrochemical experiments were performed using a homemade three-electrode electrochemical cell. The compounds 1 and 2 modified nickel foam (NiFO) as a working (WE), a homemade Ag/AgCl (3M) as a reference (RE), and Pt mesh as counter (CE) electrodes were employed to perform electrochemical studies. The preparation of compounds 1 and 2 modified electrodes was done using 20 mg of sample and 4 mg of acetylene carbon black in 4 mL of the ethanol-water mixture (3:2 ratio). 80 μL of 5 wt% aqueous Nafion binder was then added and subjected to ultra-sonication at room temperature for 30 min to make a homogenous suspension. 100 μL of this homogeneous ink was coated on the nickel foam working electrode (NiFO-WE) having a 1 cm^2 geometrical area, resulting in $\sim 0.5 \text{ mg/cm}^2$ of sample loading on the working electrode. The diluted Nafion solution was prepared by adding 40 μL (5 wt %) Nafion solution into a 60 μL of ethanol (4:6 Nafion-ethanol mixture ratio), and a drop of it was coated over the sample loaded electrode. The same amount of sample loading was maintained for all the electrochemical experiments unless otherwise mentioned. The drop-cast sample was dried under the IR-lamp (temp $\sim 70^\circ\text{C}$), and the sample loaded electrode was left at room temperature ($\sim 5 \text{ min}$) at an ambient atmosphere. All the electrochemical experiments were run under the nitrogen atmosphere. The experimentally observed potentials were converted into the RHE (reversible hydrogen electrode) scale following the relation $E_{(\text{RHE})} = E_{(\text{Ag}/\text{AgCl})} + 0.204 \text{ V} + 0.059\text{pH}$, where the pH of electrolyte was 4.0 and the Ag/AgCl electrode was used as a standard reference electrode. The cyclic voltammogram (CV) scan was initiated at the open circuit potential (OCP) and was first scanned to the cathodic side. Linear sweep voltammograms were recorded with 5 mVs^{-1} , whereas most of the CVs were done with 100 mVs^{-1} unless otherwise mentioned. All the electrochemical studies were performed in acidic pH 4.0 (0.1 M) of potassium phosphate solution which was used as a supporting electrolyte. The chronoamperometry experiments were done with a NiFO as working, and large surface Pt mesh as the counter electrode. The Tafel data were collected in a galvanostatic mode under steady-state mass flow by stirring the electrolyte solution at 480 rpm throughout the experiment and the internal cell resistance was manually calibrated. The electrochemical impedance spectra were also collected in the two-electrode mode in the electrocatalytic HER experimental condition.

S2.1 TCD-GC analysis of electrochemically generated H₂ gas mediated by compounds 1 and 2

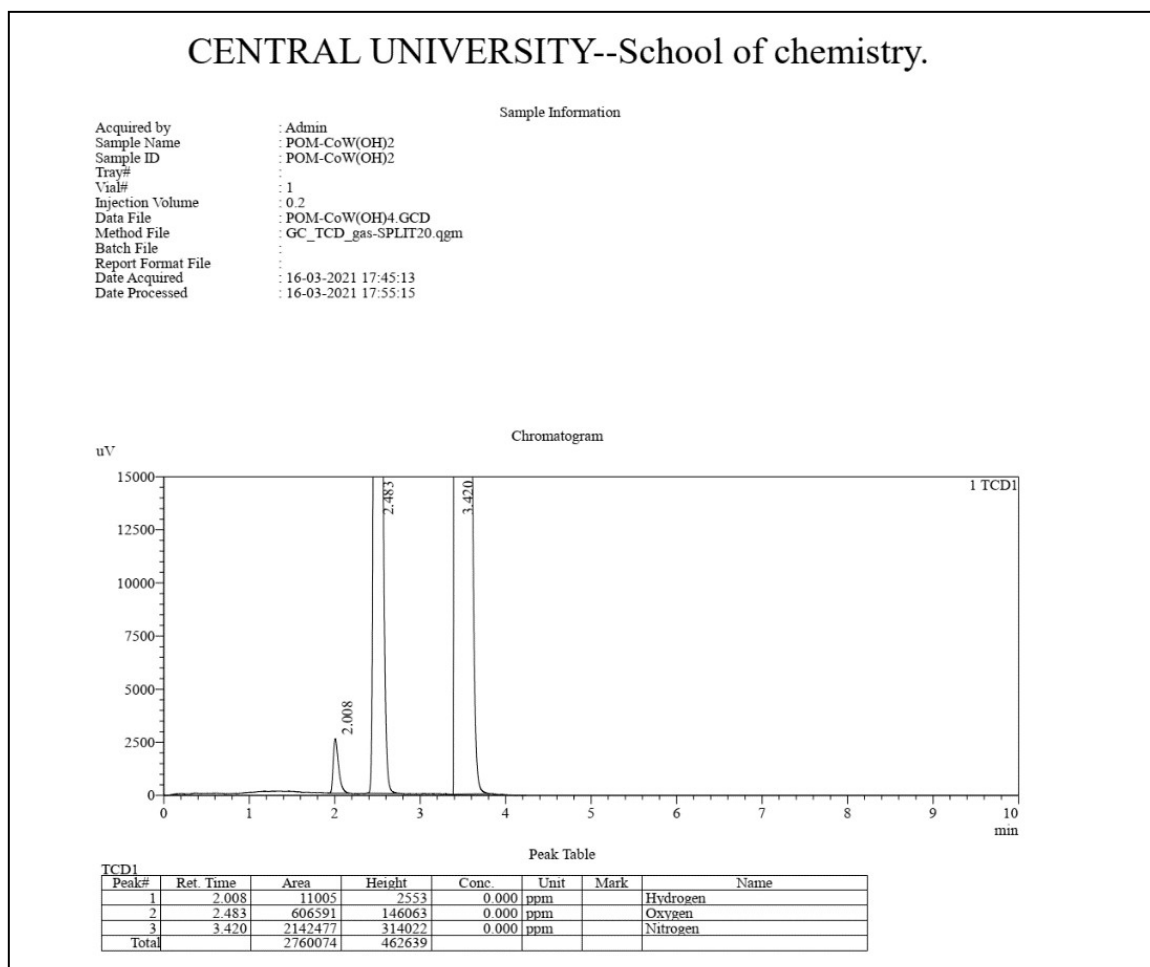


Fig. S6. TCD-GC analysis report for the electrocatalysis, catalysed by compound 1.

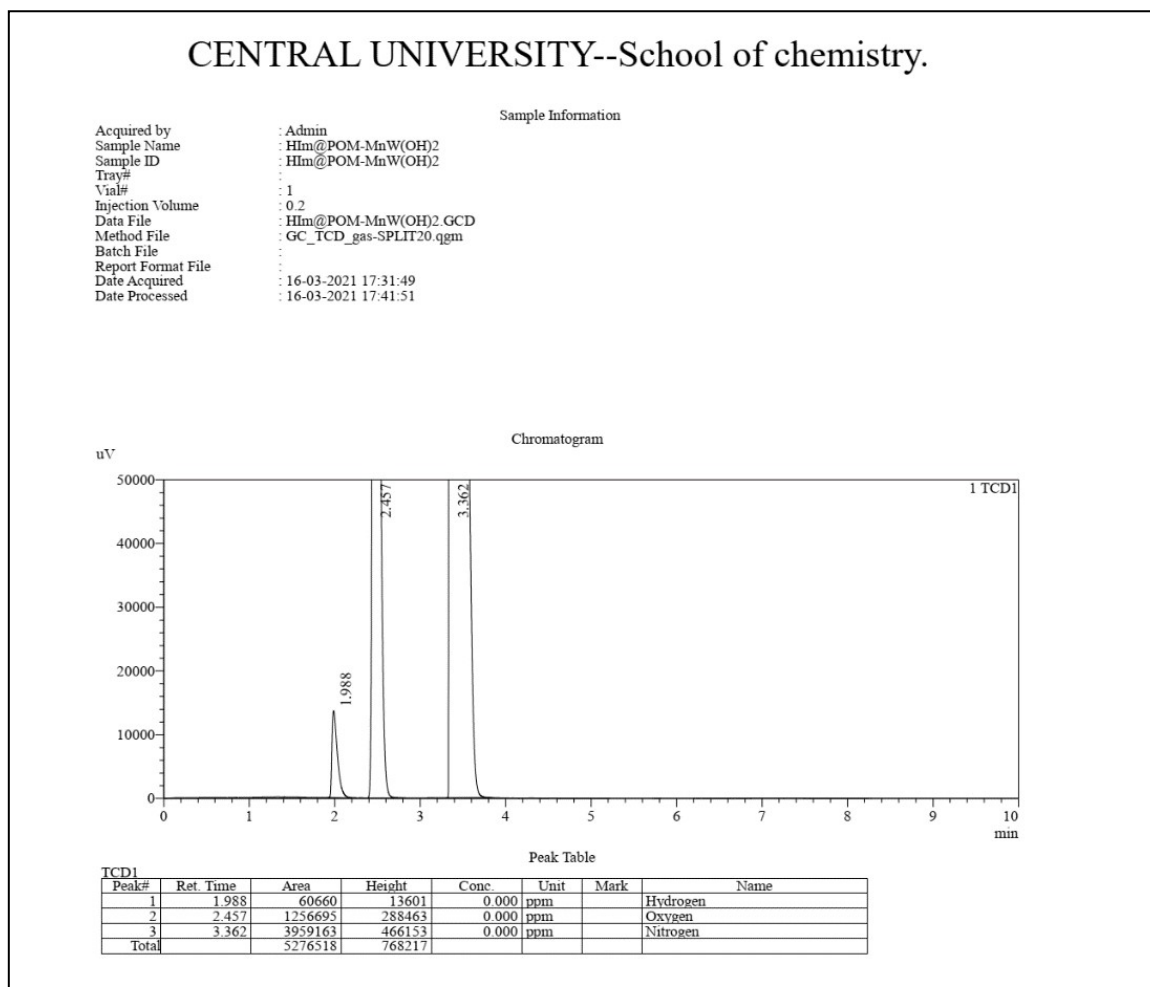


Fig. S7. TCD-GC analysis report for the electrocatalysis, catalysed by compound 2.

S2.2 Non-aqueous cyclic voltammogram

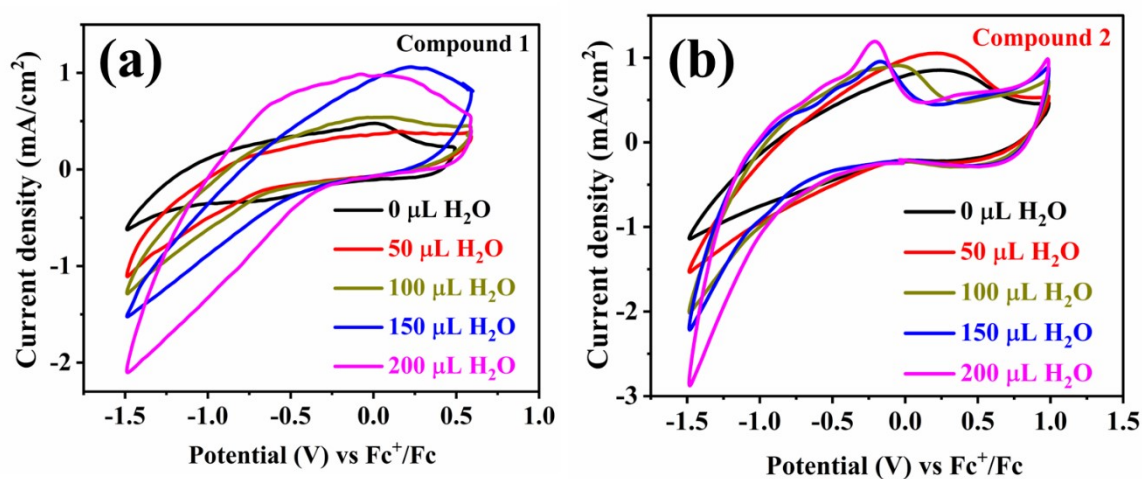


Fig. S8. Non-aqueous medium cyclic voltammograms (CVs) were performed under inert atmosphere: **a** and **b** for compounds **1** and **2**. The CVs were collected during the sequential addition of water to the electrochemical cell (dry tetrahydrofuran solution having 0.1 M tetrabutylammonium perchlorate (TBA-ClO₄) as a supporting electrolyte and the CV data were collected with 100 mVs⁻¹ scan rate).

S2.3 Raman spectra and microscopic analyses of compounds 1 and 2 electrode materials

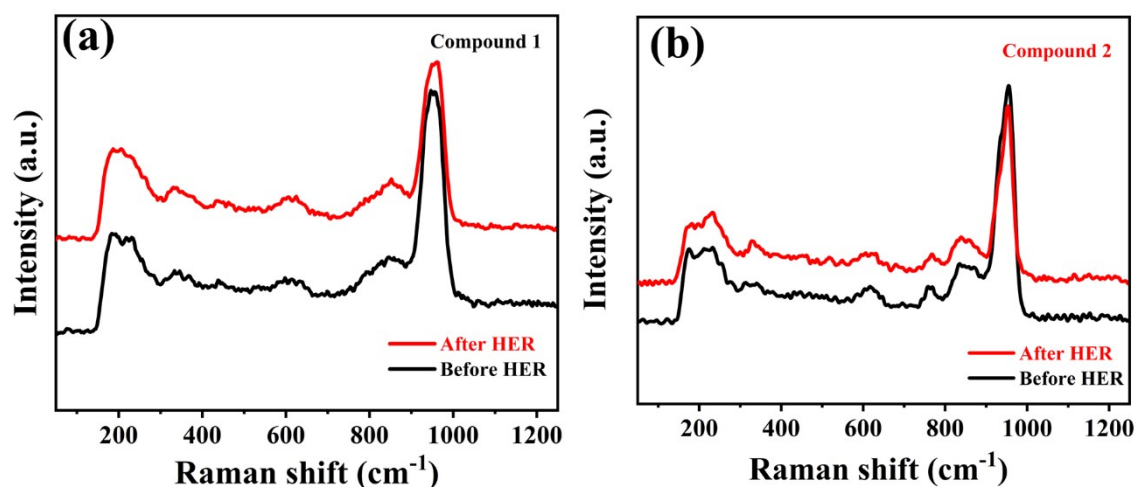


Fig. S9. (a and b) post-HER electrolysis electrode materials Raman spectral profiles for compounds 1 and 2 compared with pre-HER electrolysis profiles.

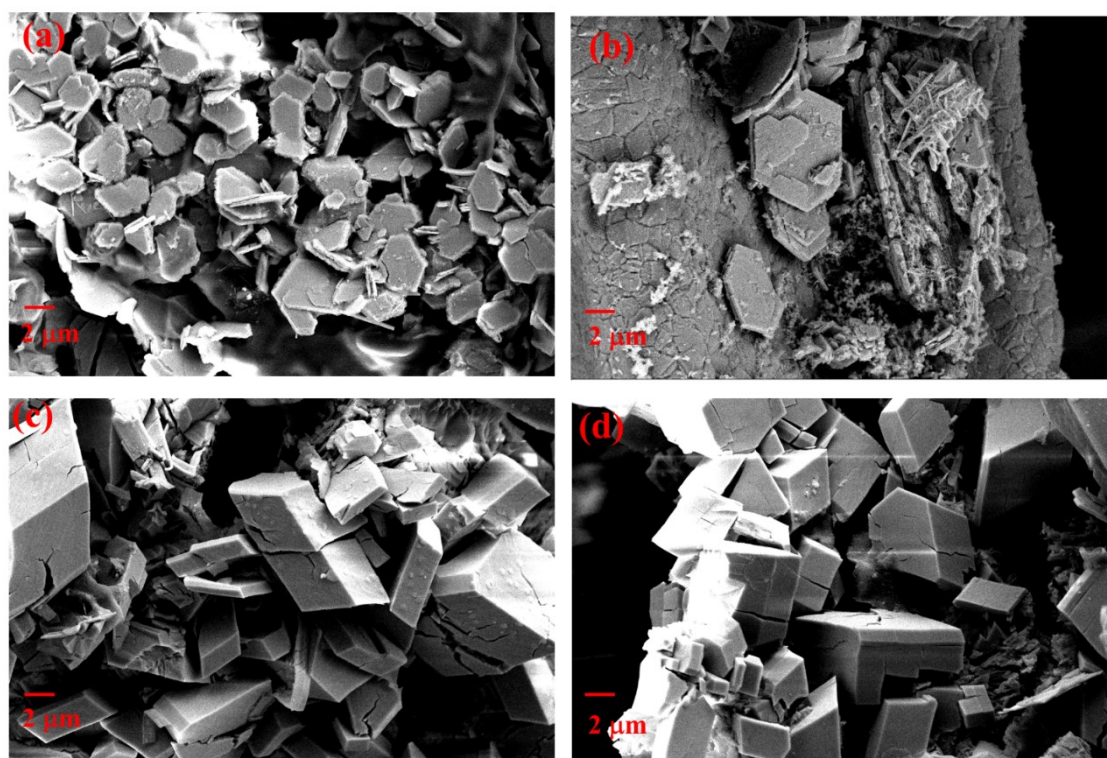


Fig. S10. FE-SEM analysis on the HER electrolysis NiFO-electrodes (at acidic pH 4.0): (a and b) before and after HER for compound 1, (c and d) before and after HER for compound 2, respectively.

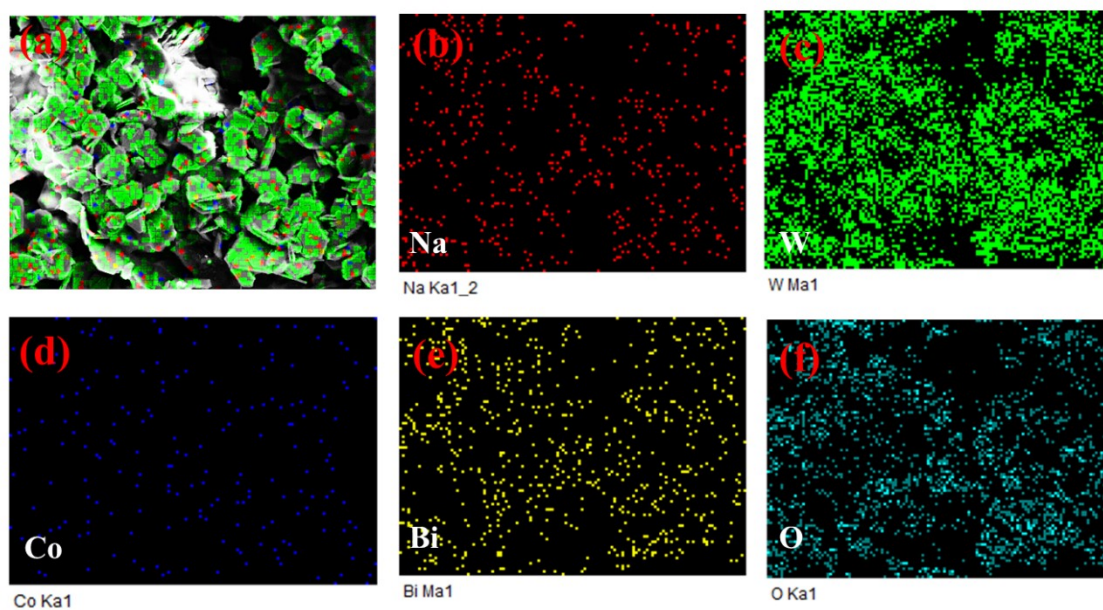


Fig. S11. Before HER electrolysis at acidic pH 4.0, the FESEM-EDX mapping has been performed on compound **1** modified NiFO-electrode.

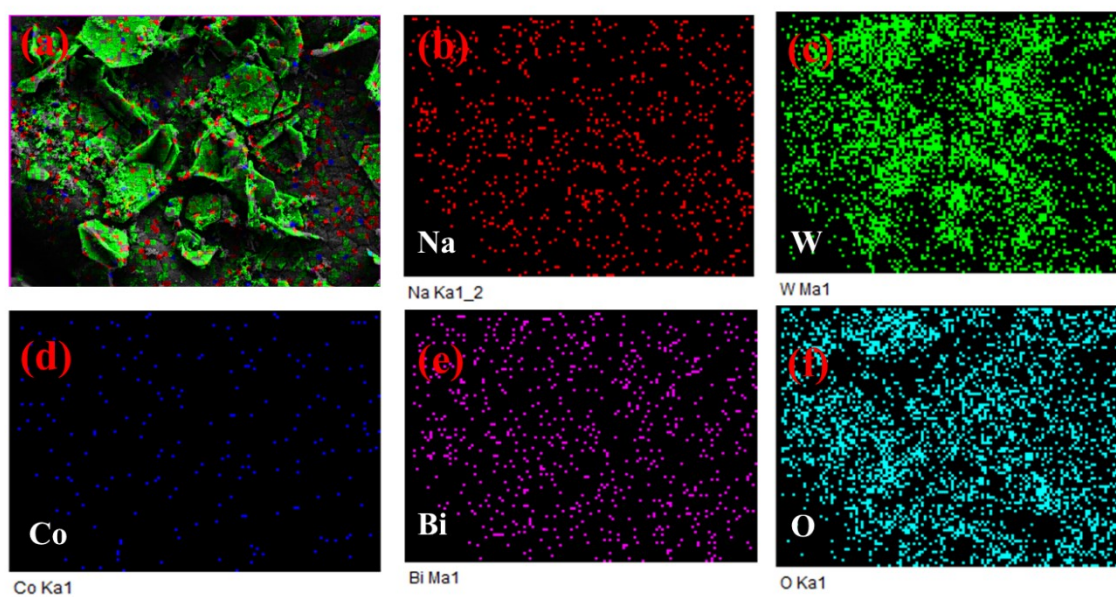


Fig. S12. After HER electrolysis at acidic pH 4.0, the FESEM-EDX mapping has been done on the same electrode of compound **1** modified NiFO-electrode.

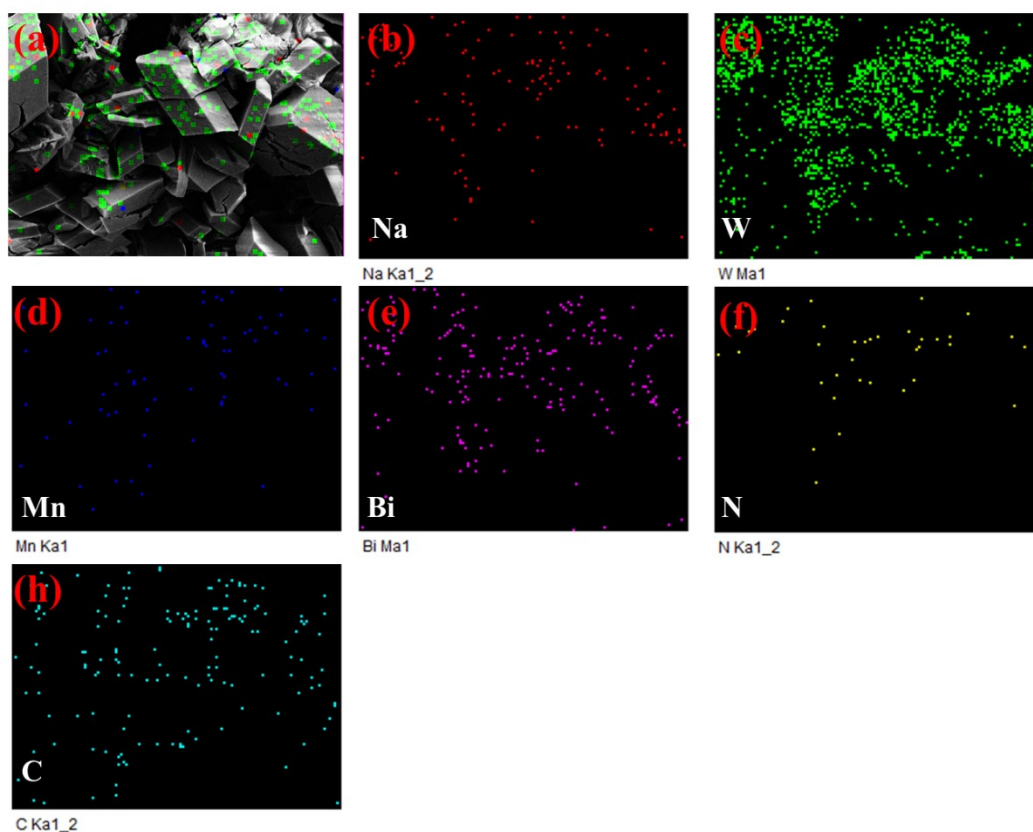


Fig. S13. Before HER electrolysis at acidic pH 4.0, the FESEM-EDX mapping has been collected on compound 2 modified NiFO-electrode.

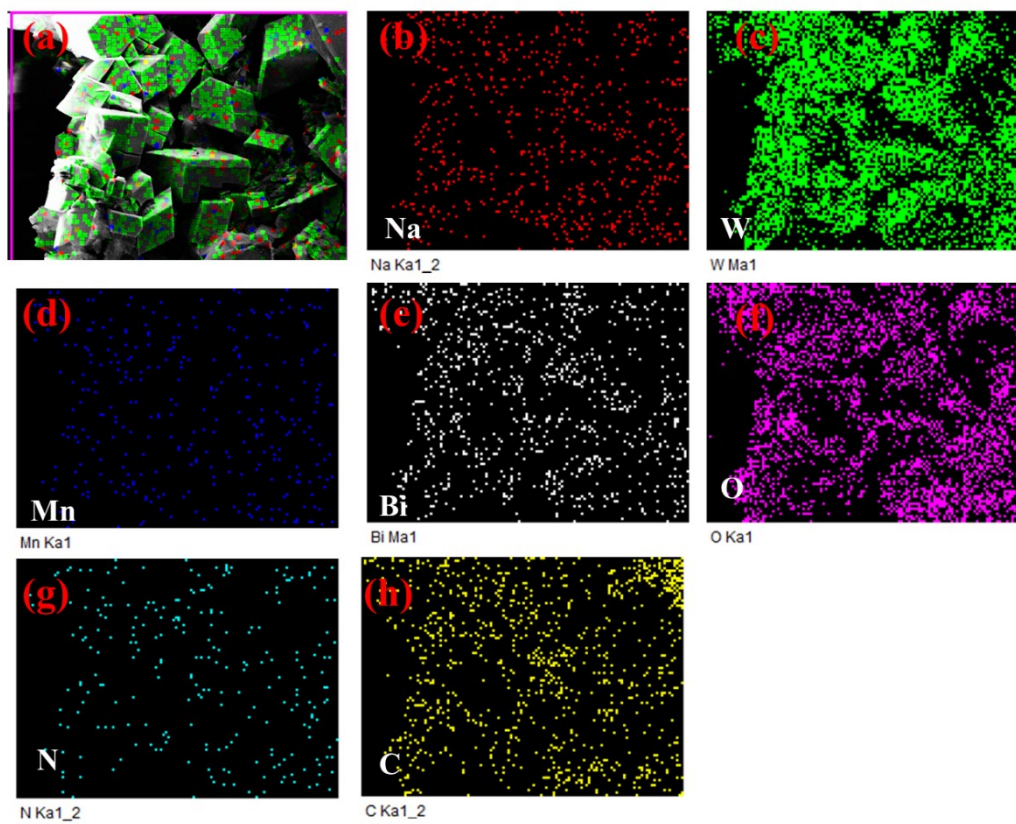
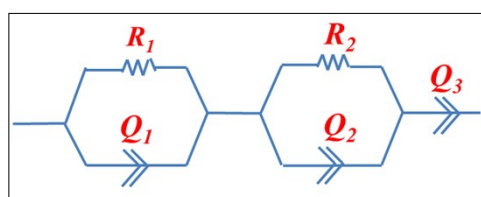


Fig. S14. After HER electrolysis at acidic pH 4.0, the FESEM-EDX mapping has been performed on the same electrode of compound 2 modified NiFO-electrode.

S2.4 Electrochemical impedance spectroscopy

The electrochemical impedance spectroscopy (EIS) measurements of compounds **1** and **2** were recorded in a two-electrode setup, where the sample modified nickel foam (NiFO) electrode acts as a working electrode (WE) and Pt mesh electrode functions as a counter electrode (CE) under the -10 mAcm^{-2} HER current operational conditions. The impedance spectra of both compounds **1** and **2** were collected in the frequency range of 1Hz to 1MHz employing the potential -0.76 V vs RHE. The experimental Nyquist plots of impedance data have been analyzed by the Randles equivalence circuit, $(R_1/Q_1)+(R_2/Q_2)+Q_3$, where R_1 and R_2 are the resistances corresponding to the charge transfer resistance (R_{ct}) of the material and the electrode-electrolyte interface resistance, Q_1 , Q_2 , and Q_3 are the constant phase elements. The observed R_{ct} values of compounds **1** and **2** have shown a similar trend with the other kinetic parameters. Compound **2** (94.37 Ohms) has lower charge transfer resistance than compound **1** (95.82 Ohms), which could be attributed to the presence of charge conducting imidazole cations in compound **2**. The equivalent circuit and fitting parameters in terms of χ^2 of the compounds **1** and **2** have been given below.



Compound name	R (Ohm)		Fitting error in χ^2
	R_1	R_2	
Compound 1	95.82	1238	0.267×10^{-3}
Compound 2	94.37	180.6	11.93×10^{-3}

S2.5 Cyclic voltammograms at different scan rates in the non-faradaic region

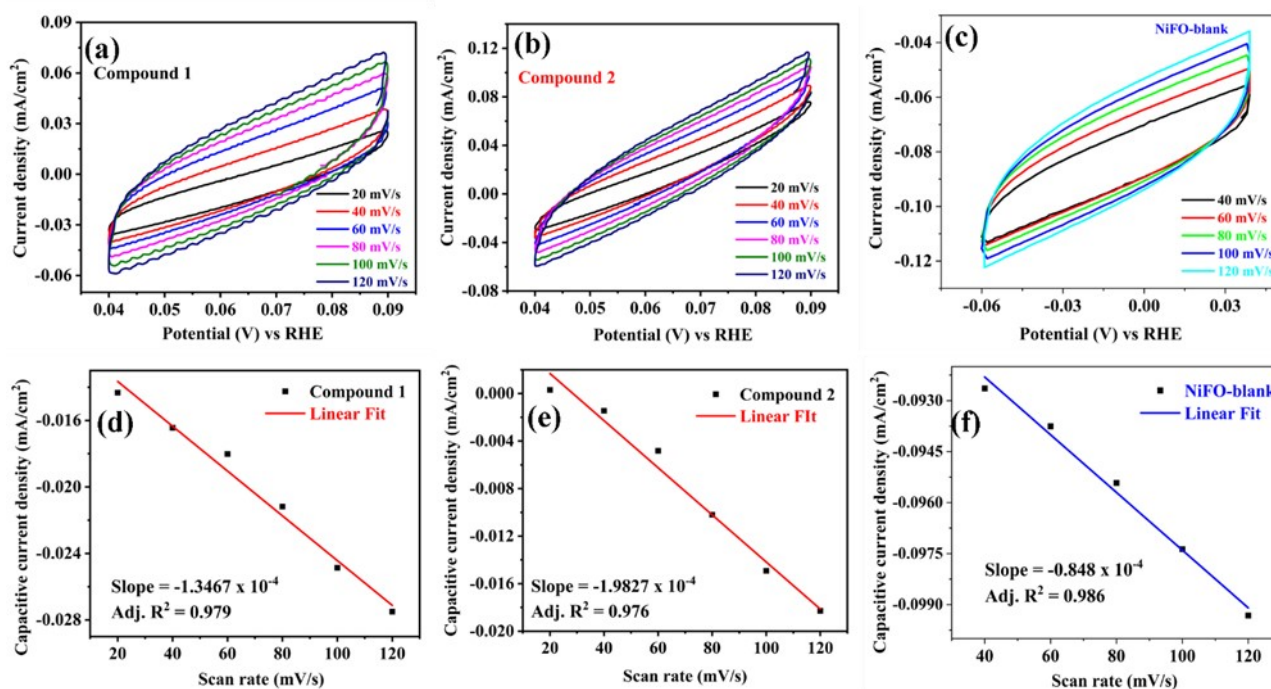


Fig. S15. (a-c) Cyclic voltammogram of compounds **1**, **2** and NiFO-blank at different scan rates in the non-faradaic region (0.04–0.09 V vs RHE) with different scan rates from 20 to 120 mVs^{-1} in pH 4 (0.1 M) potassium phosphate electrolyte, (d-f) capacitive current as a function of scan rate in the non-faradaic region (0.04–0.09 V vs RHE) of the CVs for compounds **1**, **2** and NiFO-blank.

Electrochemically active surface area (EASA) calculations for NiFO-blank, compounds **1** and **2**

Double layer capacitance NiFO-blank (C_{NiFO}) = $0.848 \times 10^{-4} \text{ Fcm}^{-2}$

Double layer capacitance of compound **1** (C_1) = $1.3467 \times 10^{-4} \text{ Fcm}^{-2}$

Double layer capacitance of compound **2** (C_2) = $1.9827 \times 10^{-4} \text{ Fcm}^{-2}$

EASA of NiFO-blank ($EASA$)_{NiFO} has been calculated by running a cyclic voltammogram with 1mM solution of $K_4[Fe(CN)_6]$ in 0.1M potassium phosphate buffer following the Randles-Sevick equation:

$$i_p = 0.4463 \text{ nFAC (nFvD/RT)}^{1/2}$$

where,

$$i_p = 0.0179 \text{ A}, n = 1, F = 96500 \text{ C/mol}, D = 1.84 \times 10^{-9} \text{ cm}^2/\text{s}, C = 0.001 \text{ mol/cm}^3, v = 0.1 \text{ V/s}, R = 1.98 \times 10^{-3} \text{ VCK}^{-1} \text{ mol}^{-1}, T = 300 \text{ K}$$

Thus,

$$0.0179 = 0.4463 \times 1 \times 96500 \times A \times 0.001 \times \{[1 \times 96500 \times 0.1 \times 1.84 \times 10^{-9} / 1.98 \times 10^{-3} \times 300]\}^{1/2}$$

$$0.0179 = 430.679 \times A \times 2.98 \times 10^{-5}$$

$$= 1.283 \times 10^{-2} \times A$$

$$A = 0.0179 / 1.283 \times 10^{-2}$$

$$(EASA)_{NiFO} = 1.388 \text{ cm}^2$$

From this, ($EASA$)₁ is calculated using the following equation:

$$(EASA)_1 / (EASA)_{NiFO} = C_1 / C_{NiFO}$$

$$(EASA)_1 / 1.388 = 1.3467 \times 10^{-4} / 0.848 \times 10^{-4}$$

$$\text{Or, } (EASA)_1 = 2.204 \text{ cm}^2$$

Similarly,

$$(EASA)_2 / (EASA)_{NiFO} = C_2 / C_{NiFO}$$

$$(EASA)_2 / 1.388 = 1.9827 \times 10^{-4} / 8.164 \times 10^{-5}$$

$$\text{Or, } (EASA)_2 = 3.245 \text{ cm}^2$$

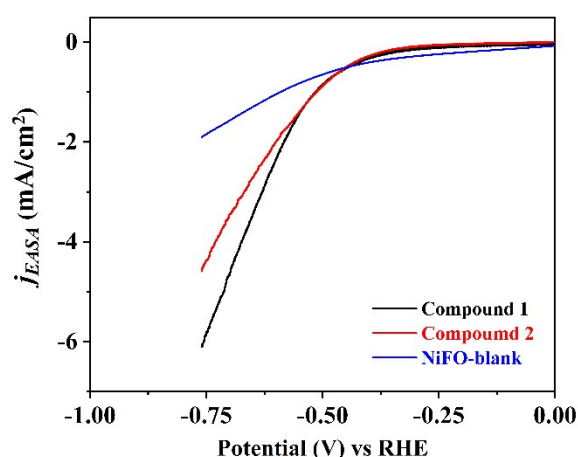


Fig. S16. ECSA-normalized polarization curves of NiFO-blank, compounds 1 and 2.

S2.6 Faradaic efficiency

Following the recent procedure,⁹ the Faradaic efficiency was determined from the evolved hydrogen (H₂) gas over a period of time. The chronopotentiometry electrolysis was carried out using a two-electrode system at 1 atm pressure. A known amount of sample coated nickel foam (NiF) electrode (1 cm² area surface) was used as a working electrode (in the present case, it works as a cathodic electrode), and a large surface area graphite rod was taken as a counter electrode (works as an anode). The catalyst loading on the NiF working electrode was maintained as 1 mg/cm², and the pH 4.0 (0.1 M) potassium phosphate solution was used as the electrolyte for both cases. A homemade setup was used to conduct the electrolysis process by employing a constant cathodic current -0.001 A or -1 mA for 3 hours.

Calculation of Faradaic efficiency

The Faradaic efficiency can be expressed as the efficiency, with which charge is utilized in the electrochemical reaction. The Faradaic efficiencies of both the catalysts were determined by the following equation:

$$\text{For HER, Faradaic efficiency} = \frac{\text{Number of moles of hydrogen evolved}}{\text{Number of moles of hydrogen that can evolve by utilizing the employed charge}} \times 100 \quad \dots\dots\dots (1)$$

In a constant current cathodic electrolysis at pH 4.0 condition, the evolved hydrogen gas was collected by a homemade setup. We found 0.38 mL/hour (1.15 mL/3 hours) and 0.40 mL/hour (1.2 mL/3 hours) of hydrogen gas under 1 atm pressure for **1**- and **2**-NiF electrodes, respectively.

Thus, the number of moles of hydrogen evolved in one hour for compound **1** = (0.38/22400) = 1.696 × 10⁻⁵ mol or 16.96 μmol

Thus, the number of moles of hydrogen evolved in one hour for compound **2** = (0.40/22400) = 1.785 × 10⁻⁵ mol or 17.85 μmol

$$H_{2 \text{ ideal}} = \frac{Q \text{ (total charge employed)}}{n(\text{number of electrons required for the chemical change}) \times 1\text{Farad}} \quad \dots\dots\dots (2)$$

Here, we employed a constant cathodic current -0.001 A and n = 2 for HER (a two-electron process).

$$\text{Thus, the } H_2 \text{ ideally should evolve} = \frac{(0.001 \times 3600)}{2 \times 96500} \text{ mol} = 1.865 \times 10^{-5} \text{ mol} \quad \dots\dots\dots (3)$$

$$\text{Faradaic efficiency} = \frac{\text{Experimentally evolved hydrogen}}{\text{Ideally evolved hydrogen}} \times 100 \quad \dots\dots\dots (4)$$

Therefore, the Faradaic efficiency:

$$\text{for compound } \mathbf{1} = 1.696 \times 10^{-5} / 1.865 \times 10^{-5} \times 100 = \mathbf{90.9\%}$$

$$\begin{aligned} \text{for compound 2} &= 1.785 \times 10^{-5} / 1.865 \times 10^{-5} \times 100 \\ &= \mathbf{95.7\%} \end{aligned}$$

S2.7 Brunauer-Emmett-Teller (BET) analysis of compounds 1 and 2

The Brunauer-Emmett-Teller (BET) isotherm profiles for compounds 1 and 2 have been recorded on Quantachrome® ASiQwin™- Automated Gas Sorption instrument. Prior to BET analysis, both the compounds 1 and 2 were subjected for degasification at 150 °C for 2 hours. The obtained BET surface area values of 11.148 and 13.763 m²/g (Fig. S16a,b) and the average pore radius (half pore width) values of 13.845 Å and 15.846 Å were obtained from their respective pore size distribution plots (Fig. S16c), confirming the presence of adequate void spaces, available for reactants to reach the HER active sites. The nature of the obtained isotherms of the compounds shows that they belong to type-III microporous kind of materials.

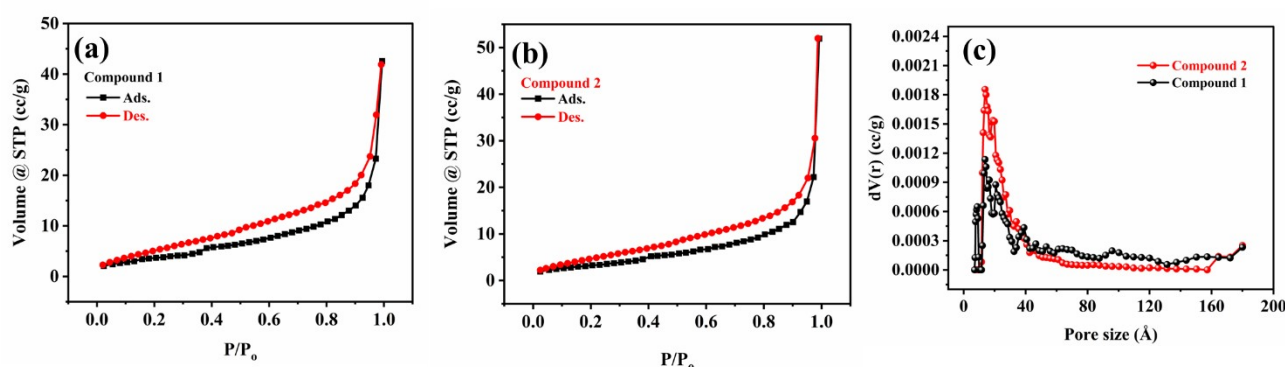


Fig. S17. (a and b) Nitrogen gas adsorption-desorption isotherms of compounds 1 and 2, (c) pore size distribution plots for compounds 1 and 2.

S2.8 Calculation of Turnover frequency (TOF)

The efficiency of a catalyst is well-expressed in terms of the turnover frequency (TOF). It is defined as the number of reactant molecules that are converted into the product molecules in unit time per active site. The TOFs of both catalysts were calculated as the following literature.¹⁰

The turnover frequency can be calculated using equation (5).

$$\text{TOF at a given overpotential} = \frac{\text{Current density at a given overpotential}}{2 \times F \times \text{no. of active sites}} \dots\dots\dots (5)$$

Here, 2 is used because hydrogen evolution reaction (HER) is a two-electron catalytic reaction process, therefore the division of a given current density (here it is 10 mAcm⁻²) by 2F gives one turnover number, and further, the turnover frequency (TOF) results from the division of this turnover number by the number active sites. In the present case, most of the elements present in both the compounds are assumed to be electrochemically active. All the coated sample on the electrode surface was considered to calculate the turnover frequency. The lower limit of TOF values 0.593 and 0.634 s⁻¹ for compounds 1 and 2 were calculated here. The actual TOFs can be much higher than the reported values in the present work.

Calculation:

The total amount of coated sample on the electrode surface was 100 μL .

The electrode ink was prepared by mixing 20 mg sample and 4 mg of acetylene carbon black in a 4 mL solution of ethanol-water (3:2 mixture) solution. The prepared ink is considered to be homogeneous in suspension and the 100 μL of ink should contain a 0.5 mg sample.

The molecular weights of compounds 1 and 2 have 5726.77 and 6118.12 g/mol respectively.

Now,

- 0.5 mg of the sample has 8.7309×10^{-8} mol of compound 1 active material.
- 0.5 mg of the sample has 8.1724×10^{-8} mol of compound 2 active material.

Thus, TOF for compound 1:

$$\text{TOF}_{j=10\text{mA/cm}^2} = [10 \times 10^{-3} / (2 \times 96500 \times 8.7309 \times 10^{-8})]$$

$$\text{TOF}_{j=10\text{mA/cm}^2} = 0.593 \text{ s}^{-1}$$

TOF for compound 2:

$$\text{TOF}_{j=10\text{mA/cm}^2} = [10 \times 10^{-3} / (2 \times 96500 \times 8.1724 \times 10^{-8})]$$

$$\text{TOF}_{j=10\text{mA/cm}^2} = 0.634 \text{ s}^{-1}$$

S2.9 Inductively coupled plasma (ICP) optical emission metal analysis result of compound 1

PENNIDEEKICIC LAONSLF PNEANJEEKEFID INDELEFF PFLIJEARKIEIYHC EONIOSCF		Report No. : LL/DR/19-20/001238	
Issued to: Prof Samar K.Das		Issue Date : 23/10/2019	
School Of Chemistry University of Hyderabad, Gachibowli, Hyderabad-500046		Customer Ref.: TRF	
Kind Attn : Dr. Sathish Kumar K		Ref.Date : 01/10/2019	
Sample Particulars : [CoW(OH) ₂]			
Qty. Received : 100mg X 1 No Vial			
Test Parameters : Tungsten as W,Sodium as Na,Cobalt as Co,Bismuth as Bi			
Date of Receipt of Sample : 01/10/2019		Date of Starting of Analysis : 22/10/2019	
Date of completion of analysis : 23/10/2019		SAMPLE TESTED AS RECEIVED	
TEST RESULTS			
S.No.	Parameters	UOM	Results
1	Tungsten as W	% by mass	62.89
2	Sodium as Na	% by mass	2.17
3	Cobalt as Co	% by mass	1.96
4	Bismuth as Bi	% by mass	7.25
Instrument Used: ICP-OES Varian 720-ES			
NOTE : This report and results relate only to the sample / items tested.			
Page No. 1/1		Srinivasu.G Authorized Signatory	

Fig. S18. Inductively coupled plasma optical emission spectra (ICP-OES) report of compound **1**.

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