Supporting Information

Three novel polyoxoanion-supported compounds: confinement of polyoxoanions in Ni-containing rigid concave surfaces with enhanced NLO properties

Yayu Dong, [a] Xiao Xu, [a] Guangpeng Zhou*,[b] Hao Miao, [a] GongHao Hu, [a] and Yan Xu *[a,c]

[a]College of Chemistry and Chemical Engineering, State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing Tech University, Nanjing 210009, PR China. E-mail: yanxu@njtech.edu.cn
[b] College of Chemistry and Chemical Engineering, Chongqing University of Technology, Chongqing 400054, P. R. China. E-mail: gpzhou@cqut.edu.cn
[c]Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, PR China

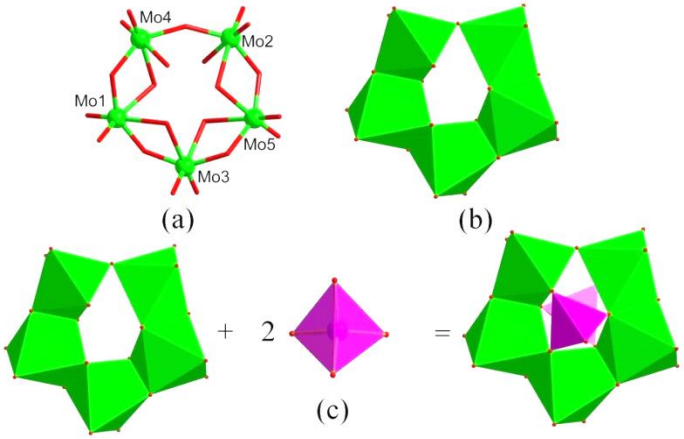

Figure S1. (a) and (b) The pentagon formed by five MoO_6 through sharing angles and edges; (c) The schematic diagram of the formation of $[H_2P_2Mo_5O_{23}]^{4-}$.

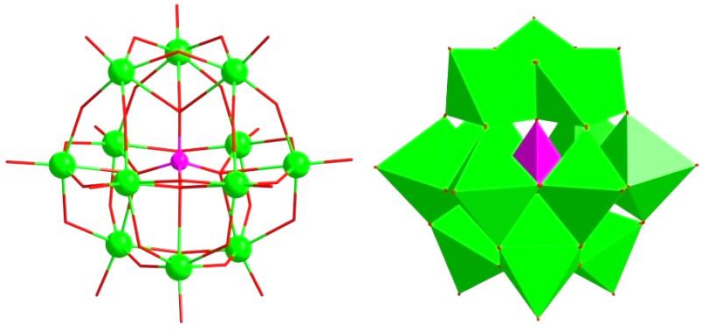

Figure S2. The $[PMo_{11}{}^{VI}Mo^{V}O_{40}]^{4-}$ cluster in compound **2** Color code: bright green; Mo, pink; P.

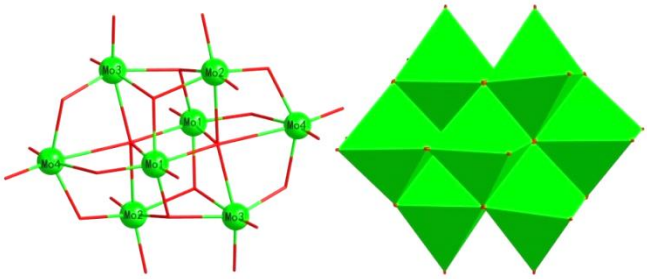

Figure S3. The $[Mo_8O_{26}]^{4-}$ cluster in compound **3**.

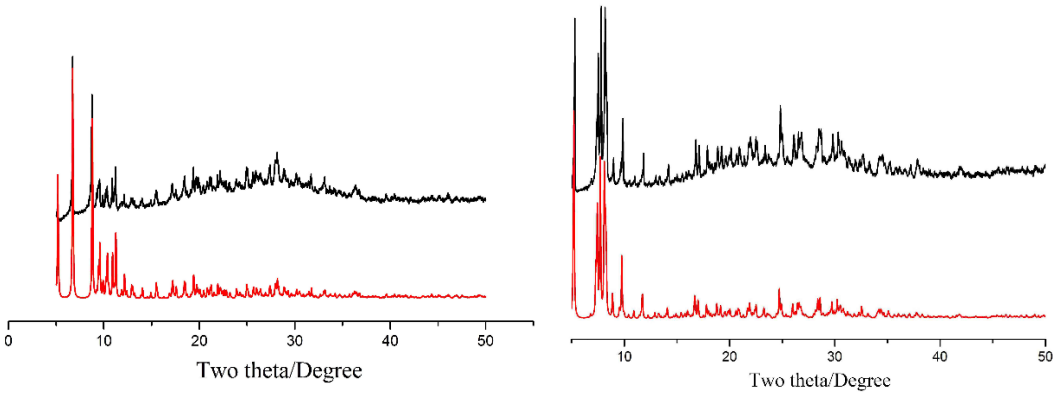

Figure S4. The experimental and simulated XRD patterns for **1** (left) and **2** (right).

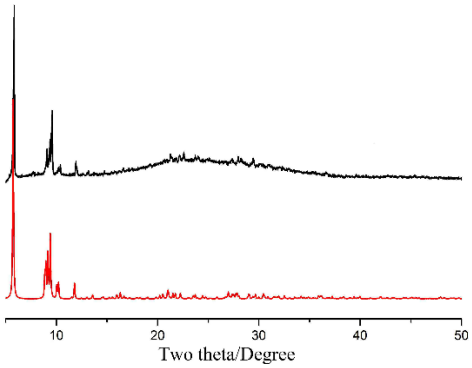

Figure S5. The experimental and simulated XRD patterns for compound **3**.

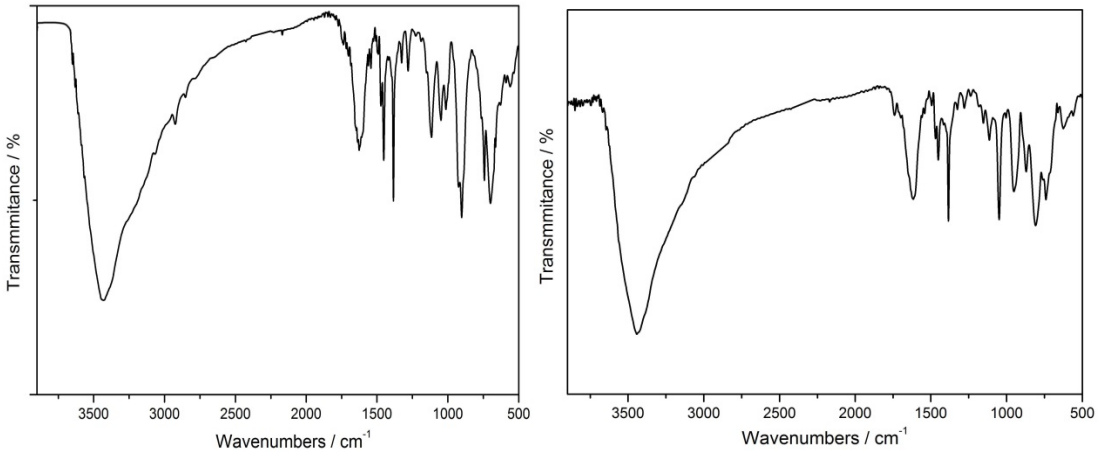

Figure S6. The IR of compound **1** (left) and **2** (right).

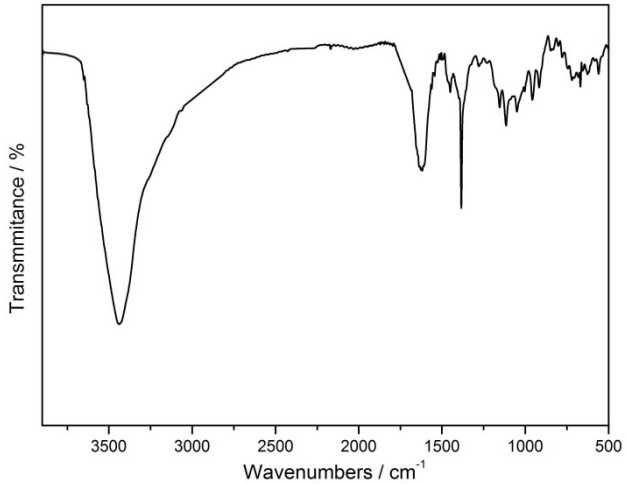

Figure S7. The IR of compound **3**.

Table S1. Selected bond lengths for compound **1** (Å).

Mo(1)-O(16)	1.691(3)	P(1)-O(8)	1.531(3)	Ni(1)-O(1W)	2.137(3)
Mo(1)-O(14)	1.712(3)	P(1)-O(21)	1.532(3)	Ni(1)-N(14)	2.201(4)
Mo(1)-O(13)	1.933(3)	P(1)-O(17)	1.568(3)	Ni(2)-N(6)	2.012(4)
Mo(1)-O(5)	1.935(3)	P(2)-O(9)	1.505(4)	Ni(2)-O(10)	2.054(3)
Mo(1)-O(8)	2.228(3)	P(2)-O(18)	1.519(3)	Ni(2)-N(2)	2.064(5)
Mo(1)-O(18)	2.387(3)	P(2)-O(6)	1.535(4)	Ni(2)-N(4)	2.067(5)
Mo(2)-O(3)	1.703(4)	P(2)-O(20)	1.575(4)	Ni(2)-O(2W)	2.152(4)
Mo(2)-O(22)	1.700(4)	Mo(5)-O(23)	1.694(3)	Ni(2)-N(7)	2.190(4)
Mo(2)-O(2)	1.906(3)	Mo(5)-O(10)	1.732(3)	P(1)-O(12)	1.513(3)
Mo(2)-O(15)	1.927(3)	Mo(5)-O(7)	1.886(3)	Ni(1)-N(9)	2.038(4)
Mo(2)-O(12)	2.315(3)	Mo(5)-O(15)	1.935(3)	Ni(1)-N(13)	2.045(4)
Mo(2)-O(6)	2.389(3)	Mo(5)-O(6)	2.202(3)	Ni(1)-N(11)	2.057(4)
Mo(3)-O(11)	1.696(4)	Mo(5)-O(21)	2.403(3)	Ni(1)-O(4)	2.060(3)
Mo(3)-O(4)	1.733(3)	Mo(4)-O(2)	1.926(3)	Mo(4)-O(19)	1.703(4)
Mo(3)-O(5)	1.896(3)	Mo(4)-O(9)	2.288(3)	Mo(4)-O(1)	1.711(4)
Mo(3)-O(7)	1.929(3)	Mo(4)-O(8)	2.387(3)	Mo(4)-O(13)	1.896(3)

Mo(3)-O(11)	1.696(4)	Mo(3)-O(18)	2.360(3)	Mo(3)-O(21)	2.297(3)

Table S2. Selected bond lengths for compound **2** (Å).

Mo(1)-O(7)	1.701(5)	Mo(10)-O(58)	1.678(7)	Mo(19)-O(46)	1.811(7)
Mo(1)-O(50)	1.804(6)	Mo(10)-O(62)	1.830(5)	Mo(19)-O(33)	1.923(5)
Mo(1)-O(59)	1.904(5)	Mo(10)-O(20)	1.885(5)	Mo(19)-O(12)	1.952(5)
Mo(1)-O(39)	1.914(5)	Mo(10)-O(42)	1.990(6)	Mo(19)-O(62)	1.960(5)
Mo(1)-O(29)	2.010(6)	Mo(10)-O(27)	1.991(5)	Mo(19)-O(69)	1.987(6)
Mo(1)-O(25)	2.438(5)	Mo(10)-O(44)	2.441(5)	Mo(19)-O(44)	2.346(5)
Mo(2)-O(23)	1.695(5)	Mo(11)-O(8)	1.675(6)	Mo(20)-O(65)	1.689(5)
Mo(2)-O(80)	1.815(5)	Mo(11)-O(13)	1.860(5)	Mo(20)-O(42)	1.828(7)
Mo(2)-O(69)	1.827(5)	Mo(11)-O(55)	1.890(5)	Mo(20)-O(60)	1.923(6)
Mo(2)-O(20)	2.000(5)	Mo(11)-O(5)	1.953(5)	Mo(20)-O(41)	1.929(6)
Mo(2)-O(4)	2.006(5)	Mo(11)-O(34)	1.968(5)	Mo(20)-O(66)	1.970(5)
Mo(2)-O(44)	2.427(5)	Mo(11)-O(24)	2.438(5)	Mo(20)-O(10)	2.419(5)
Mo(3)-O(1)	1.709(5)	Mo(12)-O(38)	1.687(6)	Mo(21)-O(40)	1.726(7)
Mo(3)-O(76)	1.855(5)	Mo(12)-O(29)	1.861(5)	Mo(21)-O(35)	1.878(7)
Mo(3)-O(15)	1.893(6)	Mo(12)-O(19)	1.896(5)	Mo(21)-O(15)	1.938(5)
Mo(3)-O(57)	1.905(6)	Mo(12)-O(70)	1.923(7)	Mo(21)-O(47)	1.956(7)
Mo(3)-O(67)	1.968(5)	Mo(12)-O(43)	1.940(5)	Mo(21)-O(54)	1.961(5)
Mo(3)-O(53)	2.462(5)	Mo(12)-O(25)	2.461(6)	Mo(21)-O(53)	2.459(6)
Mo(4)-O(36)	1.701(7)	Mo(13)-O(28)	1.700(7)	Mo(22)-O(74)	1.699(7)
Mo(4)-O(57)	1.892(6)	Mo(13)-O(63)	1.895(7)	Mo(22)-O(33)	1.870(5)
Mo(4)-O(31)	1.902(5)	Mo(13)-O(70)	1.906(7)	Mo(22)-O(6)	1.917(5)
Mo(4)-O(59)	1.915(5)	Mo(13)-O(78)	1.913(5)	Mo(22)-O(60)	1.947(5)
Mo(4)-O(19)	1.935(6)	Mo(13)-O(1A)	1.947(7)	Mo(22)-O(75)	1.969(5)
Mo(4)-O(25)	2.451(5)	Mo(13)-O(49)	2.402(5)	Mo(22)-O(10)	2.494(6)
Mo(5)-O(11)	1.683(5)	Mo(14)-O(86)	1.700(7)	Mo(23)-O(79)	1.809(7)
Mo(5)-O(34)	1.863(5)	Mo(14)-O(47)	1.843(7)	Mo(23)-O(45)	1.932(5)
Mo(5)-O(14)	1.865(6)	Mo(14)-O(64)	1.927(7)	Mo(23)-O(55)	1.936(5)
Mo(5)-O(18)	1.947(5)	Mo(14)-O(68)	1.934(5)	Mo(23)-O(80)	1.971(5)
Mo(5)-O(71)	1.989(6)	Mo(14)-O(1A)	2.040(7)	Mo(23)-O(17)	1.998(5)
Mo(5)-O(21)	2.395(5)	Mo(14)-O(49)	2.410(7)	Mo(23)-O(24)	2.373(5)
Mo(6)-O(9)	1.703(6)	Mo(15)-O(51)	1.667(7)	Mo(24)-O(61)	1.810(7)
Mo(6)-O(12)	1.827(5)	Mo(15)-O(43)	1.871(5)	Mo(24)-O(35)	1.932(6)
Mo(6)-O(45)	1.893(6)	Mo(15)-O(77)	1.879(7)	Mo(24)-O(26)	1.933(5)
Mo(6)-O(6)	1.934(5)	Mo(15)-O(78)	1.918(5)	Mo(24)-O(76)	1.972(5)
Mo(6)-O(13)	1.968(5)	Mo(15)-O(87)	2.008(7)	Mo(24)-O(50)	1.995(6)
Mo(6)-O(24)	2.429(5)	Mo(15)-O(32)	2.467(5)	Mo(24)-O(53)	2.390(5)
Mo(7)-O(22)	1.688(7)	Mo(16)-O(37)	1.647(7)	P(1)-O(10)	1.533(6)
Mo(7)-O(5)	1.900(5)	Mo(16)-O(26)	1.846(5)	P(1)-O(21)	1.533(6)
Mo(7)-O(71)	1.909(6)	Mo(16)-O(68)	1.920(7)	P(1)-O(44)	1.535(5)
Mo(7)-O(75)	1.915(5)	Mo(16)-O(39)	1.932(6)	P(1)-O(24)	1.535(5)
Mo(7)-O(66)	1.922(5)	Mo(16)-O(63)	1.997(7)	P(2)-O(25)	1.512(6)
Mo(7)-O(10)	2.442(5)	Mo(16)-O(49)	2.463(5)	P(2)-O(53)	1.511(6)

Mo(8)-O(3)	1.709(6)	Mo(17)-O(2)	1.704(7)	P(2)-O(32)	1.512(5)
Mo(8)-O(17)	1.789(5)	Mo(17)-O(31)	1.884(5)	P(2)-O(49)	1.548(5)
Mo(8)-O(4)	1.838(5)	Mo(17)-O(67)	1.899(6)	Ni(1)-N(19)	2.000(8)
Mo(8)-O(14)	1.994(5)	Mo(17)-O(48)	1.921(7)	Ni(1)-N(16)	2.014(8)
Mo(8)-O(16)	2.028(5)	Mo(17)-O(77)	1.995(7)	Ni(1)-N(18)	2.026(7)
Mo(8)-O(21)	2.506(6)	Mo(17)-O(32)	2.461(5)	Ni(1)-O(9)	2.057(5)
Mo(9)-O(30)	1.695(5)	Mo(18)-O(73)	1.690(6)	Ni(1)-O(4W)	2.131(7)
Mo(9)-O(16)	1.844(6)	Mo(18)-O(54)	1.841(5)	Ni(1)-N(21)	2.166(7)
Mo(9)-O(27)	1.842(5)	Mo(18)-O(64)	1.886(7)	Ni(2)-N(2)	2.011(7)
Mo(9)-O(18)	1.957(5)	Mo(18)-O(48)	1.921(7)	Ni(2)-N(6)	2.013(7)
Mo(9)-O(41)	2.057(6)	Mo(18)-O(87)	2.027(7)	Ni(2)-N(3)	2.015(8)
Mo(9)-O(21)	2.428(5)	Mo(18)-O(32)	2.447(5)	Ni(2)-O(1W)	2.151(7)
Ni(4)-N(23)	2.037(8)	Ni(3)-O(7)	2.110(6)	Ni(2)-O(1)	2.136(5)
Ni(4)-N(26)	2.051(8)	Ni(3)-O(2W)	2.145(7)	Ni(2)-N(3A)	2.187(7)
Ni(4)-O(23)	2.075(5)	Ni(3)-N(14)	2.166(10)	Ni(3)-N(9)	2.036(8)
Ni(4)-O(3W)	2.145(7)	Ni(3)-N(11)	2.031(8)	Ni(3)-N(13)	2.032(8)
Ni(4)-N(28)	2.153(9)	Ni(4)-N(25)	2.010(8)		

Table S3. Selected bond lengths for compound **3** (Å).

Mo(1)-O(3)	1.674(4)	Mo(2)-O(1)	2.365(4)	Mo(4)-O(7)	1.688(5)
Mo(1)-O(10)	1.752(4)	Mo(2)-O(12)	2.312(4)	Mo(4)-O(11)	1.921(4)
Mo(1)-O(6)_a	1.940(4)	Mo(3)-O(12)_a	2.225(4)	Mo(4)-O(8)_a	1.925(4)
Mo(1)-O(1)	1.919(4)	Mo(3)-O(6)	2.393(4)	Mo(4)-O(10)_a	2.269(4)
Mo(1)-O(12)_a	2.205(4)	Mo(3)-O(9)	1.724(4)	Ni(1)-N(5)	2.066(5)
Mo(1)-O(12)	2.396(4)	Mo(3)-O(11)	1.878(4)	Ni(1)-O(5)	2.183(4)
Mo(2)-O(4)	1.685(4)	Mo(3)-O(1)	1.991(4)	Ni(1)-N(7)	2.191(4)
Mo(2)-O(5)	1.708(4)	Mo(3)-O(2)	1.684(5)	Ni(1)-N(2)	2.007(5)
Mo(2)-O(8)	1.910(4)	Mo(4)-O(12)_a	2.481(4)	Ni(1)-N(4)	2.043(5)
Mo(2)-O(6)	1.956(4)	Mo(4)-O(13)	1.688(5)	Ni(1)-O(9)	2.031(4)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y,-z

Table S4. Distances and angles [Å, °] of hydrogen bonds for compound **1**.

D–H···A	**d(D–H)**	**d(H···A)**	**d(D···A)**	**∠D–H···A**
O1W-H···O18	0.88	2.50	2.935(5)	111
O1W-H···O20	0.88	2.44	3.308(5)	171
O1W-HA···O14	0.88	1.96	2.828(5)	169
O2W-HB···O6W	0.85	2.4	3.066(15)	135
O2W-HC···O4W	0.85	2.28	3.119(10)	169

N1-HV···O2	0.86	2.32	3.093(8)	149
N1-HV···O19	0.86	2.33	2.981(8)	133
N3-HW···O12	0.86	2.27	3.092(7)	159
N5-HX···O5W	0.86	2.03	2.853(15)	161
N5-HX···O8WA	0.86	2.13	2.93(3)	154
N8-HY···O8WC	0.86	1.97	2.822(15)	172
N10-HZ···O9W	0.86	2.06	2.878(6)	158
N12-H0AA···O7W	0.86	1.89	2.737(15)	169
O3W-H3WA···O10W	0.89(2)	2.16(3)	2.811(9)	130(2)
O3W-H3WA···O20	0.89(2)	2.41(3)	2.724(7)	101(2)
O3W-H3WB···O20	0.85(3)	2.42(3)	2.724(7)	101.6(18)
O4W-H4WA···O12	0.85	2.06	2.847(8)	154
O4W-H4WB···O8WC	0.85	2.23	2.86(2)	131
O6W-H6WA···O11W	0.85	2.15	2.98(2)	166
O6W-H6WB···O8WA	0.85	2.52	3.32(3)	157
O6W-H6WB···O5W	0.85	2.11	2.947(17)	170
O9W-H1CA···O11W	0.85	1.99	2.76(2)	151
O9W-H1CA···O12W	0.85	2.06	2.87(2)	159
O9W-H2CA···O9	0.85	1.93	2.744(5)	160
O10W-H3CA···O22	0.85	2.11	2.813(7)	139
O10W-H4CA···O17	0.85	1.82	2.663(7)	173
C44-HD···O9	0.97	2.5	3.277(7)	137
C46-HF···O14	0.97	2.59	3.484(7)	153
C7-HJ···O3	0.93	2.57	3.331(8)	139
C10-HM···O23	0.93	2.43	3.121(7)	131
C20-HR···O22	0.97	2.55	3.501(8)	166
C22-HT···O17	0.97	2.39	3.245(8)	147

C22-HU···O1	0.97	2.42	3.135(8)	130
C1-H1AA···O1	0.93	2.57	3.446(9)	156
C4-H4AA···O11	0.93	2.55	3.304(7)	139
C25-H7AA···O7	0.93	2.35	3.152(7)	144
C32-H2BA···O20	0.93	2.51	3.349(8)	150
C34-H4BA···O14	0.93	2.49	3.244(7)	138

Table S5. Distances and angles [Å, °] of hydrogen bonds for compound **2**.

D–H···A	**d(D–H)**	**d(H···A)**	**d(D···A)**	**∠D–H···A**
N20-H···O11	0.86	2.5	2.960(10)	114
N20-H···O71	0.86	2.17	3.012(9)	168
N5-HA···O30	0.86	2.58	2.982(9)	110
N5-HA···O41	0.86	2.15	3.008(9)	174
N4-HB···O29	0.86	2.44	3.228(10)	153
N4-HB···O39	0.86	2.47	3.132(10)	134
N27-HD···O75	0.86	2.17	2.988(11)	159
N17-HE···O15	0.86	2.5	3.321(9)	161
N17-HE···O67	0.86	2.51	3.156(10)	133
N12-HJ··· O20	0.86	2.14	2.946(9)	157
N10-HN···O60	0.86	2.48	3.242(12)	148
N1-HW···O35	0.86	2.56	3.406(10)	168
N24-HX···O55	0.86	2.07	2.863(11)	154
N22-H1AA···O87	0.86	2.28	3.009(12)	143
N8-H5AA···O1A	0.86	2.11	2.863(12)	145
N15-H5BA···O19	0.86	2.11	2.954(12)	167
C18-HI···O15	0.93	2.55	3.331(11)	142
C62-HK···O34	0.93	2.55	3.426(11)	158
C15-HP···O27	0.93	2.54	3.417(11)	156
C39-H4AA···O29	0.93	2.59	3.431(13)	151
C69-H7AA···O54	0.97	2.58	3.226(11)	124

C69-H7AA···O73	0.97	2.55	3.473(12)	160
C19-H1BA···O86	0.97	2.52	3.435(12)	157
C67-H4BA···O38	0.97	2.5	3.414(12)	158
C9B-H7BA···O11	0.97	2.48	3.282(14)	140
C9B-H8BA···O51	0.97	2.42	3.375(13)	167
C45-H2CA···O28	0.97	2.51	3.429(15)	157
C93-H8CA···O14	0.97	2.25	3.153(13)	154
C51-H1EA···O36	0.93	2.43	3.231(16)	145
C43-H2EA···O16	0.97	2.27	3.211(13)	162
C31-H3FA···O62	0.93	2.26	3.163(14)	163
C73-H6FA···O13	0.93	2.24	3.167(13)	170

Table S6. Distances and angles [Å, °] of hydrogen bonds for compound **3**.

D–H···A	**d(D–H)**	**d(H···A)**	**d(D···A)**	**∠D–H···A**
O1W-H1WA···O10	0.85	2.28	3.071(8)	154
N1-H1B···O2W	0.86	2.01	2.857(8)	169
O1W-H1WB···O4W	0.86	2.49	3.189(19)	140
O2W-H2WA···O5W	0.89	2.49	3.02(2)	119
N3-H3B···O7	0.86	2.00	2.858(6)	176
O2W-H2WB···O5W	0.90	2.52	3.02	116
O3W-H3WA···O2	0.93	2.36	2.977(11)	123
O3W-H3WB···O2	0.94	2.37	2.977(11)	122
N6-H6B···O8	0.86	1.92	2.750(6)	162
C19-H19B···O4	0.97	2.51	3.056(8)	116
C22-H22B···O13	0.97	2.55	3.501(8)	168

Table S7. BVS values of oxygen atoms in compound **1**.

O1	1.5061	O13	2.2035
O2	2.2177	O14	1.5012
O3	1.5513	O15	2.1535
O4	1.8271	O16	1.5421
O5	2.2031	O17	1.1846
O6	2.3722	O18	2.2013
O7	2.2185	O19	1.5324
O8	2.3554	O20	1.2852
O9	1.8939	O21	2.2312
O10	1.8189	O22	1.5437
O11	1.5401	O23	1.5149
O12	1.8171		