Supramolecular self-assembly for desiging non-centrosymmetric crystal based on Keggin polyoxometallates and crown ether

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Supporting Information

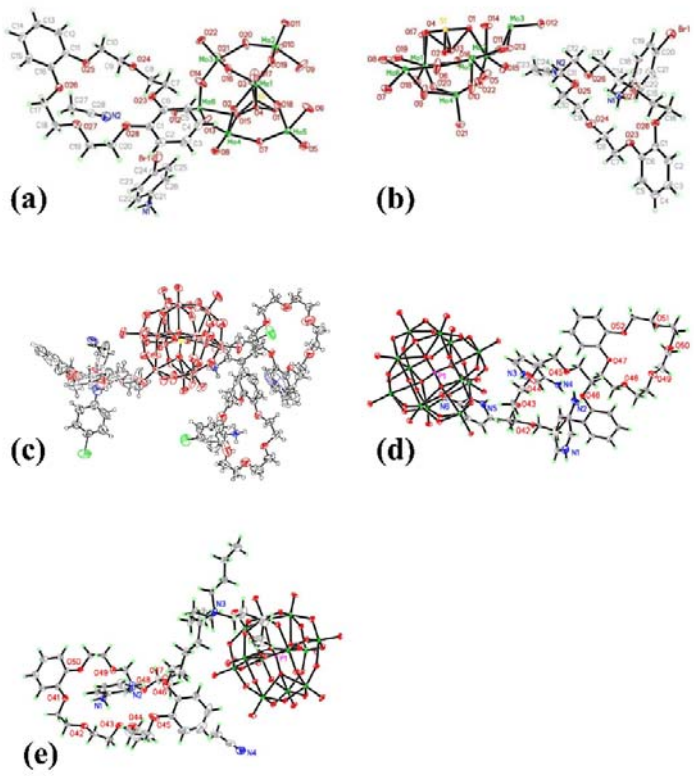

Figure S1. ORTEP diagrams of the asymmetric unit of crystals **1 (a), 2 (b), 3 (c), 4 (d)** and **5 (e)** with the atomic numbering scheme and 30% thermal ellipsoids.

Table S1. Weak intermolecular interaction of the crystal **1** (Å, °).

D–H···A	d(N–H)	d(H···A)	d(D···A)	∠DHA
N(1)–H(1A)···O(23)	0.89	2.20	2.8043	125
N(1)–H(1A)···O(24)	0.89	2.06	2.8953	155
N(1)–H(1B)···O(25)	0.89	2.35	2.9355	124
N(1)–H(1B)···O(26)	0.89	2.06	2.8912	154
N(1)–H(1C)···O(27)	0.89	2.29	2.8868	124
N(1)–H(1C)···O(28)	0.89	1.99	2.8304	156
C(10)–H(10B)···O(12)	0.97	2.49	3.2708	137
C(14)–H(14)···O(22)	0.93	2.56	3.2221	129
C(17)–H(17A)···O(5)	0.97	2.36	3.1688	140
C(17)–H(17B)···O(8)	0.97	2.27	3.1980	159
C(20)–H(20A)···O(21)	0.97	2.60	3.4760	151
C(20)–H(20B)···O(17)	0.97	2.46	3.1950	133

Table S2. Weak intermolecular interaction of the crystal **2** (Å, °).

D–H···A	d(N–H)	d(H···A)	d(D···A)	∠DHA
N(1)–H(1A)···O(23)	0.89	2.25	3.0123	144
N(1)–H(1A)···O(24)	0.89	2.26	2.9831	138
N(1)–H(1B)···O(25)	0.89	2.03	2.7979	144
N(1)–H(1B)···O(26)	0.89	2.28	2.9673	134
N(1)–H(1C)···O(27)	0.89	2.04	2.8294	147
N(1)–H(1C)···O(28)	0.89	2.18	2.8037	126
C(16)–H(16A)···O(19)	0.97	2.53	3.4395	157

Table S3. Weak intermolecular interaction of the crystal **3** (Å, °).

D–H···A	d(N–H)	d(H···A)	d(D···A)	∠DHA
N(1)–H(1A)···O(43)	0.89	2.56	2.8755	102
N(1)–H(1A)···O(44)	0.89	2.29	3.1432	160
N(1)–H(1A)···O(45)	0.89	2.53	3.0097	114
N(1)–H(1B)···O(41)	0.89	2.53	2.9031	106
N(1)–H(1B)···O(46)	0.89	2.99	2.8714	172
N(1)–H(1C)···O(41)	0.89	2.54	2.9013	105
N(1)–H(1C)···O(42)	0.89	2.04	2.9219	172
N(1)–H(1C)···O(43)	0.89	2.46	2.8755	109
N(2)–H(2A)···O(49)	0.89	2.38	3.0350	131
N(2)–H(2A)···O(50)	0.89	1.98	2.7949	151
N(2)–H(2B)···O(47)	0.89	2.25	2.8686	126
N(2)–H(2B)···O(48)	0.89	2.04	2.8487	151
N(2)–H(2C)···O(51)	0.89	2.23	2.9060	133
N(2)–H(2C)···O(52)	0.89	2.05	2.8308	146
N(3)–H(3A)···O(56)	0.89	2.34	2.8334	115
N(3)–H(3A)···O(57)	0.89	1.99	2.8467	160
N(3)–H(3B)···O(53)	0.89	1.98	2.8500	166
N(3)–H(3B)···O(58)	0.89	2.30	2.8459	119
N(3)–H(3C)···O(54)	0.89	2.40	2.9322	119
N(3)–H(3C)···O(55)	0.89	2.01	2.8690	162
C(7)–H(7A)···O(5)	0.97	2.50	3.4059	156
C(10)–H(10B)···O(15)	0.97	2.52	3.2307	130
C(13)–H(13A)···O(38)	0.97	2.42	3.3482	159
C(13)–H(13B)···O(37)	0.97	2.46	3.3964	161
C(30)–H(30A)···O(38)	0.97	2.57	3.4968	160
C(35)–H(35A)···O(20)	0.97	2.45	3.3367	153
C(36)–H(36B)···O(21)	0.97	2.55	3.3609	141
C(38)–H(38B)···O(17)	0.97	2.54	3.0385	112
C(53)–H(53A)···O(27)	0.97	2.29	3.1566	148
C(62)–H(62)···O(57)	0.93	2.49	3.2498	139
C(67)–H(67A)···O(5)	0.96	2.39	3.3053	159
C(67)–H(67B)···N(1)	0.96	2.62	3.5763	174
C(69)–H(69B)···O(11)	0.96	2.56	3.1801	122
C(69)–H(69B)···O(28)	0.96	2.52	3.4659	168

Table S4. Weak intermolecular interaction of the crystal **4** (Å, °).

D–H···A	d(N–H)	d(H···A)	d(D···A)	∠DHA
N(2)–H(2A)···O(36)	0.86	2.58	3.0431	115
N(2)–H(2A)···O(45)	0.86	2.29	3.1178	161
N(3)–H(3)···O(43)	0.86	2.23	2.8789	132
N(3)–H(3)···O(44)	0.86	2.26	2.9239	135
N(4)–H(4A)···O(11)	0.86	2.30	2.9503	133
N(4)–H(4B)···O(41)	0.86	2.19	2.9846	153
N(5)–H(5A)···O(49)	0.86	2.46	2.9349	116
N(5)–H(5A)···O(50)	0.86	2.14	2.8696	143
N(6)–H(6A)···O(32)	0.86	2.58	3.0899	119
N(6)–H(6A)···O(52)	0.86	2.15	2.9964	169
N(1)–H(20)···O(47)	0.86	2.55	3.0012	113
N(1)–H(20)···O(48)	0.86	1.95	2.7769	162
C(20)–H(1)···O(42)	0.93	2.25	3.1198	156
C(2)–H(2)···O(37)	0.93	2.53	3.4003	157
C(7)–H(7B)···O(12)	0.97	2.51	3.4489	163
C(11)–H(11B)···O(13)	0.97	2.58	3.4652	152
C(11)–H(11B)···O(22)	0.97	2.59	3.4123	142
C(15)–H(15A)···O(39)	0.97	2.55	3.4675	159
C(16)–H(16B)···O(37)	0.97	2.57	3.3743	140
C(19)–H(17)···O(46)	0.93	2.60	3.2063	124
C(17)–H(19)···O(51)	0.93	2.47	3.3235	152
C(25)–H(25)···O(20)	0.93	2.29	3.1656	156
C(26)–H(26)···O(14)	0.93	2.46	3.1203	128
C(29)–H(29)···O(6)	0.93	2.51	3.3478	149
C(34)–H(34B)···O(6)	0.97	2.47	3.2156	134
C(36)–H(36A)···O(35)	0.97	2.54	3.4439	155
C(37)–H(37B)···O(40)	0.97	2.58	3.4776	155
C(39)–H(39A)···O(37)	0.97	2.57	3.3354	136
C(39)–H(39B)···O(28)	0.97	2.53	3.3172	138
C(42)–H(42A)···O(35)	0.97	2.57	3.4387	149
C(43)–H(43)···O(51)	0.93	2.59	3.3217	136
C(45)–H(45)···O(27)	0.93	2.35	3.1253	141

Table S5. Weak intermolecular interaction of the crystal **5** (Å, °).

D–H···A	d(N–H)	d(H···A)	d(D···A)	∠DHA
N(1)–H(1A)···O(43)	0.86	2.30	2.7896	116
N(1)–H(1B)···O(41)	0.86	2.15	2.9848	163
N(1)–H(1B)···O(42)	0.86	2.32	2.8472	120
N(2)–H(2A)···O(46)	0.86	2.08	2.8580	150
N(2)–H(2A)···O(47)	0.86	2.42	3.0738	133
C(2)–H(2)···O(26)	0.93	2.51	3.3897	157
C(9)–H(9A)···O(7)	0.97	2.54	3.3347	139
C(11)–H(11A)···O(48)	0.97	2.50	3.3588	147
C(21)–H(21B)···O(9)	0.97	2.55	3.5021	166
C(26)–H(26A)···O(12)	0.97	2.52	3.1100	120
C(27)–H(27A)···O(3)	0.97	2.55	3.4462	153
C(28)–H(28A)···O(21)	0.97	2.40	3.3157	157
C(30)–H(30)···O(48)	0.93	2.17	3.0699	163
C(32)–H(32)···O(17)	0.93	2.58	3.1859	123
C(33)–H(33)···O(17)	0.93	2.58	3.1808	123
C(34)–H(34A)···O(32)	0.97	2.59	3.3736	138
C(41)–H(41B)···O(16)	0.96	2.43	3.2917	150
C(46)–H(46A)···O(19)	0.97	2.51	2.9783	110
C(46)–H(46B)···O(19)	0.97	2.58	2.9783	105
C(47)–H(47B)···O(6)	0.97	2.57	3.1800	121

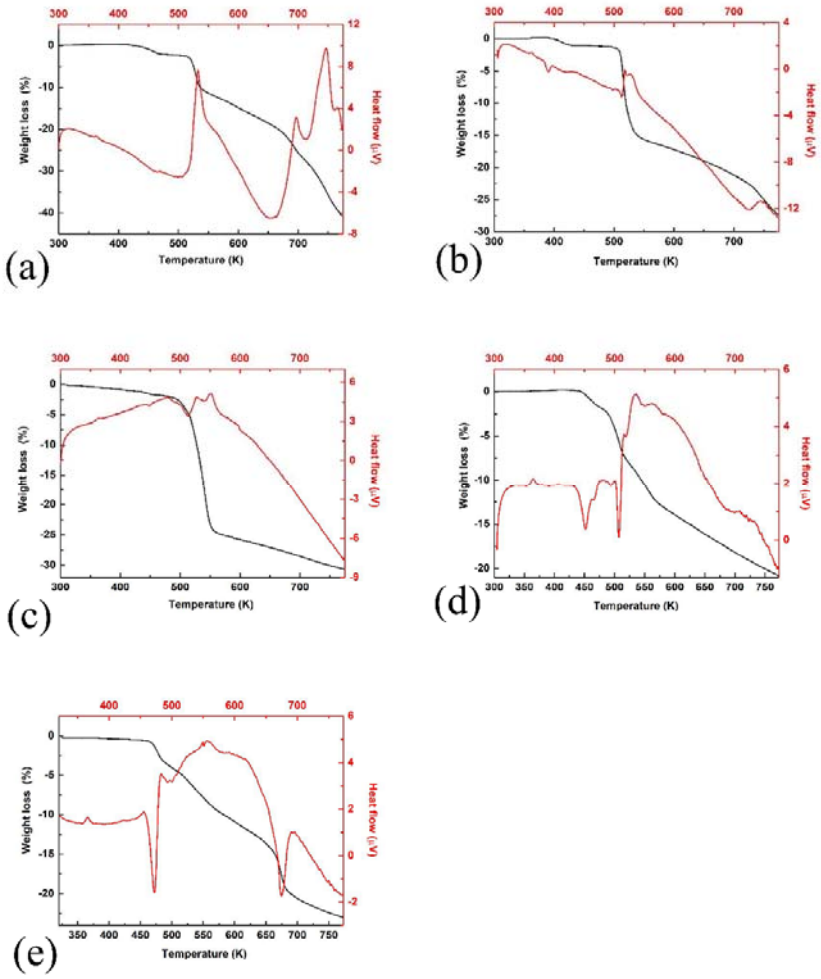

Figure S2. The TG-DTA curve of crystals **1 (a)**, **2 (b)**, **3 (c)**, **4 (d)** and **5 (e)**, respectively.

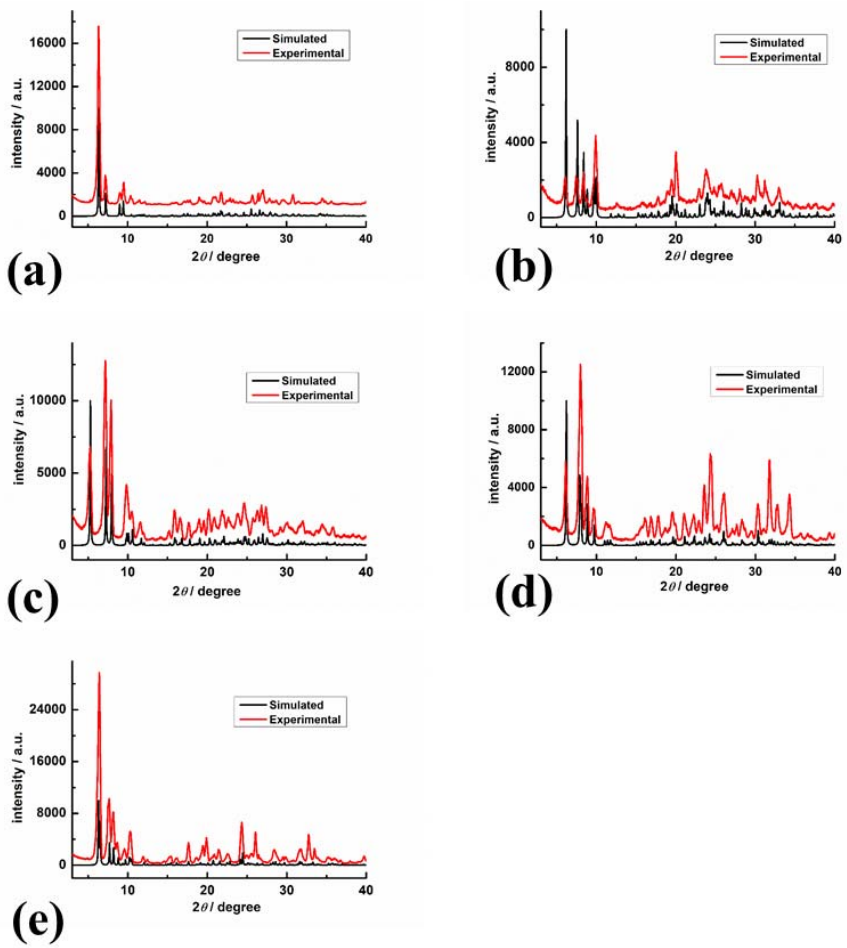

Figure S3. XRD patterns of crystal **1 (a)**, **2 (b)**, **3 (c)**, **4 (d)** and **5 (e)**, respectively.

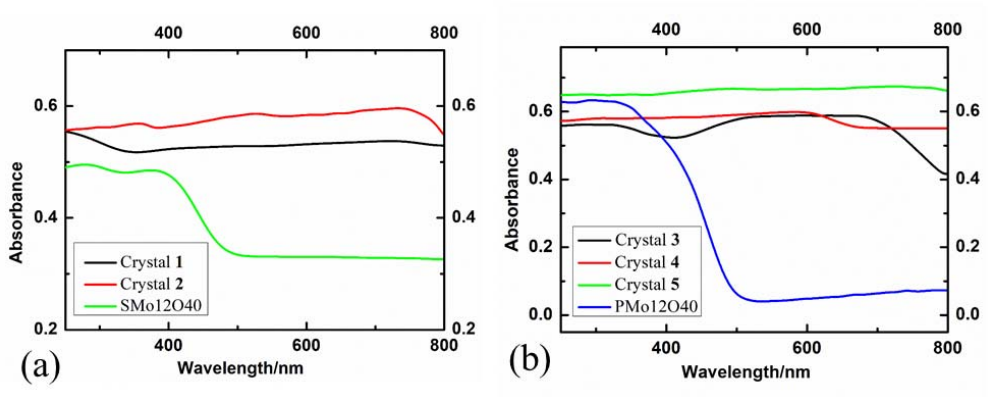

Figure S4. Diffuse reflectance spectra of crystals **1-5**. (a) Crystals based on $SMo_{12}O_{40}$; (b) Crystals based on $PMo_{12}O_{40}$.