Supplemental Material for:

A novel POMos-based hybrid with penta-coordinated Mo in trigonal bipyramid: structure and an efficient precursor for hydrodesulfurization catalyst

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Experimental Section

All reagents were purchased commercially and used without further purification. FT-IR spectra were measured on a Thermo Nicolet Nexus Fourier-transform infrared spectrometer using KBr pellets in the 4000-400 cm^{-1} region. TG was carried out on a SDT Q600 Thermal Analyzer in N_2 atmosphere with a heating rate of 10 ℃·min^{-1} from 25 to 800 ℃. Elemental analysis was carried out on a Perkin-Elmer 2400 CHN Elemental Analyzer (C, H and N), and on a Leaman inductively coupled plasma spectrometer (Ni and Mo). Powder X-ray diffraction (PXRD) patterns were recorded on a Panalytical X'Pert Pro MPD diffractometer (Netherlands) using Cu Kα radiation at a scan rate (2θ) of 5 °·min^{-1}. The accelerating voltage and applied current were 40 kV and 40 mA, respectively. XPS was undertaken with a Thermo ESCALAB 250 spectrometer combined with an Al Kα (1486.6 eV) achromatic X-ray source. The HRTEM micrograph of the sulfided catalyst was obtained with a JEOL 2010 transmission electron microscope operating at 200 kV with 1.9 Å point to point resolution.

Catalytic experiment

The HDS activity test was performed in a batch reactor at 300 ℃ and 7.3 MPa

total pressure for 4 h with constant stirring. Prior to the HDS activity test, the hybrid was sulfided ex situ in a tubular furnace at 400 ℃ for 4 h under a flow (100 mL•min^{-1}) of a H_2S/H_2 (10:90) mixture. The sulfided hybrid was transferred in an inert atmosphere (Ar) to a batch reactor with 60 mL of n-hexadecane solution containing DBT (850 ppm of S). The liquid product was collected and analyzed by an Agilent 6890 GC installed with an MS 80 mass spectrometer.

Table S1.Crystal data and structure refinement of **1**.

Empirical formula	$C_{15}H_{12}Mo_2N_3NiO_7$
CCDC	943446
Formula weight	596.87
Crystal system	triclinic
Space group	P-1
a (Å)	7.1747(5)
b (Å)	11.1258(13)
c (Å)	11.4017(8)
α	98.021(8)
β	90.098(6)
γ	106.227(8)
V (Å^3)	864.53(13)
Z	2
D_{calc} (g/cm^3)	2.293
μ(mm^{-1})	2.553
F(000)	582.0
θ range/°	2.95-28.43
T (K)	293
λ (Å)	0.71073
Data/restraints/parameters	3110/1/256
R_1[a], wR_2[b] ($I > 2\sigma(I)$)	0.0370, 0.0833
R_1[a] ,wR_2[b] (all data)	0.0537, 0.0925
Goodness-of-fit on F^2	1.021

[a]$R_1 = \sum||F_o|-|F_c||/\sum|F_o|$. [b]$wR_2 = \sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$

Table S2 Selected bond angles (°) and bond lengths (Å)

O1-Mo1-O2	118.036(152)	O7-Ni1-O3	93.091(124)
O1-Mo1-O3	116.150(154)	O2-Ni2-O2	180.000(131)
O1-Mo1-O4	96.550(161)	O2-Ni2-O6	88.919(131)
O1-Mo1-N1	81.985(171)	O2^{iii}-Ni2-N3	88.466(134)
O2-Mo1-O3	120.534(156)	O2^{iii}-Ni2-O6	91.081(131)
O2-Mo1-O4	98.179(141)	O2^{iii}-Ni2-N3^{i}	91.534(134)
O2-Mo1-N1	83.840(153)	Mo1-O1	1.7292(44)
O3-Mo1-O4	98.277(143)	Mo1-O2	1.7526(33)

O3-Mo1-N1	81.093(153)	Mo1-O3	1.7623(35)
O4-Mo1-N1	177.911(145)	Mo1-O4	1.9534(27)
O5-Mo2-O6	108.217(156)	Mo1-N1	2.3140(37)
O5-Mo2-O7	108.778(157)	Mo2-O5	1.7214(31)
O5-Mo2-O4	108.207(157)	Mo2-O6	1.7376(37)
O6-Mo2-O7	110.082(159)	Mo2-O7	1.7484(33)
O6-Mo2-O4	110.328(158)	Mo2-O4	1.8529(28)
O7-Mo2-O4	111.148(141)	Ni1-N2^{vi}	2.0687(34)
N2-Ni1-N2	180.000(159)	Ni1-N2	2.0687(34)
N2^{vi}-Ni1-O7^{ii}	90.774(131)	Ni1-O7	2.0837(33)
N2^{vi}-Ni1-O3^{iv}	86.578(137)	Ni1-O7^{ii}	2.0837(33)
N2-Ni1-O3	93.422(137)	Ni1-O3^{iii}	2.0872(36)
N2^{vi}-Ni1-O7	89.226(131)	Ni1-O3^{vi}	2.0872(36)
N2-Ni1-O7	90.774(131)	Ni2-O2^{iii}	2.0160(33)
N2-Ni1-O3^{iv}	93.422(137)	Ni2-O2^{v}	2.0160(33)
O7^{iii}-Ni1-O3^{ii}	86.909(124)	Ni2-O6^{i}	2.0683(38)
O2^{v}-Ni2-N3^{i}	88.466(134)	Ni2-O6	2.0683(38)
O6-Ni2-N3^{i}	89.671(142)	Ni2-N3^{i}	2.1374(39)
O6-Ni2-N3	90.329(142)	Ni2-N3	2.1374(39)

Symmetry code: (i) 1-x, -y, -z; (ii) 1-x, -y, 1-z, (iii) -1+x, y, z, (iv) 2-x, -y, 1-z, (v) 2-x, -y, -z, (vi) 3-x, 1-y, 1-z.

Crystal Data: CCDC 943446 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Table S3 Bond valence sum calculations

Mo1 and Mo2			
Mo1-O1	1.62	Mo2-O4	1.16
Mo1-O2	1.52	Mo2-O5	1.65
Mo1-O3	1.48	Mo2-O6	1.58
Mo1-O4	0.88	Mo2-O7	1.54
Mo1-N1	0.46	∑	5.93
∑	5.96		

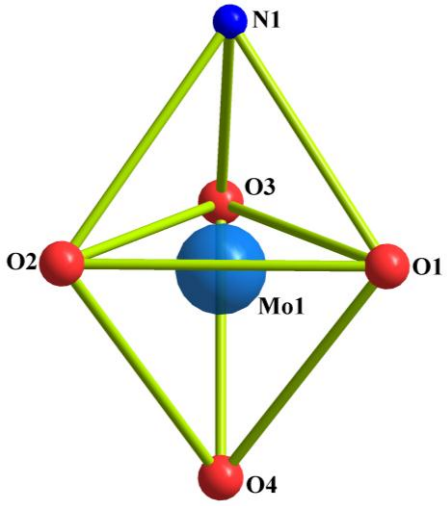

Fig. S1 Trigonal bipyramidal geometry of the Mo1 site

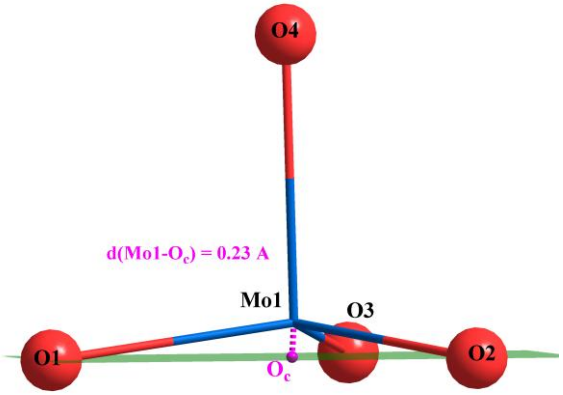

Fig. S2 Displaced Mo1 toward the equatorial plane of the three oxygen atoms

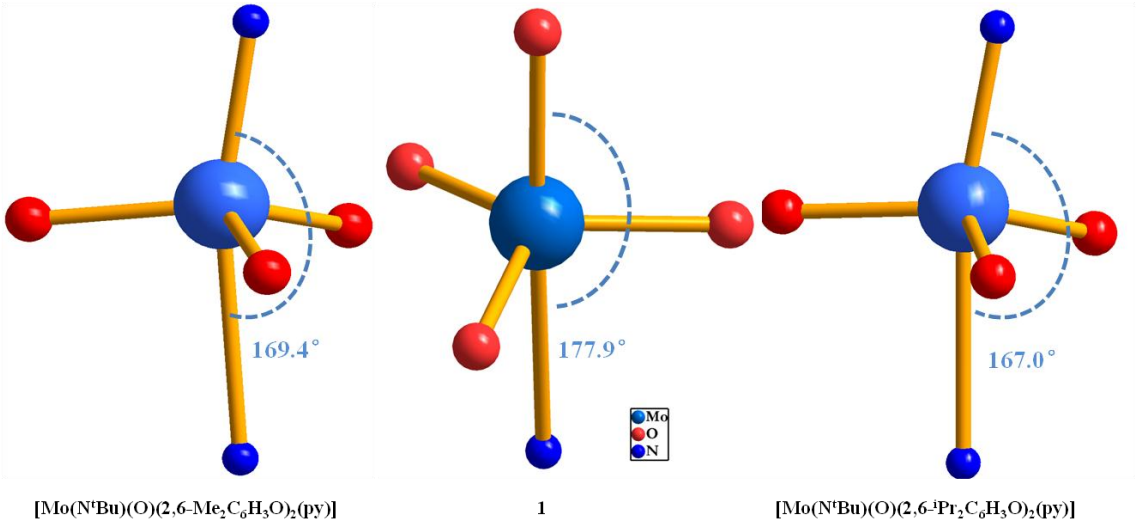

Fig. S3 Trigonal bipyramidal geometry of the Mo in **1** compared with the reported compounds

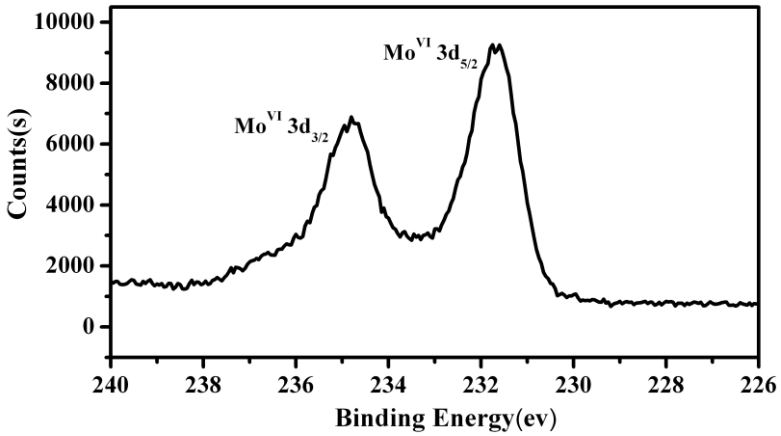

Fig. S4 XPS spectra for Mo in **1**.

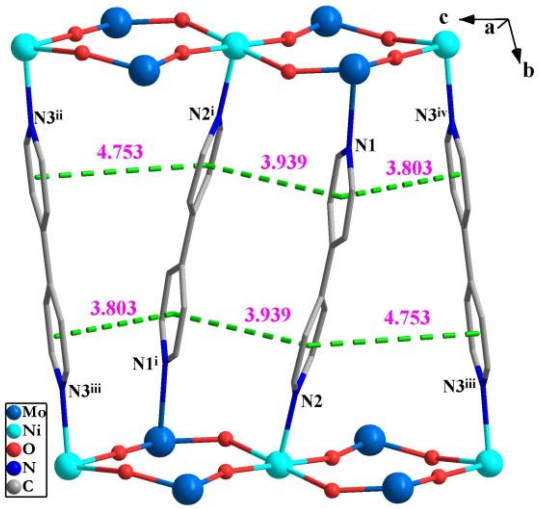

Fig. S5 Layered structure with π···π interactions in the hybrid. Distances are in Å unit. Symmetry code: (i) 4-x, 1-y, 1-z; (ii) 2-x, -y, 1-z, (iii) 2+x, 1+y, 1+z, (iv) 2-x, -y, -z.

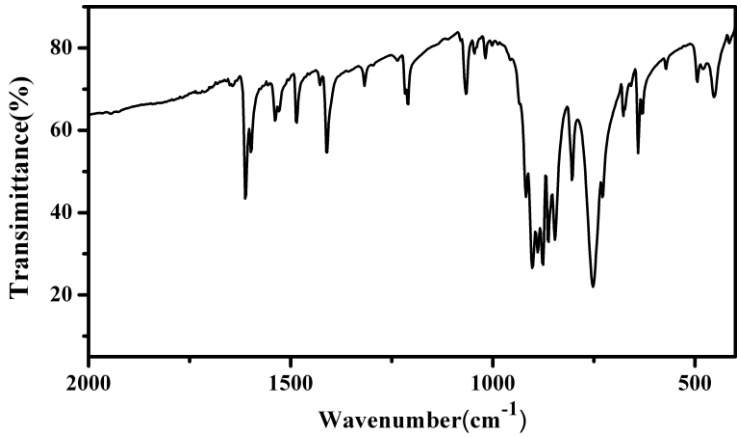

Fig. S6 The IR spectrum of compound **1**.

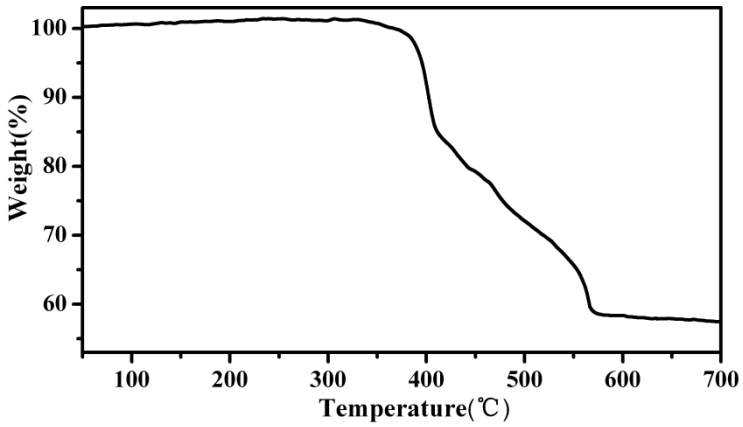

Fig. S7 The TG curve of compound **1**.