Supplementary Material (ESI) for CrystEngComm

Supporting Information

Polyoxometalate Charge Directed Coordination Assemblies: Macrocycles and Polymer Chains

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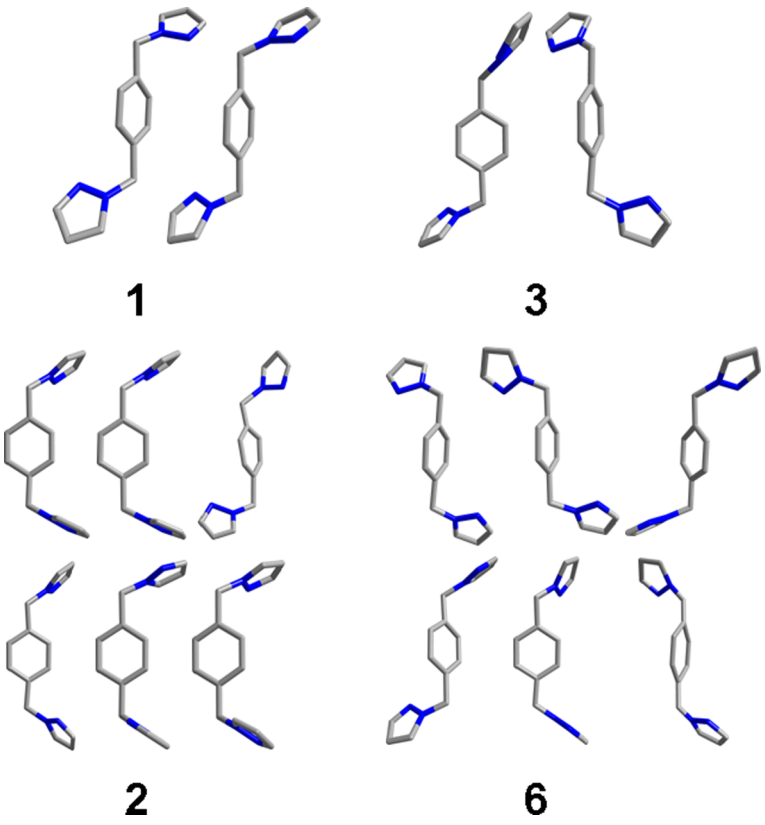


Figure S1 Conformations of the L molecules.

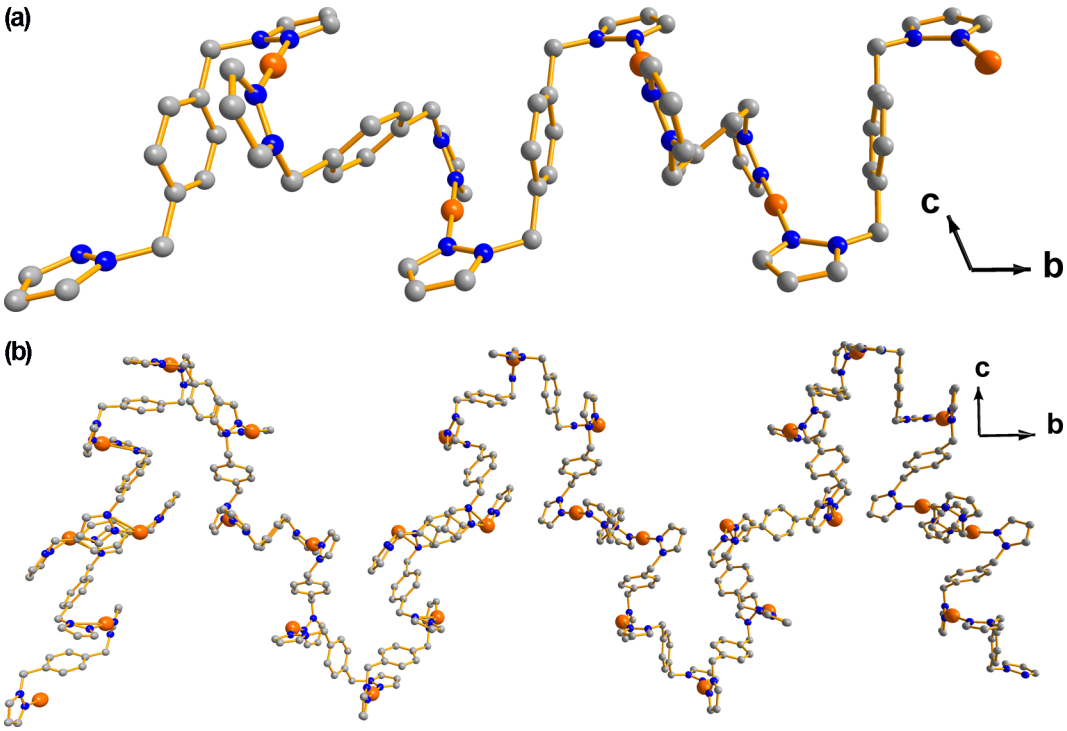


Figure S2 1D cationic chains in **1** and **6**.

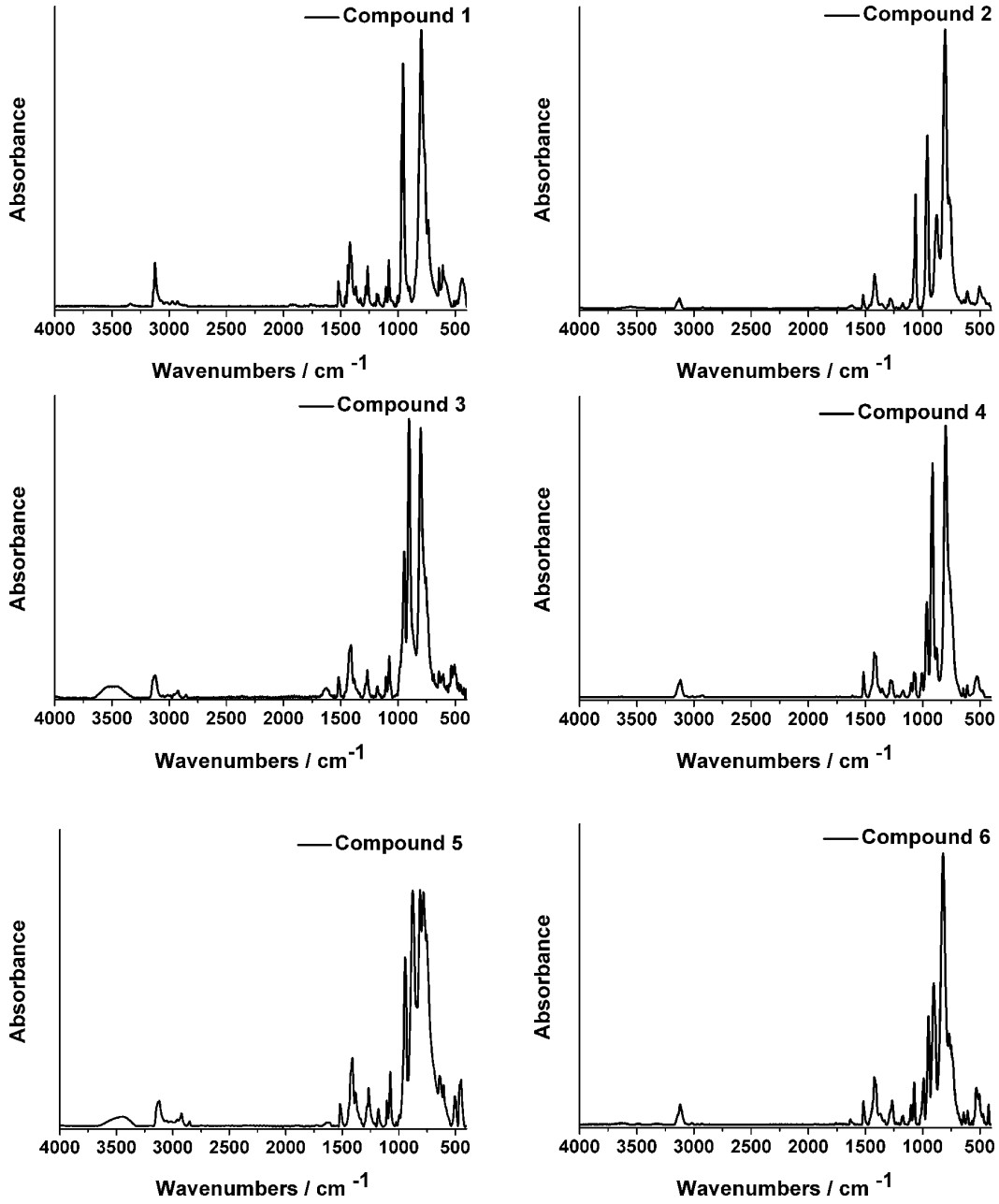


Figure S3 The IR spectra of compounds **1**–**6**.

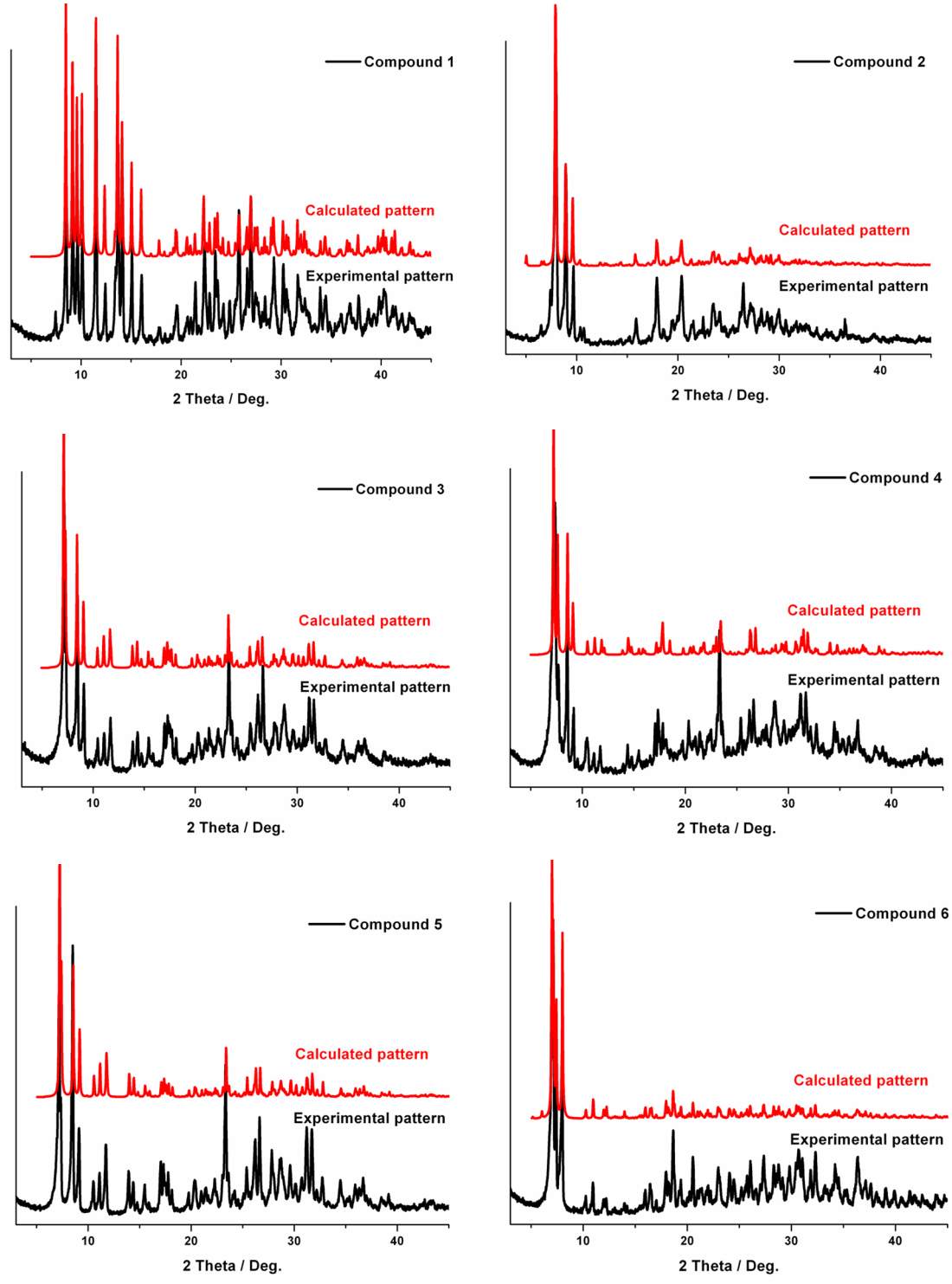
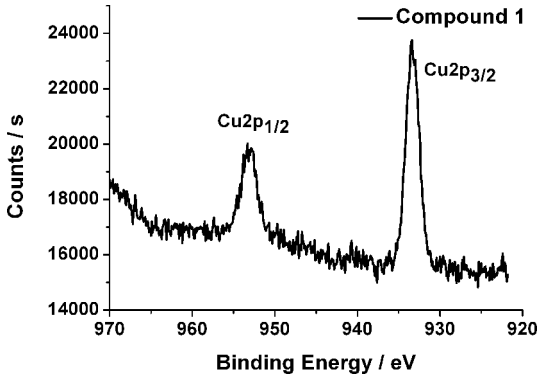
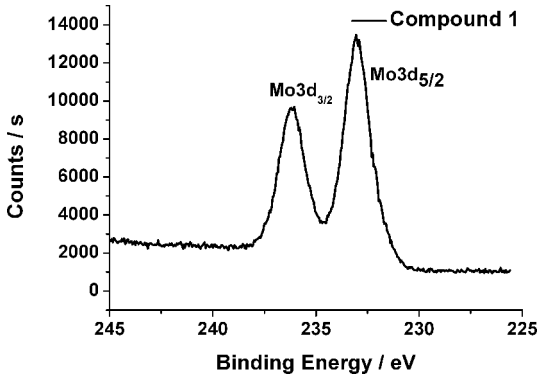
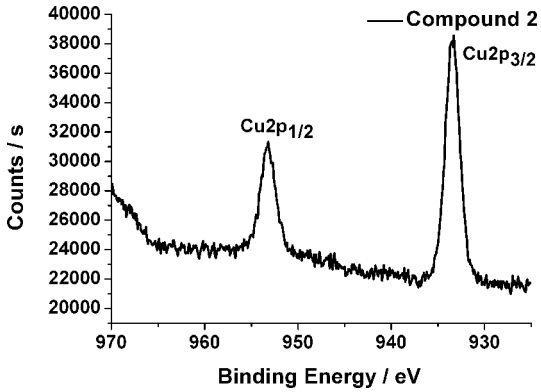
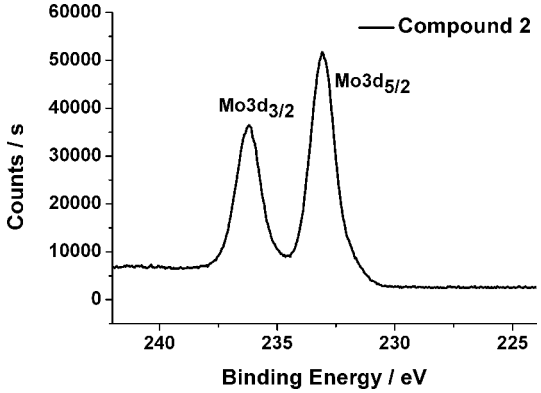


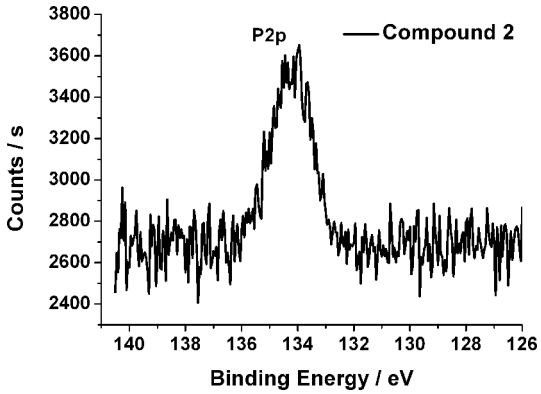
Figure S4 The powder X-ray diffraction patterns and the simulated patterns of compounds **1**–**6**.

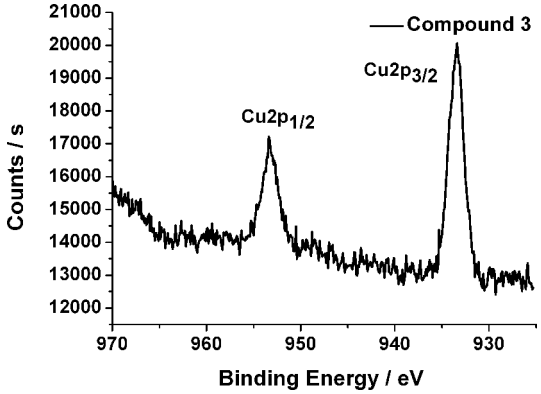


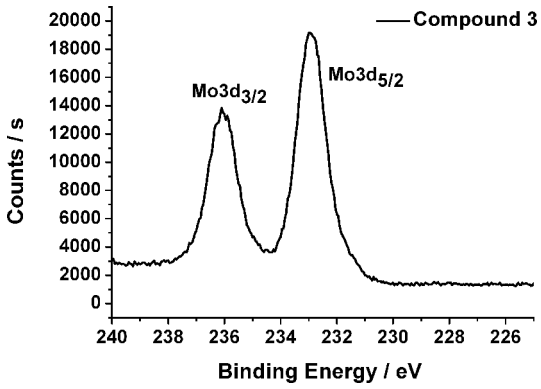


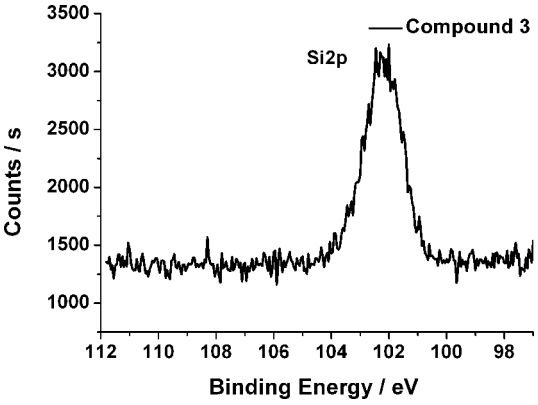


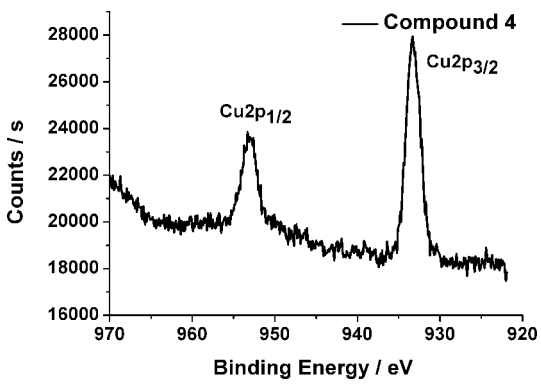


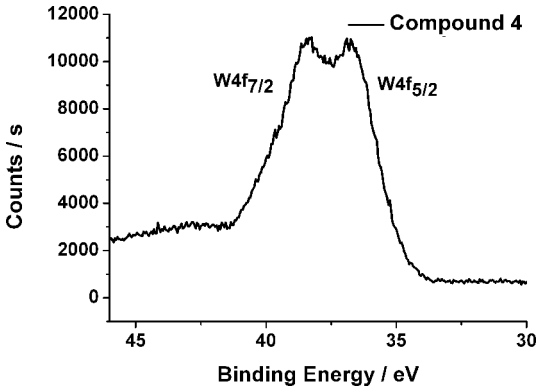


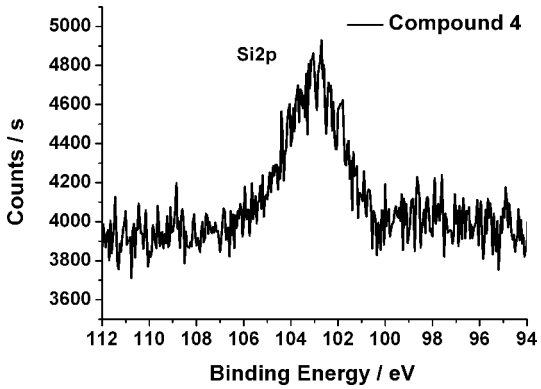


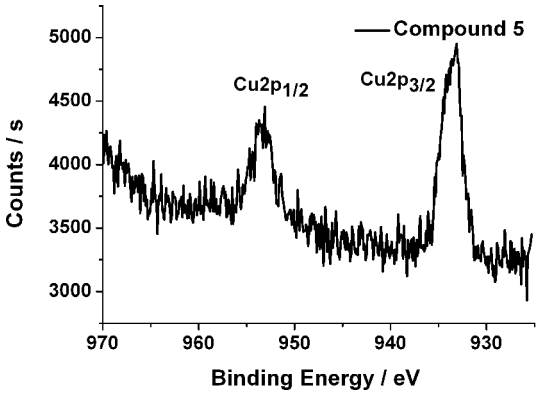


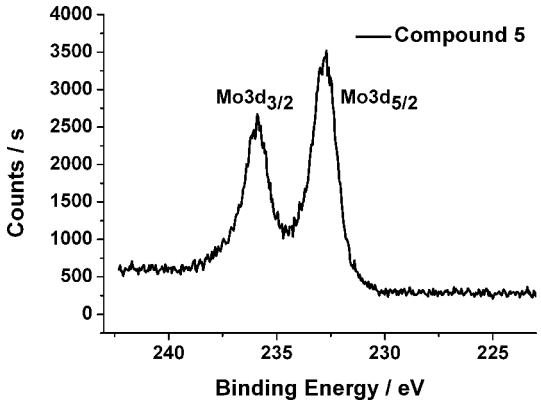


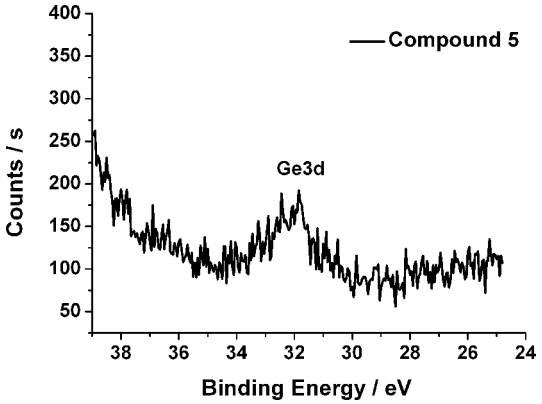


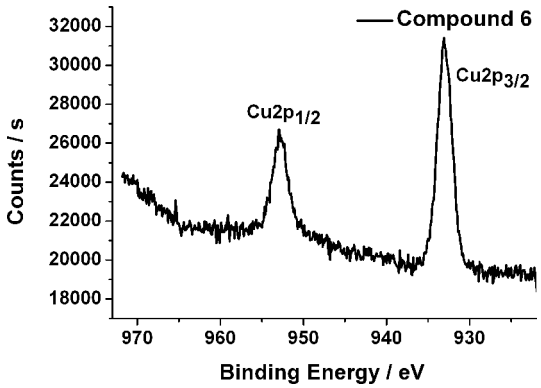


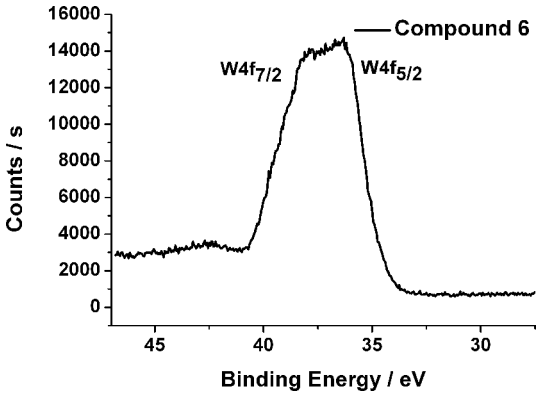












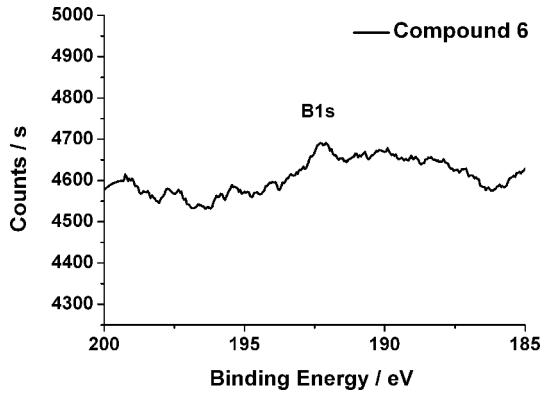
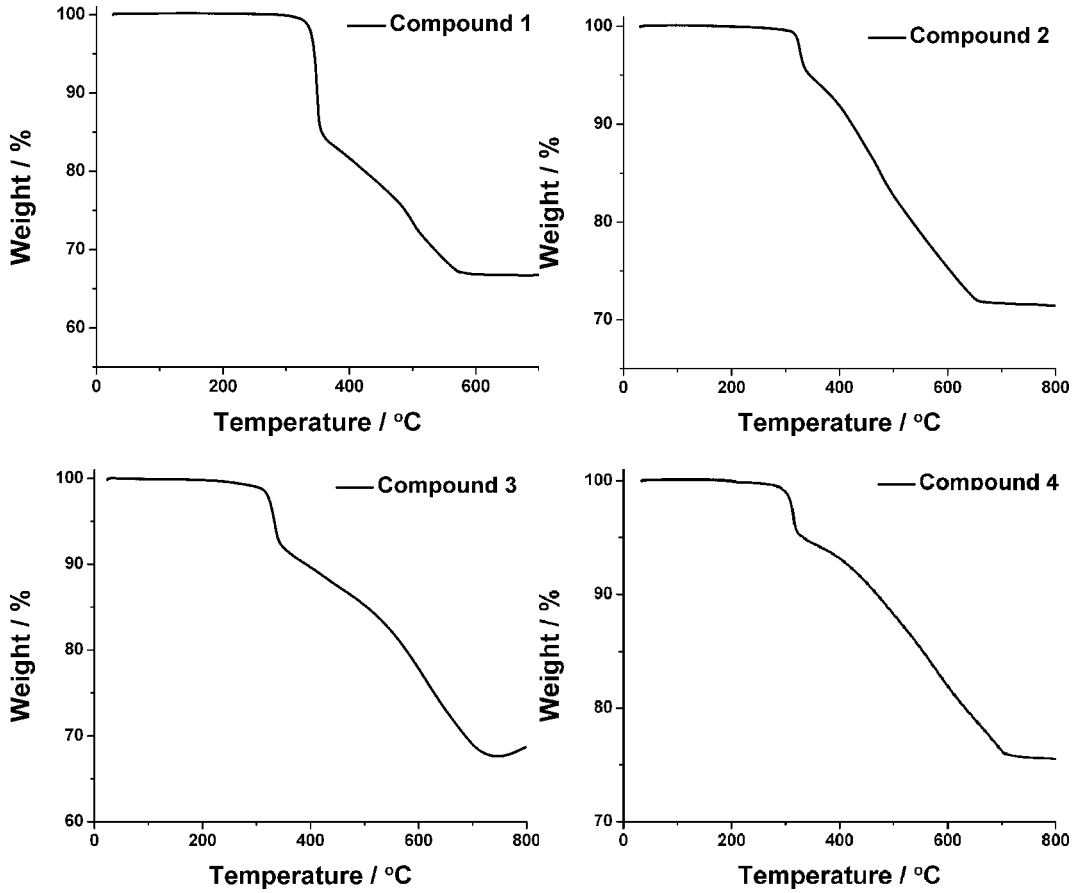


Figure S5 X-ray photoelectron spectra of compounds **1–6**



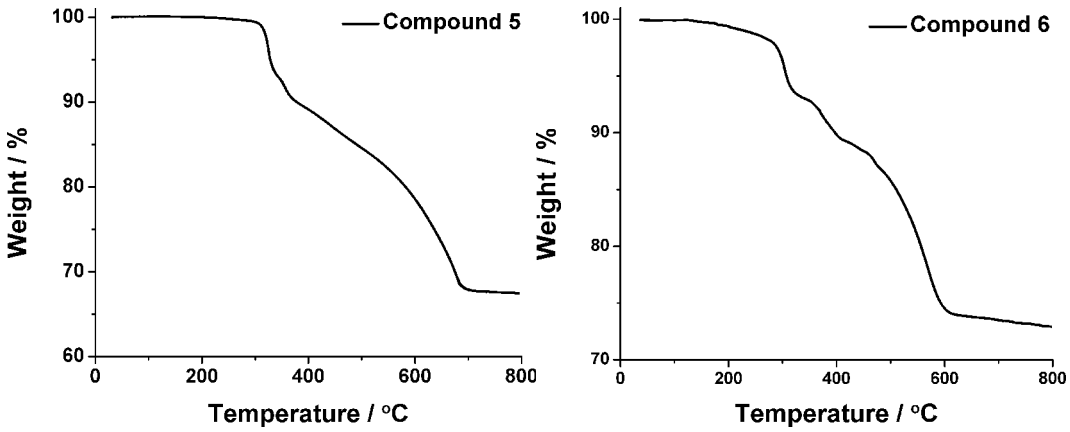


Figure S6 TGA curves of compounds **1**–**6**.

Table S1 TGA of compounds **1**–**6**.

Compound	Formula	Stable temperature / °C	Lost weight range / °C	Lost weight %	
				Exp.	Calcd.
1	$C_{28}H_{28}N_8Cu_2Mo_6O_{19}$	322	322-585	34.2	32.5
2	$C_{84}H_{84}N_{24}Cu_6P_2Mo_{24}O_{80}$	313	313-672	27.4	26.2
3	$C_{56}H_{56}N_{16}Cu_4SiMo_{12}O_{40}$	309	309-720	32.1	31.5
4	$C_{56}H_{56}N_{16}Cu_4\ SiW_{12}O_{40}$	305	305-706	23.9	23.3
5	$C_{56}H_{56}N_{16}Cu_4GeMo_{12}O_{40}$	306	306-703	31.9	31.1
6	$C_{70}H_{72}N_{20}Cu_5BW_{12}O_{41}$	296	296-614	26.9	27.6

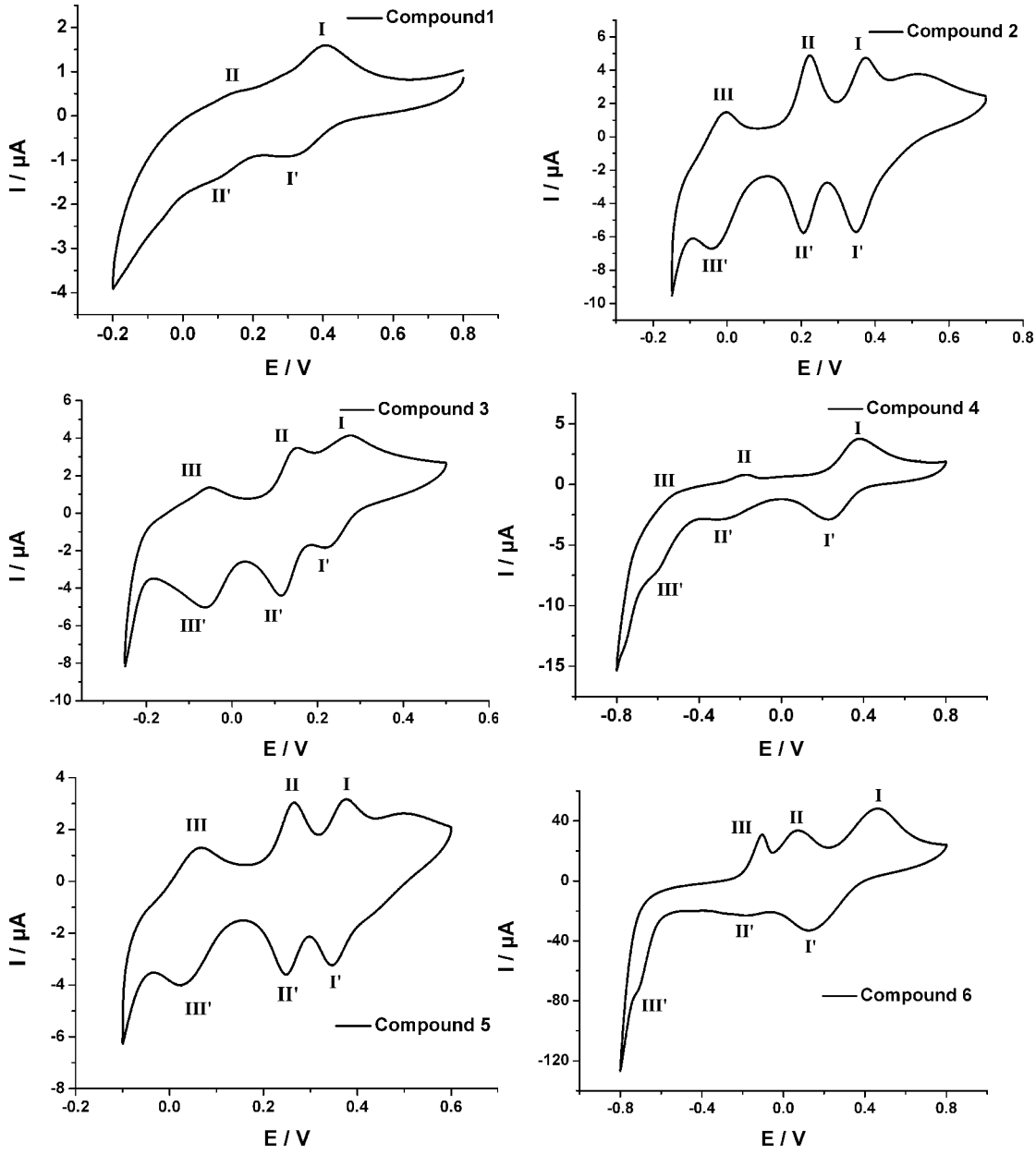


Figure S7 The Cyclic voltammograms of **1**-CPE, **3**-CPE, **4**-CPE and **6**-CPE in 1M H_2SO_4 under scan rate 50 $mV \cdot s^{-1}$.

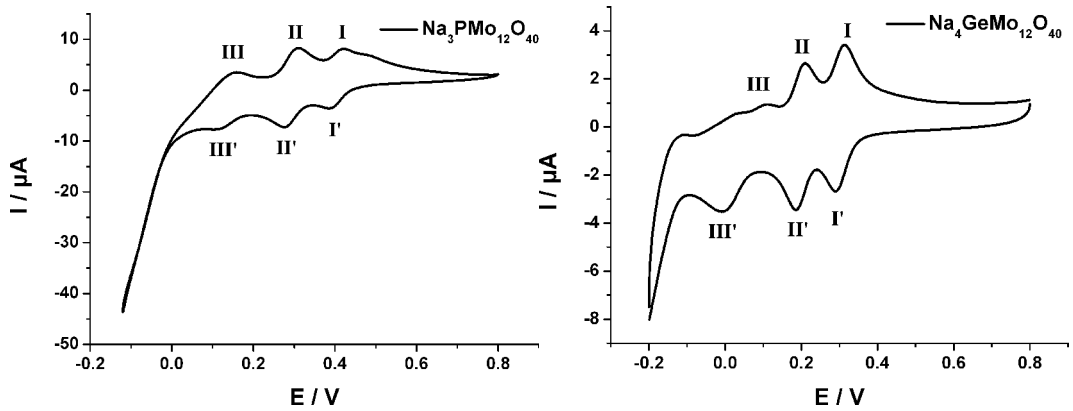


Figure S8 The cyclic voltammograms of $[PMo_{12}O_{40}]^{3-}$ and $[GeMo_{12}O_{40}]^{4-}$ -CPE in 1 M H_2SO_4 under scan rate 50 $mV{\cdot}s^{-1}$.

Some special restraints are used during the refinement of **2**–**6**: In **2**, a total of 27 restraints are caused by the commands 'Dfix 1.50 0.01 C36 C39 N10 C32 N12 C39' and 'Isor 0.01 N12 N10 C35 C40' to restrain the bond distance and thermal ellipsoid. In **3**, a total of 36 restraints are caused by the commands 'Isor 0.01 O6 O7 O9 O13 O14 O16' to restrain the thermal ellipsoid. In **4**, a total of 96 restraints are caused by the commands ' Isor 0.001 O19 O21 and Isor 0.01 C12 O20 N7 C13 O2 O4 O6 O7 O9 O11 O12 O13 O14 O16' to restrain the thermal ellipsoid. In **5**, a total of 30 restraints are caused by the commands ' Isor 0.01 O11 O13 and Isor 0.005 O7 O14 O16' to restrain the thermal ellipsoid. In **6**, a total of 2 restraints are caused by the commands 'DFIX 1.40 0.01 C68 C69 C68 C70'.

Table S2: Selected Bond Lengths and Angles for Compounds **1**–**6**.

Compound **1**			
Cu(1)−N(3)	1.877(4)	Cu(1)−N(1)	1.880(4)
Cu(1)−O(9)	2.579(4)		
N(3)−Cu(1)−N(1)	178.54(18)	N(3)−Cu(1)−O(9)	94.55(15)
N(1)−Cu(1)−O(9)	84.05(16)		
Compound **2**			
Cu(1)−N(11)	1.837(8)	Cu(1)−N(1)	1.850(7)
Cu(2)−N(3)	1.854(9)	Cu(2)−N(5)	1.870(9)
Cu(3)−N(7)	1.845(8)	Cu(3)−N(9)	1.851(9)
Cu(4)−N(13)	1.839(8)	Cu(4)−N(23)	1.849(7)
Cu(5)−N(19)	1.873(8)	Cu(5)−N(21)	1.876(8)
Cu(6)−N(15)	1.842(8)	Cu(6)−N(17)	1.850(7)

Cu(4)−O(40)	2.785(7)	P(1)−O(3)	1.545(5)
P(1)−O(13)	1.525(5)	P(1)−O(16)	1.534(5)
P(1)−O(21)	1.527(6)	P(2)−O(44)	1.527(5)
P(2)−O(46)	1.532(5)	P(2)−O(47)	1.532(5)
P(2)−O(54)	1.540(5)		
N(11)−Cu(1)−N(1)	174.1(4)	N(3)−Cu(2)−N(5)	177.2(4)
N(7)−Cu(3)−N(9)	175.6(4)	N(13)−Cu(4)−N(23)	179.5(4)
N(19)−Cu(5)−N(21)	172.8(4)	N(15)−Cu(6)−N(17)	176.7(4)
O(40)−Cu(4)−N(23)	88.2(3)	O(40)−Cu(4)−N(13)	91.7(3)
Compound **3**			
Cu(1)−N(1)	1.825(13)	Cu(2)−N(3)	1.872(12)
Cu(2)−N(5)	1.878(11)	Cu(3)−N(7)	1.861(9)
Si−O(19)	1.673(13)	Si−O(20)	1.678(13)
Si−O(21)	1.541(12)	Si−O(22)	1.603(12)
N(1)#1−Cu(1)−N(1)	166.4(9)	N(3)−Cu(2)−N(5)	165.5(6)
N(7)−Cu(3)−N(7)#1	174.8(6)		
Symmetry Code: #1 -x, y, -z+1/2			
Compound **4**			
Cu(1)−N(1)	1.841(16)	Cu(2)−N(3)	1.861(17)
Cu(2)−N(5)	1.879(15)	Cu(3)−N(7)	1.862(14)
Si−O(19)	1.674(19)	Si−O(20)	1.63(2)
Si−O(21)	1.564(18)	Si−O(22)	1.557(19)
N(1)#1−Cu(1)−N(1)	169.0(12)	N(3)−Cu(2)−N(5)	164.3(9)
N(7)−Cu(3)−N(7)#1	175.7(10)		
Symmetry Code: #1 -x, y, -z+1/2			
Compound **5**			
Cu(1)−N(1)	1.828(10)	Cu(2)−N(3)	1.849(12)
Cu(2)−N(5)	1.860(10)	Cu(3)−N(7)	1.874(9)
Ge(1)−O(19)	1.802(12)	Ge(1)−O(20)	1.779(12)
Ge(1)−O(21)	1.717(11)	Ge(1)−O(22)	1.627(12)

N(1)−Cu(1)−N(1)#1	168.4(7)	N(3)−Cu(2)−N(5)	165.1(6)
N(7)#1−Cu(3)−N(7)	174.8(6)		
Symmetry Code: #1 -x, y, -z+1/2			
Compound **6**			
Cu(1)−N(1)	1.891(11)	Cu(1)−N(7)	1.906(11)
Cu(1)−O(34)	2.205(8)	Cu(2)−N(3)	1.883(14)
Cu(2)−N(5)	1.914(13)	Cu(3)−N(9)	1.860(12)
Cu(3)−N(11)	1.878(11)	Cu(3)−O(37)#3	2.776(9)
Cu(4)−N(15)	1.891(15)	Cu(4)−N(20)	1.969(14)
Cu(4)−O(15)	2.195(8)	Cu(5)−N(14)#2	1.886(13)
Cu(5)−N(17)#1	1.905(12)	Cu(5)−O(10)	2.429(9)
B(1)−O(26)	1.515(17)	B(1)−O(27)	1.520(17)
B(1)−O(9)	1.547(17)	B(1)−O(21)	1.547(16)
N(1)−Cu(1)−N(7)	150.7(5)	N(1)−Cu(1)−O(34)	112.4(4)
N(7)−Cu(1)−O(34)	92.8(4)	N(3)−Cu(2)−N(5)	172.5(7)
N(9)−Cu(3)−N(11)	171.7(5)	N(9)−Cu(3)−O(37)#3	91.4(4)
N(11)−Cu(3)−O(37)#3	91.1(4)	N(15)−Cu(4)−N(20)	145.0(7)
N(15)−Cu(4)−O(15)	107.6(5)	N(20)−Cu(4)−O(15)	107.3(5)
N(14)#2−Cu(5)−N(17)#1	162.7(5)	N(14)#2−Cu(5)−O(10)	101.4(4)
N(17)#1−Cu(5)−O(10)	94.8(4)		
Symmetry Code: #1 -x+2, -y, -z+2; #2 x, y-1, z; #3 -x-1, -y-1, -z-1			

Table S3. Selected Hydrogen Bond Interactions in Compounds **1**–**6**.

Compound **1**				
D−H···A	D−H/ Å	H···A/ Å	D···A/ Å	∠D − H···A/deg
C(3)−H(3)···O(4)#4	0.93	2.47	3.259(6)	142
C(10)−H(10)···O(1)#5	0.93	2.31	3.237(6)	178
C(13)−H(13)···O(6)#6	0.93	2.40	3.283(6)	159
Symmetry Code: #1 -x, -y+1, -z+1; #2 -x, -y, -z+1; #3 -x+1, -y+2, -z+2; #4 -x+1, -y+1, -z+1; #5 x-1, y-1, z; #6 x, y-1, z				

Compound **2**				
D−H···A	D−H/ Å	H···A/ Å	D···A/ Å	∠D − H···A/deg
C(1)−H(1)···O(49)#1	0.93	2.58	3.315(11)	137
C(4)−H(4B)···O(51)	0.97	2.52	3.307(11)	138
C(9)−H(9)···O(74)#7	0.93	2.56	3.387(11)	148
C(11)−H(11A)···O(74)#7	0.97	2.36	3.261(11)	155
C(12) −H(12)···O(1)	0.93	2.58	3.083(12)	114
C(18)−H(18A)···O(70)#7	0.97	2.53	3.467(11)	163
C(25)−H(25B)···O(58)#6	0.97	2.46	3.331(12)	149
C(28) −H(28)···O(43)#2	0.93	2.56	3.281(15)	135
C(32)−H(32A)···O(56)#2	0.97	2.68	3.583(16)	154
C(32)−H(32B)···O(26)	0.97	2.30	3.224(16)	160
C(40)−H(40)···O(23)#5	0.93	2.53	3.417(17)	158
C(45)−H(45)···O(67)#1	0.93	2.38	3.311(13)	179
C(48)−H(48)···O(38)#1	0.93	2.59	3.490(12)	162
C(53)−H(53B)···O(79)#2	0.97	2.49	3.353(12)	148
C(57)−H(57)···O(36)#1	0.93	2.53	3.182(12)	128
C(58)−H(58)···O(71)#1	0.93	2.55	3.426(12)	157
C(59)−H(59)···O(43)#1	0.93	2.42	3.138(12)	134
C(60)−H(60A)···O(7)#4	0.97	2.60	3.556(13)	168
C(67)−H(67A)···O(2)#3	0.97	2.26	3.215(10)	169
C(73)−H(73)···O(74)#2	0.93	2.54	3.292(11)	138
C(81)−H(81A)···O(28)	0.97	2.55	3.172(12)	122
C(81)−H(81A)···O(37)	0.97	2.59	3.549(13)	168
C(82)−H(82)···O(49)#2	0.93	2.35	3.131(12)	142
C(83)−H(83)···O(60)#2	0.93	2.38	3.277(12)	162
C(84)−H(84)···O(39)#1	0.93	2.45	3.166(12)	134
Symmetry Code: #1 x-1,-y+1/2,z-1/2 #2 -x+1,-y,-z+1 #3 x,-y+1/2,z-1/2 #4 x-1,y,z-1 #5 -x+1,y-1/2,-z+3/2 #6 x-1,y,z #7 -x+2,-y,-z+2				
Compound ***3***				

C(4)−H(4A)···O(11)	0.97	2.47	3.30(2)	144
C(10)−H(10)···O(1)#2	0.93	2.60	3.42(2)	148
C(11)−H(11B)···O(16)#3	0.97	2.38	3.20(2)	142
C(15)−H(15)···O(2)#2	0.93	2.52	3.241(16)	135
C(17)−H(17)···O(7)#4	0.93	2.49	3.376(19)	160
C(18)−H(18B)···O(6)#4	0.97	2.55	3.44(2)	152
C(20)−H(20)···O(2)#5	0.93	2.59	3.470(17)	159
C(26)−H(26)···O(13)#3	0.93	2.53	3.275(15)	137
Symmetry Code: #1 -x, y, -z+1/2 #2 -x+1/2, -y+1/2, -z+1 #3 -x+1/2, y+1/2, -z+1/2 #4 -x, -y+1, -z+1 #5 x, y+1, z				
Compound **4**				
C(4)−H(4A)···O(11)	0.97	2.45	3.29(3)	144
C(10)−H(10)···O(1)#2	0.93	2.57	3.39(3)	149
C(11)−H(11A)···O(16)#3	0.97	2.49	3.30(3)	141
C(15)−H(15)···O(2)#2	0.93	2.52	3.22(2)	132
C(17)−H(17)···O(7)#4	0.93	2.50	3.39(3)	159
C(18)−H(18B)···O(6)#4	0.97	2.57	3.46(3)	151
C(20)−H(20)···O(2) #5	0.93	2.56	3.47(2)	164
C(26)−H(26)···O(13)#3	0.93	2.57	3.31(2)	137
Symmetry Code: #1 -x,y,-z+1/2 #2 -x+1/2,-y+1/2,-z+1 #3 -x+1/2,y+1/2,-z+1/2 #4 -x,-y+1,-z+1 #5 x,y+1,z				
Compound **5**				
C(4)−H(4A)···O(11)	0.97	2.47	3.294(19)	143
C(10)−H(10)···O(1)#2	0.93	2.62	3.434(19)	147
C(11)−H(11A)···O(16)#3	0.97	2.42	3.25(2)	143
C(15)−H(15)···O(2)#2	0.93	2.52	3.253(15)	136
C(17)−H(17)···O(7)#4	0.93	2.50	3.392(18)	162
C(18)−H(18B)···O(6)#4	0.97	2.60	3.48(2)	151
C(20)−H(20)···O(2)#5	0.93	2.62	3.497(15)	157
C(26)−H(26)···O(13)#3	0.93	2.53	3.278(14)	138
Symmetry Code: #1 -x,y,-z+1/2 #2 -x+1/2,-y+1/2,-z+1 #3 -x+1/2,y+1/2,-z+1/2 #4 -x,-y+1,-z+1 #5 x,y+1,z				

Compound **6**				
C(3)-H(3)...O(1)#5	0.93	2.47	3.143(15)	129
C(14)-H(14)...O(6)#2	0.93	2.49	3.060(18)	120
C(14)-H(14)...O(14)#2	0.93	2.55	3.446(18)	163
C(16)-H(16)...O(28)#5	0.93	2.59	3.138(19)	118
C(18)-H(18B)...O(31)#2	0.97	2.55	3.41(2)	149
C(21)-H(21)...O(31)#2	0.93	2.46	3.245(19)	143
C(24)-H(24)...O(2)#6	0.93	2.41	3.327(18)	170
C(28)-H(28)...O(36)#7	0.93	2.53	3.42(2)	160
C(32)-H(32A)...O(17)#7	0.97	2.58	3.369(18)	138
C(33)-H(33)...O(40)#5	0.93	2.48	3.291(19)	146
O(41)-H(142)...O(29)	0.85	2.19	3.027(17)	171
O(41)-H(141)...O(28)	0.85	2.29	3.13(2)	173
C(46)-H(46A)...O(41)#4	0.97	2.50	3.44(3)	165
C(47)-H(47)...O(18)#5	0.93	2.44	3.34(3)	164
C(61)-H(61)...O(3)#9	0.93	2.60	3.332(18)	136
C(61)-H(61)...O(11)#9	0.93	2.49	3.145(18)	127
C(63)-H(63)...O(29)#1	0.93	2.51	3.430(18)	169
C(66)-H(66)...O(30)#9	0.93	2.24	2.917(18)	129
C(66)-H(66)...O(38)#9	0.93	2.20	2.997(17)	144
C(67)-H(67A)...O(24)	0.97	2.24	3.10(2)	148
Symmetry Code: #1 -x+2, -y, -z+2; #2 -x+2, -y+1, -z+2; #3 x, y-1, z; #4 x, y+1, z; #5 -x+1, y+1/2, -z+3/2; #6 -x+2, y+1/2, -z+3/2; #7 -x+1 ,-y+1 ,-z+1; #8 x+1, -y+1/2, z+1/2; #9 x, -y+1/2, z+1/2				