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Supplementary Information

Synthesis, Characterization and Catalytic Performance of a Novel Picolinic Acid-12-Molybdophosphoric Acid Hybrid Catalyst

Lijun Liu, Honghong Wang, Shuwen Gong,* Jing Lu* and Qian Zhang

Institute of Organic Functional Molecules and Materials, School of Chemistry and Chemical Engineering, Liaocheng University, 252000Liaocheng, China

Table S1. Refinement crystal data of PI-HPM

Empirical formula	$C_{24}H_{49}Mo_{14}N_4O_{67}P$
Formula weight	2839.80
Temperature / K	293(2)
Wavelength / Å	0.71073
Crystal system	triclinic
Space group	P-1
Unit cell dimension / Å	a =10.3564(13)
	b =12.1077(15)
	c = 16.583(2)
Unit cell dimension / degree	α = 92.599(11)
	β = 105.030(12)
	γ = 111.746(12)
Volume / Å^3	1842.0(4)
Calculated density / (g cm^{-3})	2.560
Z	1
Absorption coefficient / mm^{-1}	2.441
F(000)	1360
Crystal size / mm^3	0.30 × 0.20 × 0.20
Theta range for collection data / degree	2.40 to 25.02
Limiting indices	$-12 \le h \le 12$, $-14 \le k \le 14$, $-19 \le l \le 19$
Reflections collected/unique	12304/6500
R(int)	0.0794
Completeness to theta 25.02 / %	99.9
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6409 and 0.5279
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6500/1512/517
Goodness-of-fit on F^2	1.048
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0910, wR2 = 0.2159
R indices(all data)	R1 = 0.1841, wR2 = 0.3167
Largest diff. peak and hole / Å^3	3.256 and –1.372

Z: Number of formula units in the unit cell; F(000): structure factor evaluated in the zeroth-order case; R: residual factor.

*e-mail: gshw76@163.com; lujinglcu@163.com

Table S2. Selected bond distances (Å) and angles (°) of PI-HPM

	Bond distance / Å		Bond distance / Å
Mo(1)–O(2)	1.660(12)	Mo(1)–O(1)	1.877(14)
Mo(1)–O(4)	1.888(15)	Mo(1)–O(19)	1.905(14)
Mo(1)–O(3)	1.905(13)	Mo(1)–O(5)	2.46(2)
Mo(1)–O(18)	2.48(2)	Mo(2)–O(6)	1.638(12)
Mo(2)–O(4)	1.869(15)	Mo(2)–O(7)	1.879(14)
Mo(2)–O(13)#1	1.895(15)	Mo(2)–O(15)#1	1.906(14)
Mo(2)–O(5)	2.45(2)	Mo(2)–O(17)#1	2.45(2)
Mo(3)–O(9)	1.633(14)	Mo(3)–O(11)	1.822(15)
Mo(3)–O(10)	1.885(14)	Mo(3)–O(7)	1.920(13)
Mo(3)–O(8)	1.960(14)	Mo(3)–O(20)#1	2.41(2)
Mo(3)–O(17)#1	2.51(3)	Mo(4)–O(12)	1.659(12)
Mo(4)–O(13)	1.875(15)	Mo(4)–O(3)#1	1.891(14)
Mo(4)–O(10)	1.897(15)	Mo(4)–O(14)	1.939(14)
Mo(4)–O(20)#1	2.44(2)	Mo(4)–O(5)#1	2.49(2)
Mo(5)–O(8)#1	1.849(14)	Mo(5)–O(19)	1.885(14)
Mo(5)–O(16)	1.899(15)	Mo(5)–O(15)	1.917(13)
Mo(5)–O(18)	2.48(3)	Mo(5)–O(17)	2.49(3)
Mo(5)–O(32)	1.652(14)	Mo(6)–O(21)	1.663(13)
Mo(6)–O(14)	1.881(13)	Mo(6)–O(16)	1.896(15)
Mo(6)–O(1)	1.902(14)	Mo(6)–O(11)	1.935(15)
Mo(6)–O(20)#1	2.46(2)	Mo(7)–O(25)	1.692(16)
Mo(7)–O(26)	1.702(16)	Mo(7)–O(24)	1.867(2)
Mo(7)–O(22)	2.124(16)	Mo(7)–N(1)	2.246(18)
Mo(7)–O(27)	2.306(14)		
	Bond angle / degree		Bond angle / degree
O(2)–Mo(1)–O(1)	101.9(7)	O(2)–Mo(1)–O(4)	103.5(7)
O(1)–Mo(1)–O(4)	88.6(6)	O(2)–Mo(1)–O(19)	101.1(7)
O(1)–Mo(1)–O(19)	86.7(6)	O(4)–Mo(1)–O(19)	155.4(7)
O(2)–Mo(1)–O(3)	101.9(7)	O(1)–Mo(1)–O(3)	156.2(6)
O(4)–Mo(1)–O(3)	87.3(6)	O(19)–Mo(1)–O(3)	87.3(6)
O(2)–Mo(1)–O(5)	159.7(8)	O(1)–Mo(1)–O(5)	92.7(7)
O(4)–Mo(1)–O(5)	62.4(7)	O(19)–Mo(1)–O(5)	93.7(7)
O(3)–Mo(1)–O(5)	64.7(7)	O(2)–Mo(1)–O(18)	159.8(8)
O(1)–Mo(1)–O(18)	65.2(7)	O(4)–Mo(1)–O(18)	92.1(8)
O(19)–Mo(1)–O(18)	64.1(8)	O(3)–Mo(1)–O(18)	91.4(7)
O(5)–Mo(1)–O(18)	40.5(8)	O(6)–Mo(2)–O(4)	104.4(8)
O(6)–Mo(2)–O(7)	100.6(8)	O(4)–Mo(2)–O(7)	87.2(6)
O(6)–Mo(2)–O(13)#1	103.0(8)	O(4)–Mo(2)–O(13)#1	88.2(6)
O(7)–Mo(2)–O(13)#1	156.4(6)	O(6)–Mo(2)–O(15)#1	98.4(7)
O(4)–Mo(2)–O(15)#1	157.0(6)	O(7)–Mo(2)–O(15)#1	86.5(6)
O(13)#1–Mo(2)–O(15)#1	88.8(6)	O(6)–Mo(2)–O(5)	160.9(9)
O(4)–Mo(2)–O(5)	62.9(7)	O(7)–Mo(2)–O(5)	93.3(7)
O(13)#1–Mo(2)–O(5)	64.2(7)	O(15)#1–Mo(2)–O(5)	95.4(7)
O(6)–Mo(2)–O(17)#1	158.0(9)	O(4)–Mo(2)–O(17)#1	92.0(8)
O(7)–Mo(2)–O(17)#1	65.2(8)	O(13)#1–Mo(2)–O(17)#1	91.9(8)
O(15)#1–Mo(2)–O(17)#1	65.4(7)	O(5)–Mo(2)–O(17)#1	41.1(8)
O(9)–Mo(3)–O(11)	101.7(8)	O(9)–Mo(3)–O(10)	102.1(7)
O(11)–Mo(3)–O(10)	87.8(6)	O(9)–Mo(3)–O(7)	101.5(6)
O(11)–Mo(3)–O(7)	89.0(6)	O(10)–Mo(3)–O(7)	156.3(7)
O(9)–Mo(3)–O(8)	102.2(7)	O(11)–Mo(3)–O(8)	156.1(7)
O(10)–Mo(3)–O(8)	88.1(6)	O(7)–Mo(3)–O(8)	85.3(6)
O(9)–Mo(3)–O(20)#1	158.2(8)	O(11)–Mo(3)–O(20)#1	63.8(7)
O(10)–Mo(3)–O(20)#1	62.9(7)	O(7)–Mo(3)–O(20)#1	94.8(7)

Table S2. Selected bond distances (Å) and angles (°) of PI-HPM (cont.)

	Bond angle / degree		Bond angle / degree
O(8)–Mo(3)–O(20)#1	93.5(7)	O(9)–Mo(3)–O(17)#1	159.1(8)
O(11)–Mo(3)–O(17)#1	92.7(8)	O(10)–Mo(3)–O(17)#1	93.3(7)
O(7)–Mo(3)–O(17)#1	63.4(7)	O(8)–Mo(3)–O(17)#1	64.0(7)
O(20)#1–Mo(3)–O(17)#1	42.7(8)	O(12)–Mo(4)–O(13)	104.1(7)
O(12)–Mo(4)–O(3)#1	104.3(7)	O(13)–Mo(4)–O(3)#1	88.8(6)
O(12)–Mo(4)–O(10)	100.6(7)	O(13)–Mo(4)–O(10)	155.0(7)
O(3)#1–Mo(4)–O(10)	89.2(6)	O(12)–Mo(4)–O(14)	98.4(7)
O(13)–Mo(4)–O(14)	86.2(6)	O(3)#1–Mo(4)–O(14)	157.3(6)
O(10)–Mo(4)–O(14)	86.1(6)	O(12)–Mo(4)–O(20)#1	155.3(8)
O(13)–Mo(4)–O(20)#1	93.0(7)	O(3)#1–Mo(4)–O(20)#1	93.7(7)
O(10)–Mo(4)–O(20)#1	62.3(7)	O(14)–Mo(4)–O(20)#1	64.5(7)
O(12)–Mo(4)–O(5)#1	161.8(7)	O(13)–Mo(4)–O(5)#1	63.4(7)
O(3)#1–Mo(4)–O(5)#1	64.1(7)	O(10)–Mo(4)–O(5)#1	93.5(8)
O(14)–Mo(4)–O(5)#1	94.0(7)	O(20)#1–Mo(4)–O(5)#1	42.9(8)
O(32)–Mo(5)–O(8)#1	101.8(7)	O(32)–Mo(5)–O(19)	102.0(7)
O(8)#1–Mo(5)–O(19)	90.5(6)	O(32)–Mo(5)–O(16)	100.5(7)
O(8)#1–Mo(5)–O(16)	157.7(7)	O(19)–Mo(5)–O(16)	85.8(6)
O(32)–Mo(5)–O(15)	100.3(7)	O(8)#1–Mo(5)–O(15)	87.0(6)
O(19)–Mo(5)–O(15)	157.6(7)	O(16)–Mo(5)–O(15)	88.2(6)
O(32)–Mo(5)–O(18)	160.2(8)	O(8)#1–Mo(5)–O(18)	93.0(8)
O(19)–Mo(5)–O(18)	64.4(7)	O(16)–Mo(5)–O(18)	65.6(7)
O(15)–Mo(5)–O(18)	93.5(7)	O(32)–Mo(5)–O(17)	159.9(8)
O(8)#1–Mo(5)–O(17)	65.9(8)	O(19)–Mo(5)–O(17)	94.2(7)
O(16)–Mo(5)–O(17)	92.5(8)	O(15)–Mo(5)–O(17)	64.5(7)
O(18)–Mo(5)–O(17)	39.8(8)	O(21)–Mo(6)–O(16)	101.0(7)
O(21)–Mo(6)–O(14)	100.1(7)	O(14)–Mo(6)–O(16)	91.1(6)
O(21)–Mo(6)–O(1)	102.0(6)	O(14)–Mo(6)–O(1)	157.8(6)
O(16)–Mo(6)–O(1)	86.2(6)	O(21)–Mo(6)–O(11)	103.1(7)
O(14)–Mo(6)–O(11)	87.4(6)	O(16)–Mo(6)–O(11)	155.7(7)
O(1)–Mo(6)–O(11)	86.2(6)	O(21)–Mo(6)–O(20)#1	157.5(7)
O(14)–Mo(6)–O(20)#1	64.7(7)	O(16)–Mo(6)–O(20)#1	95.9(7)
O(1)–Mo(6)–O(20)#1	93.7(7)	O(11)–Mo(6)–O(20)#1	61.6(7)
O(25)–Mo(7)–O(26)	104.7(8)	O(25)–Mo(7)–O(24)	102.1(6)
O(26)–Mo(7)–O(24)	106.8(6)	O(25)–Mo(7)–O(22)	93.8(7)
O(26)–Mo(7)–O(22)	152.3(7)	O(24)–Mo(7)–O(22)	88.8(4)
O(25)–Mo(7)–N(1)	92.7(7)	O(26)–Mo(7)–N(1)	85.3(7)
O(24)–Mo(7)–N(1)	157.5(5)	O(22)–Mo(7)–N(1)	73.2(6)
O(25)–Mo(7)–O(27)	168.5(7)	O(26)–Mo(7)–O(27)	82.3(7)
O(24)–Mo(7)–O(27)	84.1(4)	O(22)–Mo(7)–O(27)	76.6(6)
N(1)–Mo(7)–O(27)	78.7(6)		

Symmetry transformations used to generate equivalent atoms (#1): –x + 1, –y, –z + 2.