<Supporting Information>

Assembly of a Phospho-molybdic Wells-Dawson-based Silver Coordination Polymer Derived from Keggin Polyoxoanion Cluster

Dong-Bin Dang, Bing An, Yan Bai* and Jing-Yang Niu*

Institute of Molecular and Crystal Engineering, School of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, P. R. China

Contents:

Table S1. Selected Bond Distances (Å) and Bond Angles (°) for **1**.

P(1)–O(55)	1.532(8)	Mo(11)–O(50)	1.924(8)
P(1)–O(57)	1.536(8)	Mo(11)–O(48)	2.189(8)
P(1)–O(56)	1.543(9)	Mo(11)–O(59)	2.300(8)
P(1)–O(58)	1.575(8)	Mo(12)–O(12)	1.696(9)
P(2)–O(60)	1.530(8)	Mo(12)–O(44)	1.780(8)
P(2)–O(61)	1.531(8)	Mo(12)–O(40)	1.911(8)
P(2)–O(59)	1.548(9)	Mo(12)–O(49)	1.917(8)
P(2)–O(62)	1.566(8)	Mo(12)–O(39)	2.083(8)
Mo(1)–O(1)	1.692(10)	Mo(12)–O(60)	2.336(8)
Mo(1)–O(19)	1.800(8)	Mo(13)–O(13)	1.689(8)
Mo(1)–O(22)	1.843(9)	Mo(13)–O(38)	1.759(8)
Mo(1)–O(20)	2.064(9)	Mo(13)–O(41)	1.877(8)
Mo(1)–O(21)	2.075(9)	Mo(13)–O(40)	1.954(8)
Mo(1)–O(58)	2.380(9)	Mo(13)–O(47)	2.126(8)
Mo(2)–O(2)	1.704(9)	Mo(13)–O(60)	2.332(8)
Mo(2)–O(25)	1.773(9)	Mo(14)–O(14)	1.691(9)
Mo(2)–O(23)	1.846(9)	Mo(14)–O(46)	1.798(8)
Mo(2)–O(22)	2.028(9)	Mo(14)–O(42)	1.890(8)
Mo(2)–O(24)	2.068(9)	Mo(14)–O(41)	1.913(8)
Mo(2)–O(58)	2.390(8)	Mo(14)–O(37)	2.091(8)
Mo(3)–O(3)	1.701(9)	Mo(14)–O(61)	2.356(8)
Mo(3)–O(26)	1.800(9)	Mo(15)–O(15)	1.707(9)
Mo(3)–O(21)	1.809(10)	Mo(15)–O(36)	1.769(8)
Mo(3)–O(23)	2.031(9)	Mo(15)–O(43)	1.879(8)
Mo(3)–O(27)	2.052(9)	Mo(15)–O(42)	1.922(8)
Mo(3)–O(58)	2.391(8)	Mo(15)–O(53)	2.163(8)
Mo(4)–O(4)	1.694(9)	Mo(15)–O(61)	2.359(8)
Mo(4)–O(20)	1.777(9)	Mo(16)–O(16)	1.704(8)
Mo(4)–O(29)	1.877(9)	Mo(16)–O(48)	1.752(8)
Mo(4)–O(28)	1.910(9)	Mo(16)–O(54)	1.828(8)
Mo(4)–O(34)	2.148(9)	Mo(16)–O(45)	2.039(9)
Mo(4)–O(55)	2.375(8)	Mo(16)–O(44)	2.074(8)
Mo(5)–O(5)	1.680(9)	Mo(16)–O(62)	2.365(8)
Mo(5)–O(35)	1.776(9)	Mo(17)–O(17)	1.674(9)
Mo(5)–O(30)	1.868(9)	Mo(17)–O(47)	1.775(8)
Mo(5)–O(29)	1.930(9)	Mo(17)–O(45)	1.839(8)
Mo(5)–O(26)	2.139(9)	Mo(17)–O(52)	2.033(8)
Mo(5)–O(55)	2.285(8)	Mo(17)–O(46)	2.056(8)
Mo(6)–O(6)	1.694(9)	Mo(17)–O(62)	2.395(8)
Mo(6)–O(27)	1.797(9)	Mo(18)–O(18)	1.681(9)
Mo(6)–O(31)	1.875(9)	Mo(18)–O(53)	1.760(8)

Mo(6)–O(30)	1.909(8)	Mo(18)–O(52)	1.828(8)
Mo(6)–O(36)	2.109(9)	Mo(18)–O(51)	2.036(9)
Mo(6)–O(56)	2.343(8)	Mo(18)–O(54)	2.063(9)
Mo(7)–O(7)	1.692(8)	Mo(18)–O(62)	2.408(8)
Mo(7)–O(37)	1.776(8)	Ag(1)–O(69)	2.250(15)
Mo(7)–O(32)	1.862(8)	Ag(1)–O(70)	2.271(14)
Mo(7)–O(31)	1.948(8)	Ag(1)–Ag(2)	3.286(3)
Mo(7)–O(25)	2.138(8)	Ag(1)–O(11A)	2.520(9)
Mo(7)–O(56)	2.301(8)	Ag(1)–O(16)	2.288(8)
Mo(8)–O(8)	1.677(8)	Ag(2)–N(1)	2.157(13)
Mo(8)–O(24)	1.787(8)	Ag(2)–N(4)	2.198(10)
Mo(8)–O(33)	1.869(9)	Ag(2)–O(63)	2.709(14)
Mo(8)–O(32)	1.925(9)	Ag(3)–O(71)	2.252(10)
Mo(8)–O(38)	2.126(8)	Ag(3)–N(3)	2.270(11)
Mo(8)–O(57)	2.349(8)	Ag(3)–O(40)	2.575(8)
Mo(9)–O(9)	1.689(9)	Ag(3)–O(65)	2.697(11)
Mo(9)–O(39)	1.780(8)	Ag(4)–N(5)	2.245(12)
Mo(9)–O(28)	1.871(9)	Ag(4)–O(72)	2.412(10)
Mo(9)–O(33)	1.952(8)	Ag(4)–O(6)	2.539(9)
Mo(9)–O(19)	2.115(8)	Ag(4)–O(7B)	2.367(8)
Mo(9)–O(57)	2.334(9)	Ag(5)–O(73)	2.24(3)
Mo(10)–O(10)	1.686(9)	Ag(5)–O(68)	2.629(10)
Mo(10)–O(51)	1.797(9)	Ag(5)–N(6)	2.339(11)
Mo(10)–O(50)	1.884(8)	Ag(5)–O(15C)	2.437(9)
Mo(10)–O(43)	1.911(8)	Ag(5)–O(72C)	2.350(10)
Mo(10)–O(35)	2.105(9)	Ag(6)–O(74)	2.16(3)
Mo(10)–O(59)	2.364(8)	Ag(6)–O(75)	2.32(2)
Mo(11)–O(11)	1.683(9)	Ag(6)–O(5)	2.523(10)
Mo(11)–O(34)	1.749(9)	Ag(6)–O(4W)	2.61(6)
Mo(11)–O(49)	1.879(8)		
O(55)–P(1)–O(57)	111.4(5)	O(71)–Ag(3)–N(3)	137.3(4)
O(55)–P(1)–O(56)	111.2(5)	O(71)–Ag(3)–O(40)	110.5(3)
O(57)–P(1)–O(56)	110.4(5)	N(3)–Ag(3)–O(40)	97.6(3)
O(55)–P(1)–O(58)	108.0(5)	O(71)–Ag(3)–O(65)	78.9(4)
O(57)–P(1)–O(58)	108.1(5)	N(3)–Ag(3)–O(65)	66.8(4)
O(56)–P(1)–O(58)	107.5(5)	O(40)–Ag(3)–O(65)	95.0(3)
O(60)–P(2)–O(61)	111.4(4)	N(5)–Ag(4)–O(7B)	139.9(4)
O(60)–P(2)–O(59)	110.7(5)	N(5)–Ag(4)–O(72)	131.8(4)
O(61)–P(2)–O(59)	109.9(5)	O(7B)–Ag(4)–O(72)	87.2(3)
O(60)–P(2)–O(62)	107.3(4)	N(5)–Ag(4)–O(6)	106.5(4)
O(61)–P(2)–O(62)	109.3(5)	O(7B)–Ag(4)–O(6)	88.7(3)
O(59)–P(2)–O(62)	108.2(4)	O(72)–Ag(4)–O(6)	77.3(3)
O(69)–Ag(1)–O(70)	102.0(6)	O(73)–Ag(5)–N(6)	101.2(10)
O(69)–Ag(1)–O(16)	128.3(4)	O(73)–Ag(5)–O(72C)	128.9(10)

O(70)–Ag(1)–O(16)	116.7(4)	N(6)–Ag(5)–O(72C)	126.9(4)
O(69)–Ag(1)–O(11A)	92.2(4)	O(73)–Ag(5)–O(15C)	84.0(10)
O(70)–Ag(1)–O(11A)	83.7(4)	N(6)–Ag(5)–O(15C)	113.4(4)
O(16)–Ag(1)–O(11A)	123.4(3)	O(72C)–Ag(5)–O(15C)	90.7(3)
O(69)–Ag(1)–Ag(2)	74.6(4)	O(73)–Ag(5)–O(68)	116.9(10)
O(70)–Ag(1)–Ag(2)	112.9(4)	N(6)–Ag(5)–O(68)	67.2(3)
O(16)–Ag(1)–Ag(2)	59.9(2)	O(72C)–Ag(5)–O(68)	74.4(4)
O(11A)–Ag(1)–Ag(2)	160.4(2)	O(15C)–Ag(5)–O(68)	158.9(4)
N(1)–Ag(2)–N(4)	155.9(5)	O(74)–Ag(6)–O(75)	146.1(10)
N(1)–Ag(2)–Ag(1)	85.0(4)	O(74)–Ag(6)–O(5)	102.0(8)
N(4)–Ag(2)–Ag(1)	118.9(3)	O(75)–Ag(6)–O(5)	108.7(6)
N(1)–Ag(2)–O(63)	69.3(5)	O(74)–Ag(6)–O(4W)	100.1(17)
N(4)–Ag(2)–O(63)	104.3(4)	O(75)–Ag(6)–O(4W)	94.2(16)
O(63)–Ag(2)–Ag(1)	106.7(2)	O(5)–Ag(6)–O(4W)	89.5(14)

Symmetry transformations used to generate equivalent atoms: A 2 – *x*, – *y*, 1 – *z*; B 1 – *x*, – *y*, 2 – *z*; C 2 – *x*, – *y*, 2 – *z*.

Table S2. Hydrogen Bonding Interactions (A˚ and °) of **1**.

D–H···A	D–H	H···A	D···A	∠DHA	Symmetry Codes
C(1)–H(1A)···O(33)	0.93	2.36	3.24(2)	159	1 – *x*, – *y*, 1 – *z*
C(3)–H(3A)···O(52)	0.93	2.55	3.41(2)	154	2 – *x*, – 1 – *y*, 1 – *z*
C(5)–H(5A)···O(17)	0.93	2.55	3.34(2)	143	2 – *x*, – 1 – *y*, 1 – *z*
C(8)–H(8A)···O(54)	0.93	2.40	3.30(2)	161	
C(9)–H(9A)···O(1)	0.93	2.50	3.26(2)	139	1 + *x*, – 1 + *y*, *z*
C(10)–H(10A)···O(9)	0.93	2.43	3.23(2)	144	1 + *x*, – 1 + *y*, *z*
C(12)–H(12A)···O(4)	0.93	2.59	3.46(2)	156	*x*, – 1 + *y*, *z*
C(18)–H(18A)···O(40)	0.93	2.52	3.421(19)	162	1 – *x*, – *y*, 1 – *z*
C(20)–H(20A)···O(69)	0.93	2.48	3.01(2)	116	
C(20)–H(20A)···O(50)	0.93	2.59	3.40(2)	145	2 – *x*, – *y*, 1 – *z*
C(21)–H(21A)···O(41)	0.93	2.57	3.47(2)	162	1 – *x*, – *y*, 2 – *z*
C(25)–H(25A)···O(15)	0.93	2.58	3.49(2)	165	2 – *x*, – *y*, 2 – *z*
C(26)–H(26A)···O(6)	0.93	2.54	3.43(2)	159	
C(29)–H(29A)···O(8)	0.93	2.50	3.20(2)	132	1 + *x*, *y*, *z*
C(29)–H(29A)···O(10)	0.93	2.32	3.01(2)	130	
C(32)–H(32B)···O(29)	0.97	2.45	3.09(3)	124	2 – *x*, – *y*, 1 – *z*
C(33)–H(33A)···O(69)	0.96	2.33	2.74(3)	105	
C(33)–H(33C)···O(5)	0.96	2.38	3.32(3)	165	2 – *x*, – *y*, 1 – *z*
C(34)–H(34A)···O(11)	0.93	2.46	3.13(3)	129	2 – *x*, – *y*, 1 – *z*
C(36)–H(36A)···O(70)	0.96	2.27	2.72(3)	107	
C(37)–H(37A)···O(12)	0.93	2.59	3.24(2)	127	1 – *x*, – *y*, 1 – *z*
C(38)–H(38A)···O(71)	0.96	2.36	2.77(3)	105	
C(38)–H(38B)···O(54)	0.96	2.57	3.27(3)	131	– 1 + *x*, *y*, *z*
C(40)–H(40A)···O(7)	0.93	2.55	3.161(16)	124	1 – *x*, – *y*, 2 – *z*
C(41)–H(41A)···O(72)	0.96	2.44	2.84(2)	104	
C(49)–H(49A)···O(21)	0.93	2.48	3.40(3)	171	
C(50)–H(50A)···O(75)	0.96	2.45	2.82(4)	102	
C(51)–H(51A)···O(1)	0.96	2.58	3.41(3)	145	

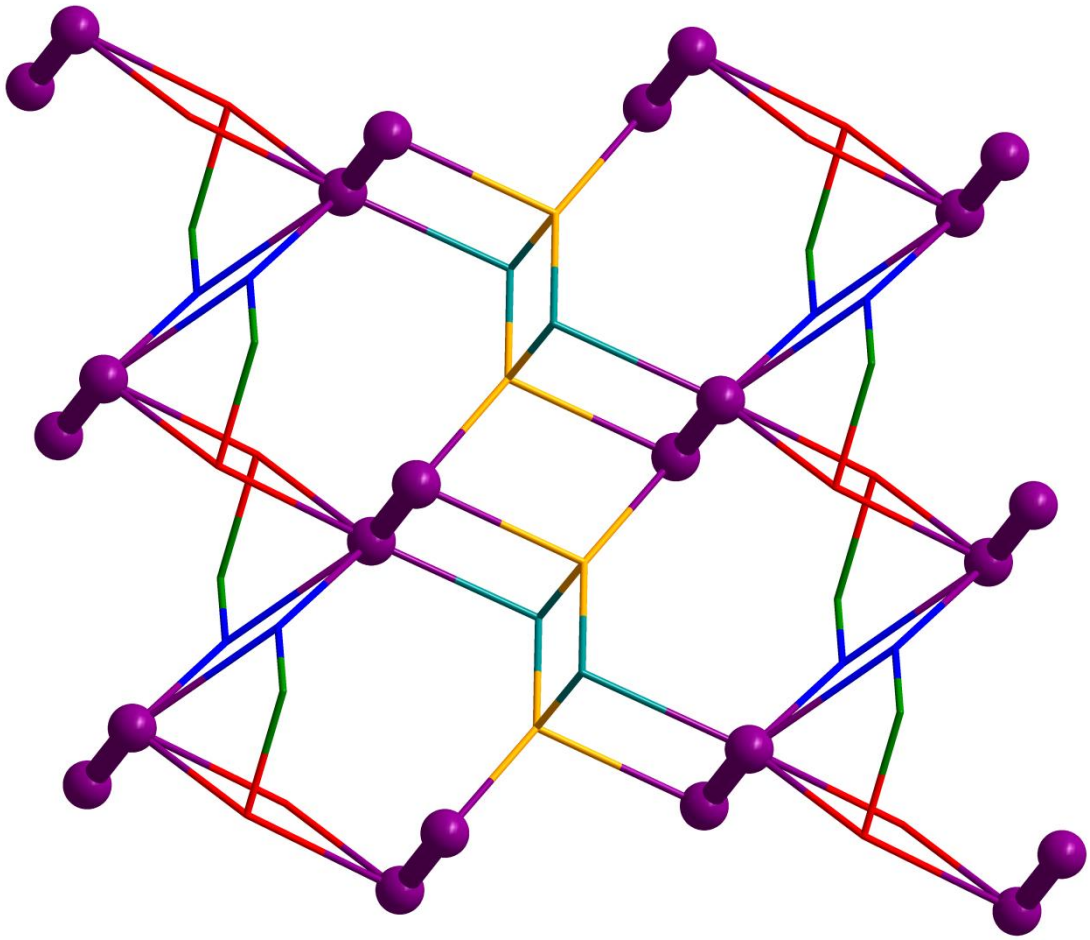


Figure S1. The 2D topologic structure with dumbbells diagram indicating $[P_2Mo_{18}O_{62}]^{6-}$.

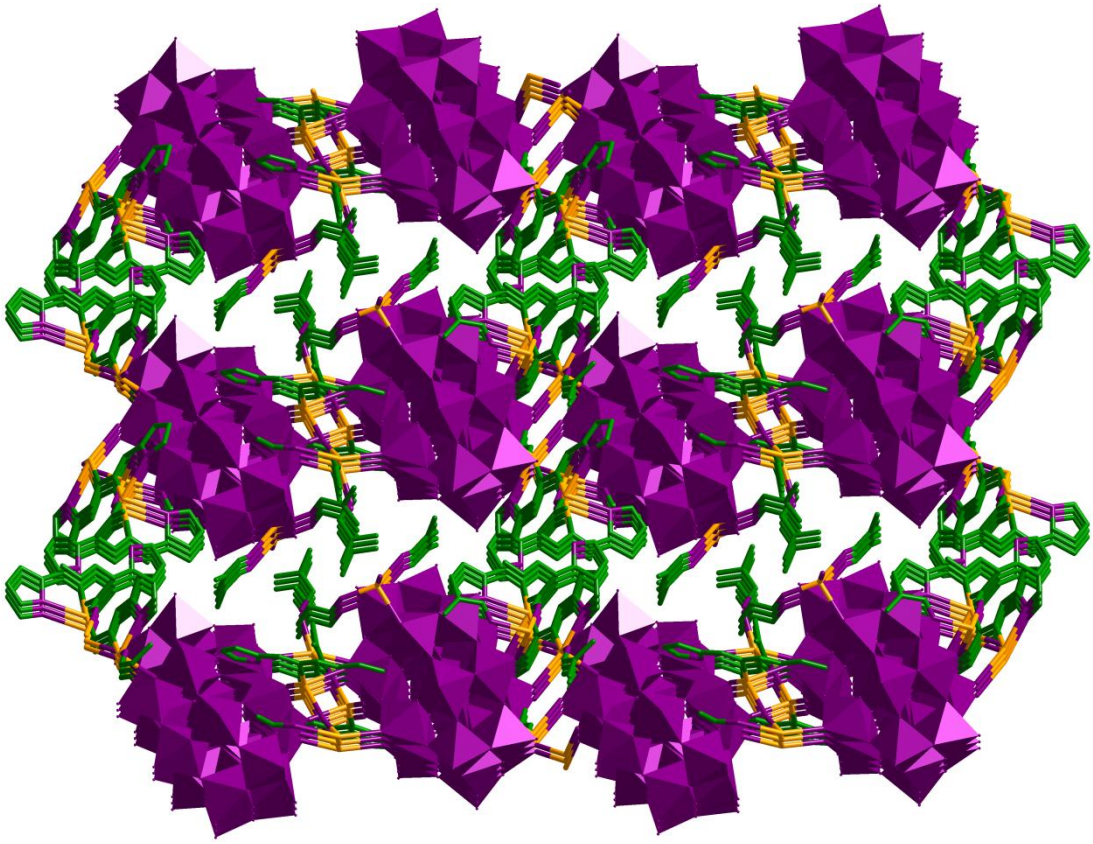


Figure S2. View of 3D structure of **1**.

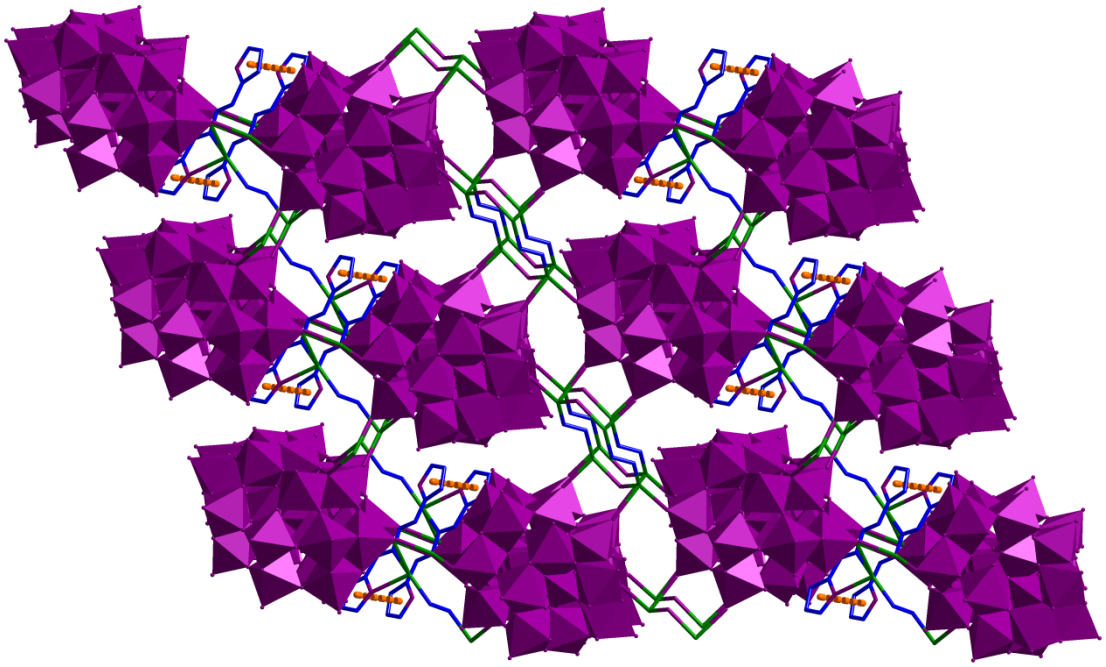


Figure S3. The 3D supramolecular framework of **1** showing π···π interactions in dashed lines.

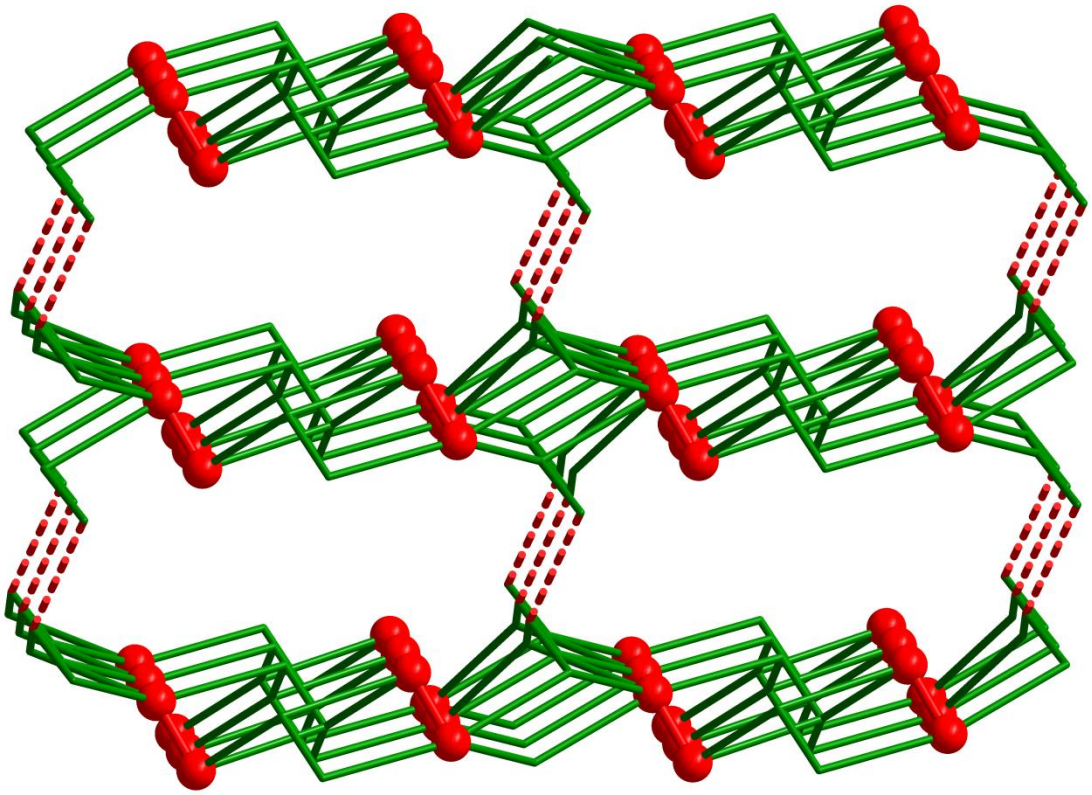


Figure S4. The 3D topologic structure of **1** showing π···π interactions in dashed lines.

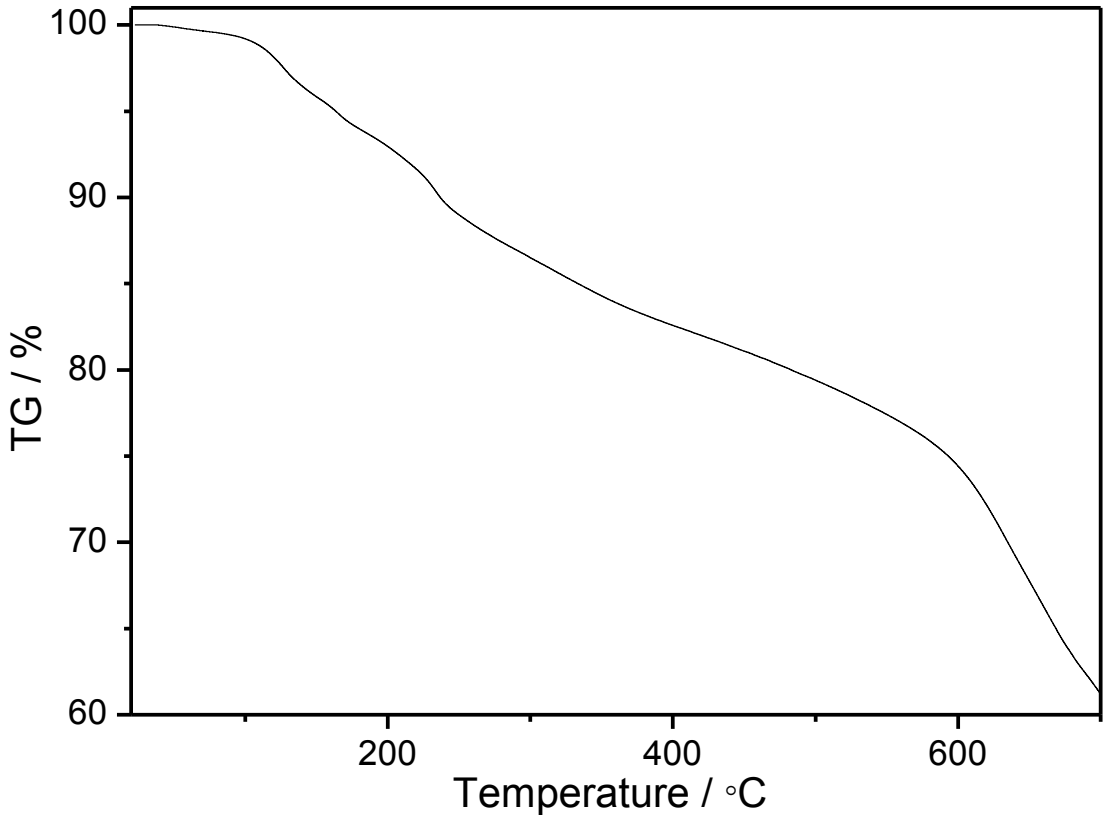


Figure S5. TGA curve for **1**.

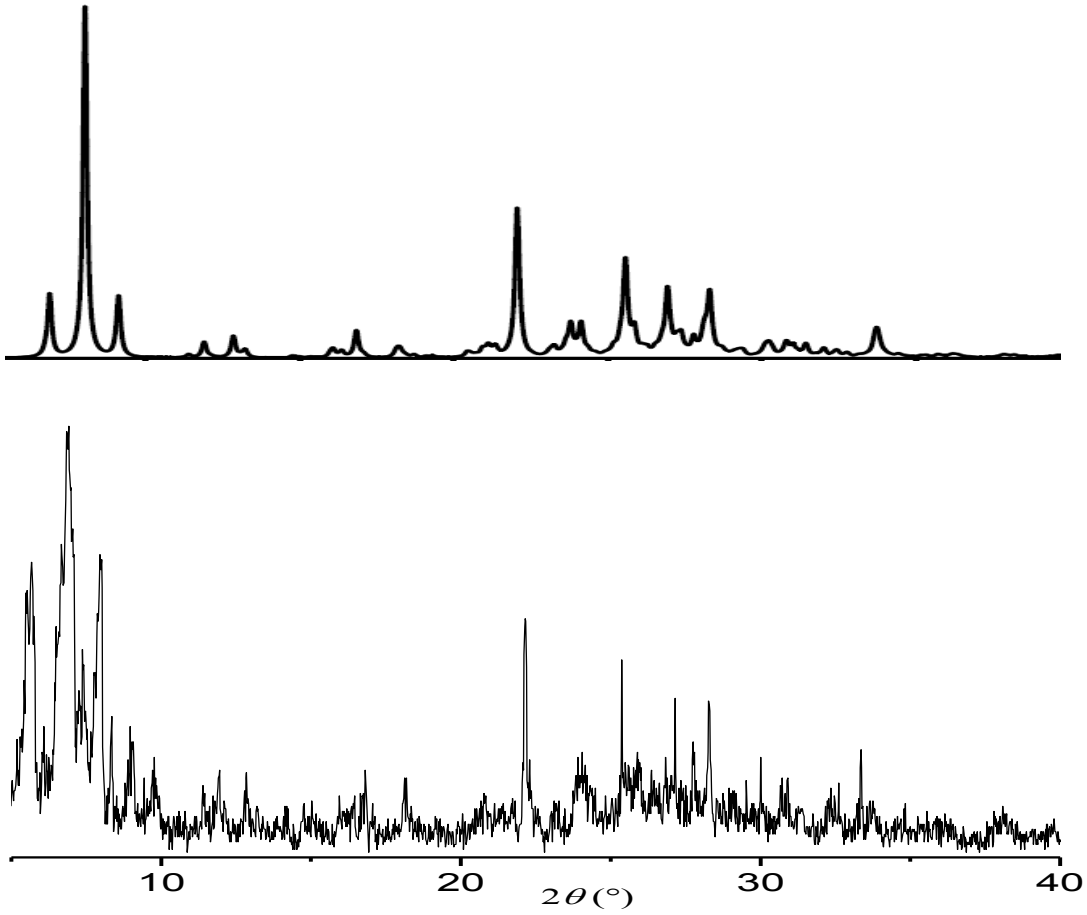
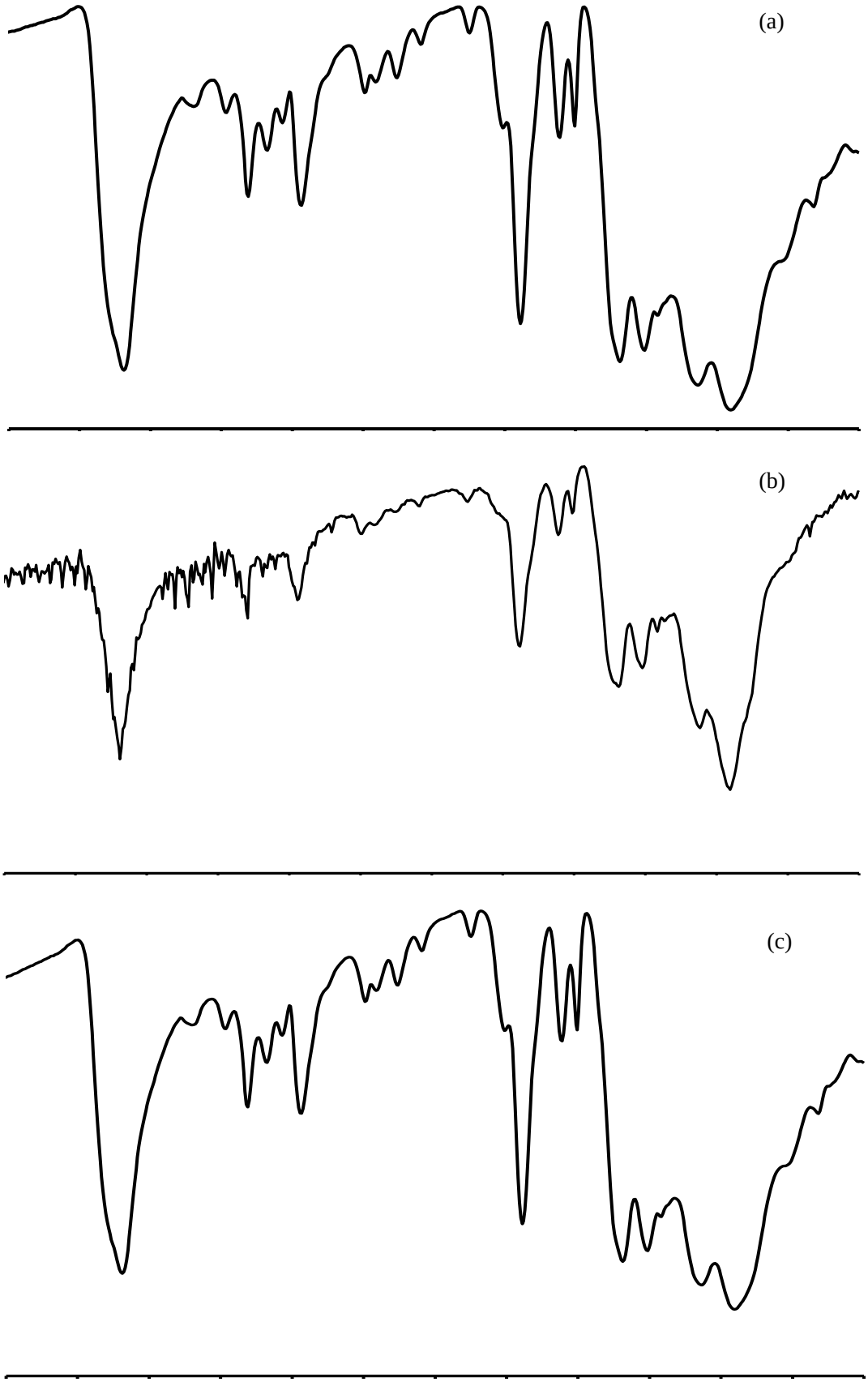


Figure S6. The pattern calculated from the single-crystal data for polymer **1** (top) and the power X-ray diffraction pattern of the samples at 296 K (bottom).



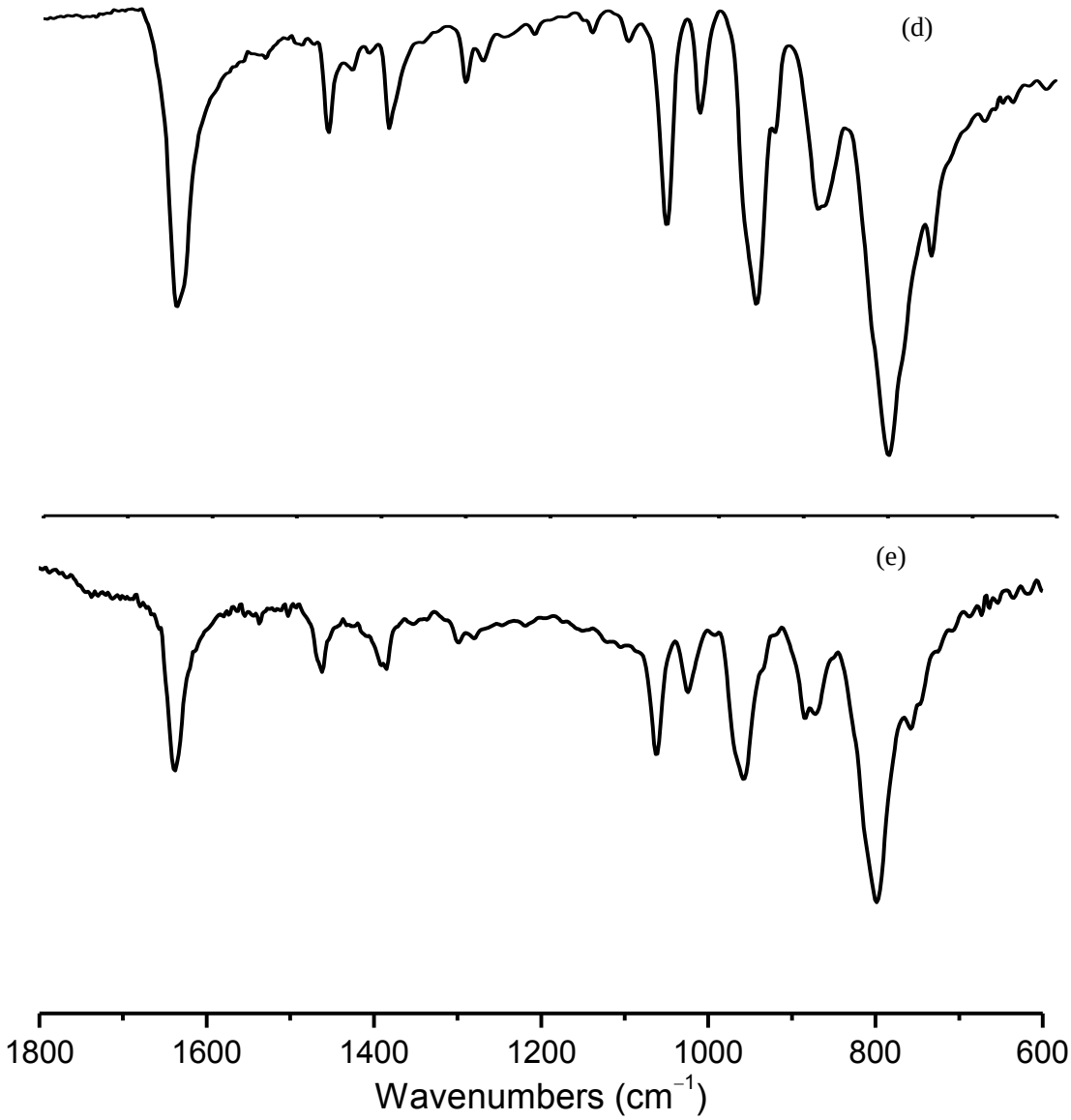


Figure S7. The IR spectra of (a)–(e) represent the solid products obtained under different pH values in DMF/CH_3OH solution system, 2.8, 3.4, 3.8, 1.8 and 2.2, respectively.

Products under 2.8 (*a*) is the crystals of polymer **1** (Dawson-based compounds), besides, the bands of (*b*) and (*c*) exhibit the characteristic bands of Dawson anion $[P_2Mo_{18}O_{62}]^{6-}$, which agrees well with Dawson-based compounds.

The IR spectra of (*d*) and (*e*) show the characteristic bands of Keggin anion $[PMo_{12}O_{40}]^{3-}$, which can be assigned to Keggin-based compounds.

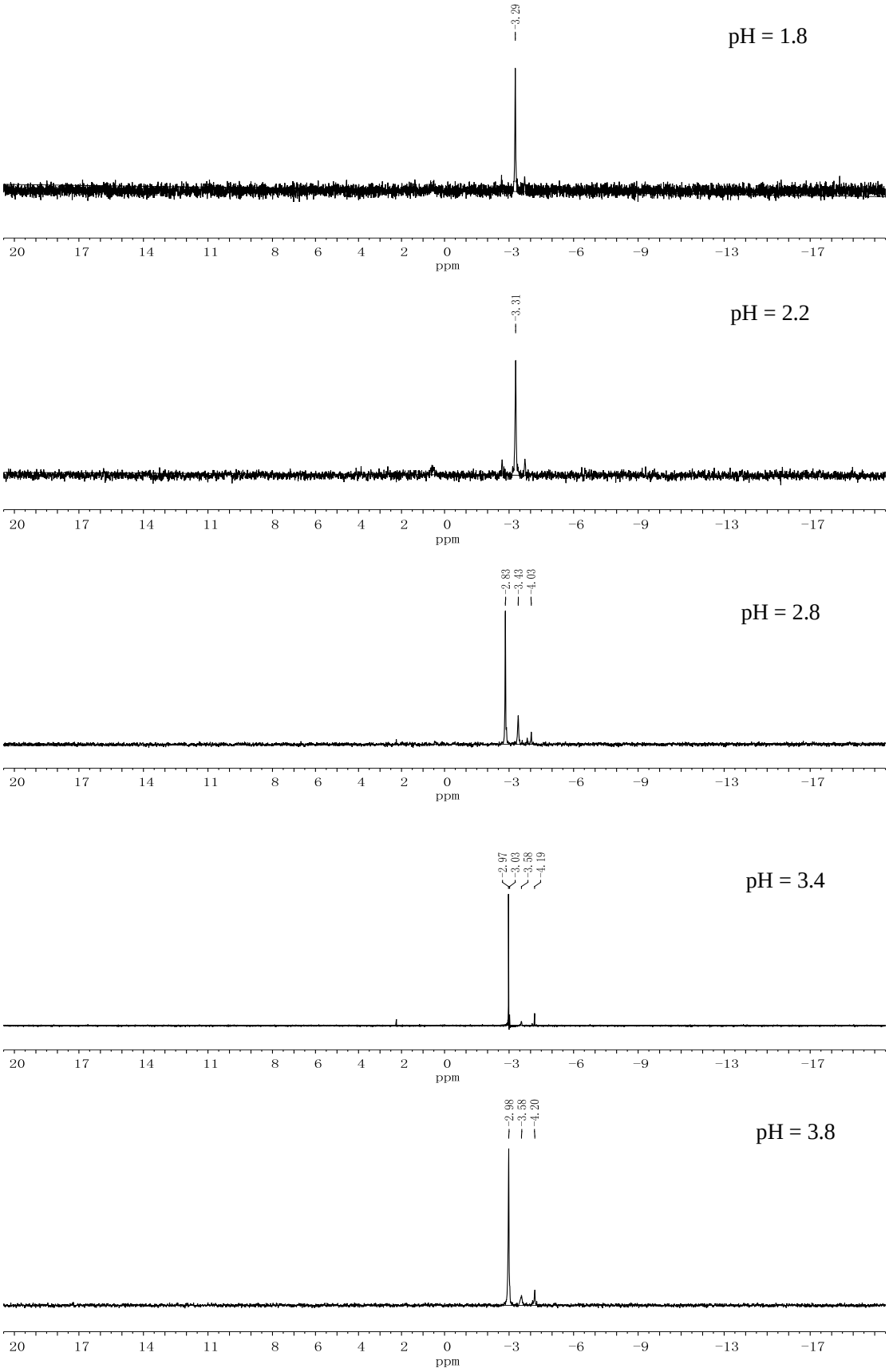


Figure S8. ^{31}P NMR spectra for $H_3PMo_{12}O_{40}$ alone in DMF solution at different pH values.

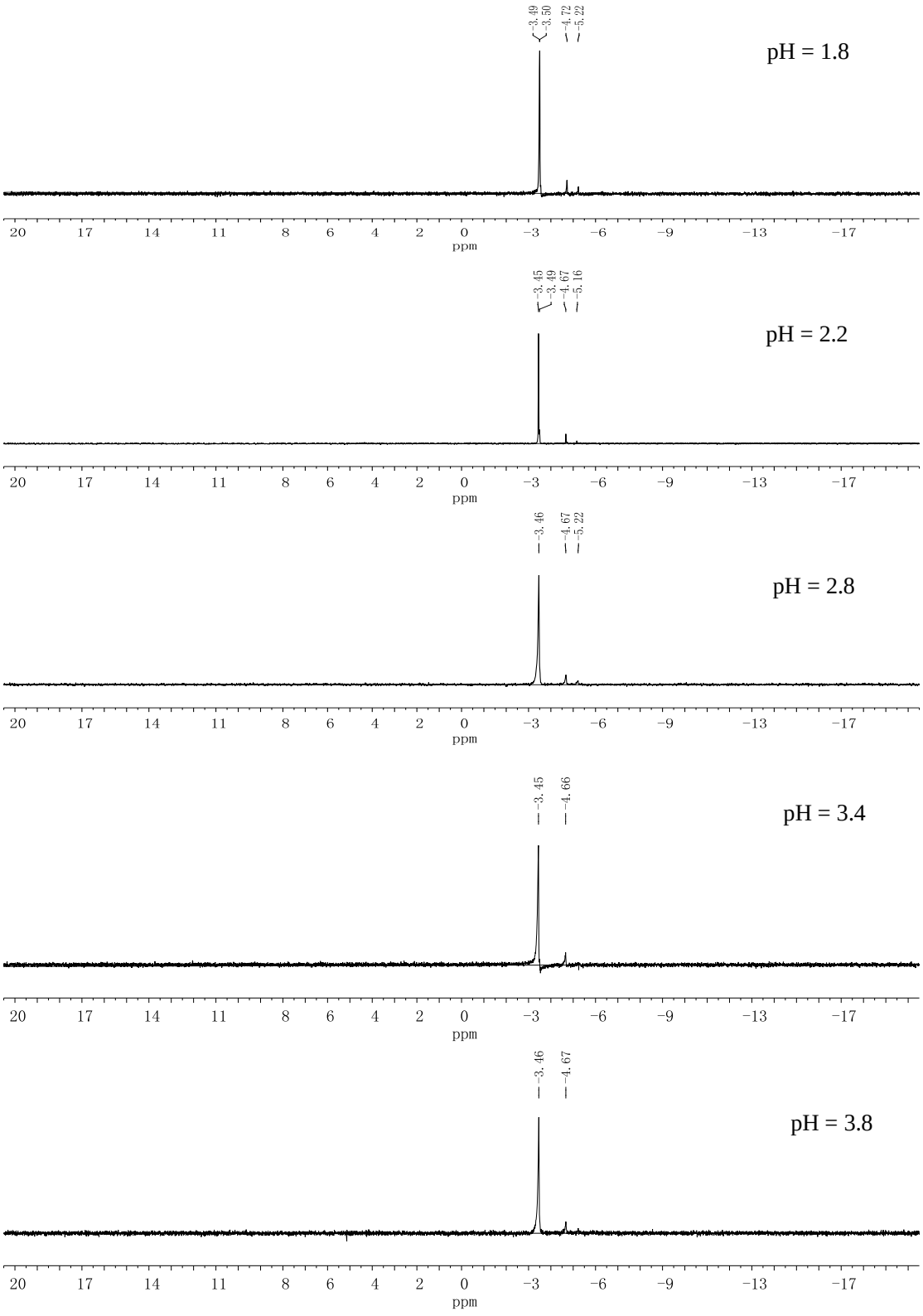
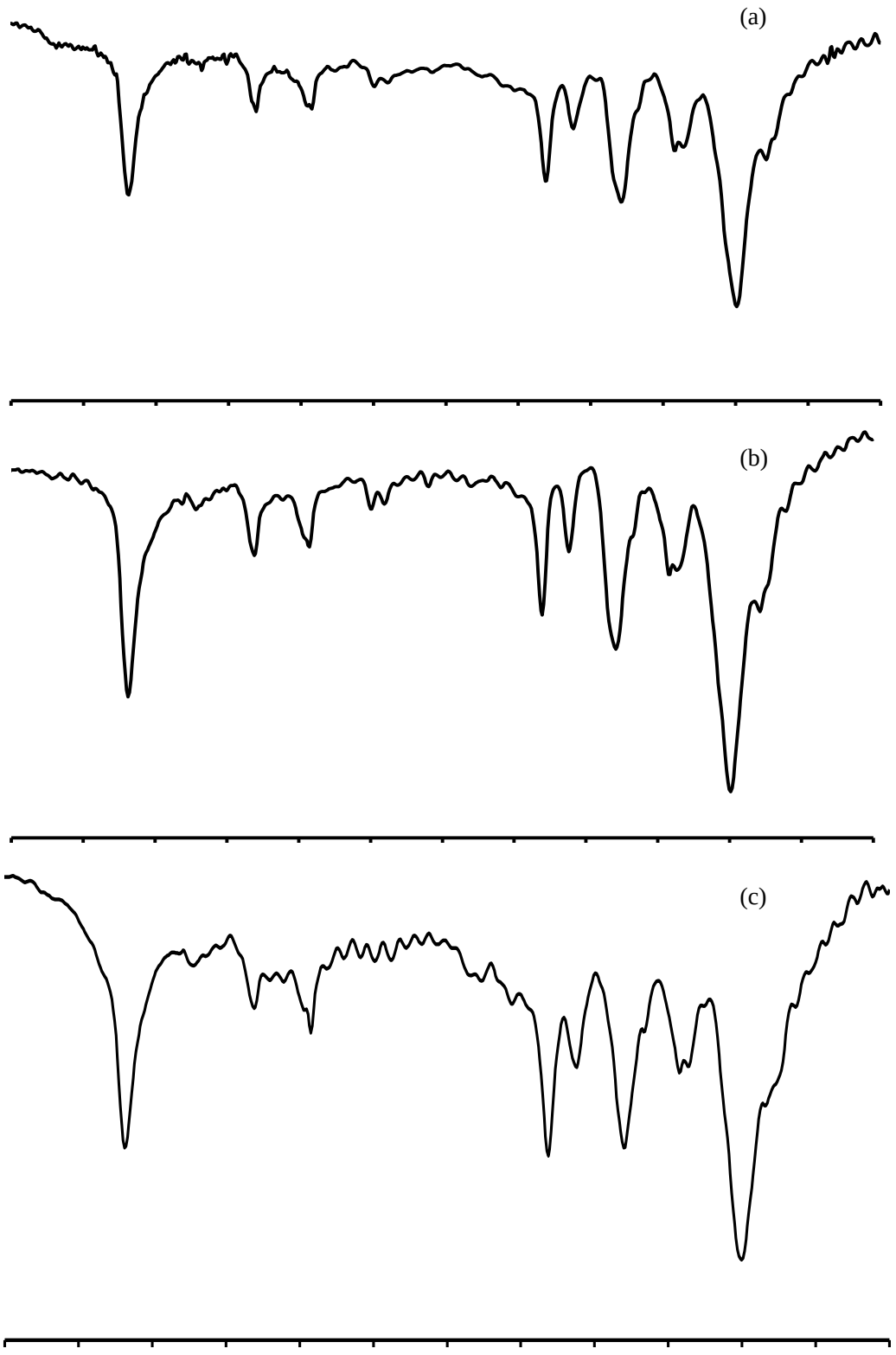


Figure S9. ^{31}P NMR spectra for $H_6P_2Mo_{18}O_{62}$ alone in DMF solution at different pH values.



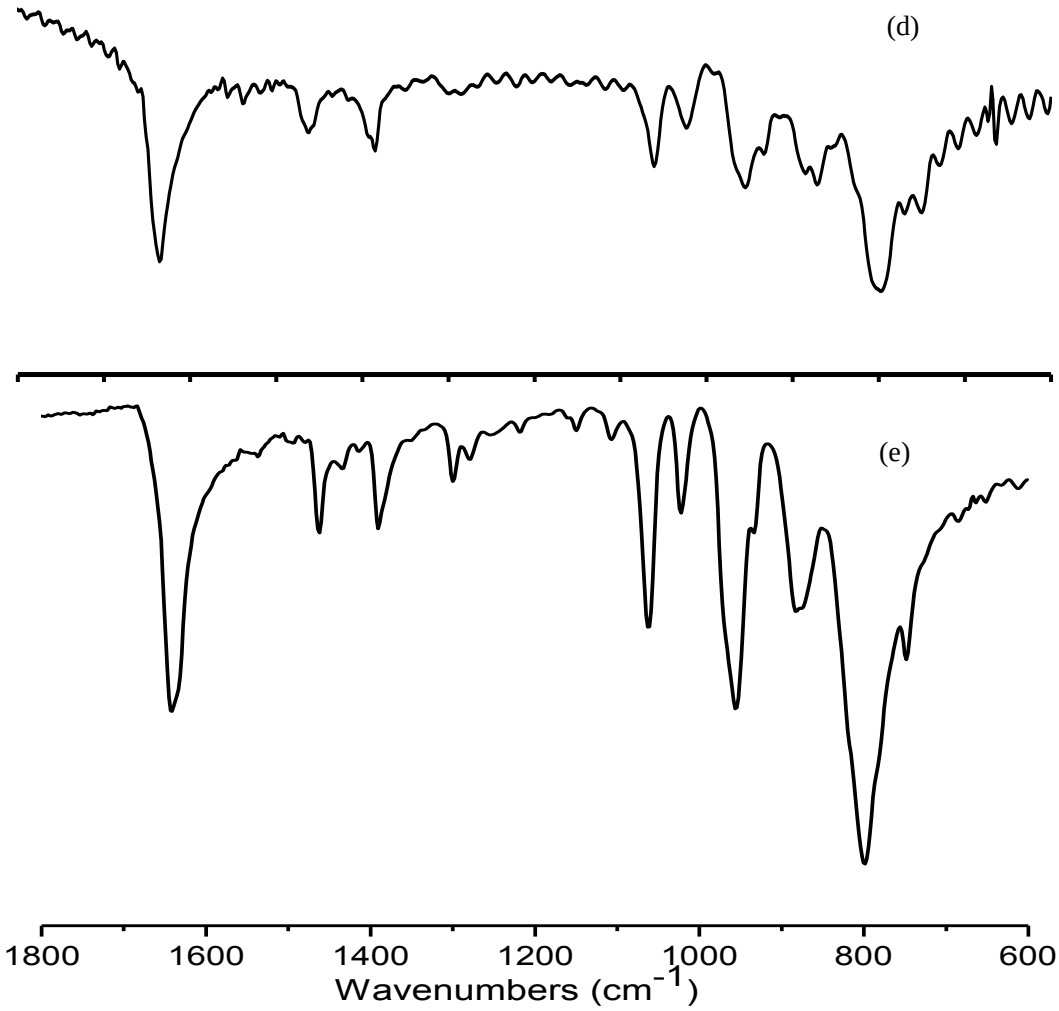


Figure S10. The IR spectra of (a)–(e) represent the solid products obtained under different pH values in H_2O/CH_3OH solution system, 1.8, 2.2, 2.8, 3.4 and 3.8, respectively. All the IR spectra show the characteristic bands of Keggin anion $[PMo_{12}O_{40}]^{3-}$, which can be assigned to Keggin-based compounds.