Electronic Supplementary Information (ESI)

Cooperative Effects of Metal Cations and Coordination Modes on Luminescent s-Block Metal-Organic Complexes Constructed from V-shaped 4,4'-Sulfonyldiphenol

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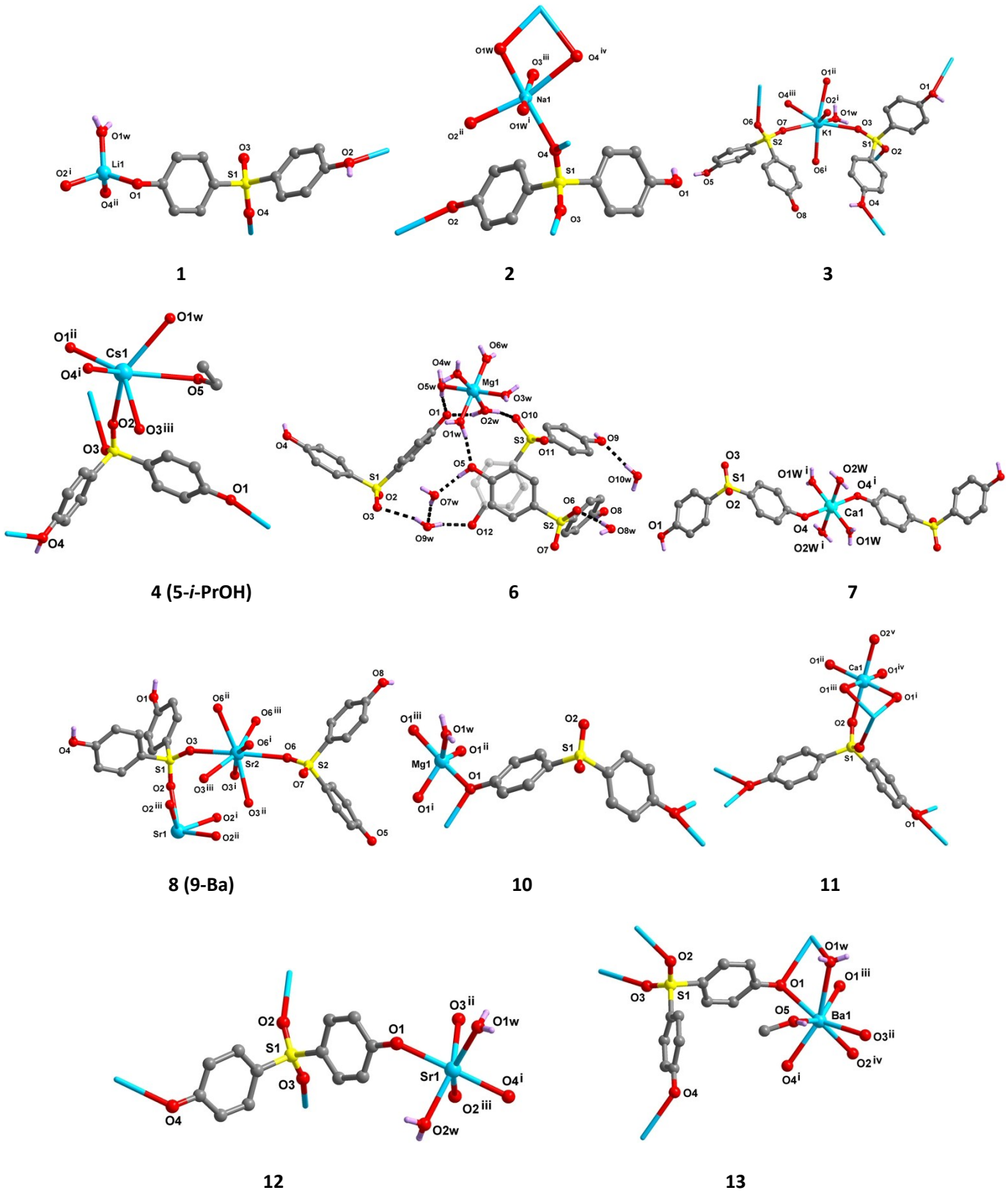


Fig. S1 Molecular structures of complexes **1-13** with the hydrogen-bonding interactions denoted as black dashed lines.

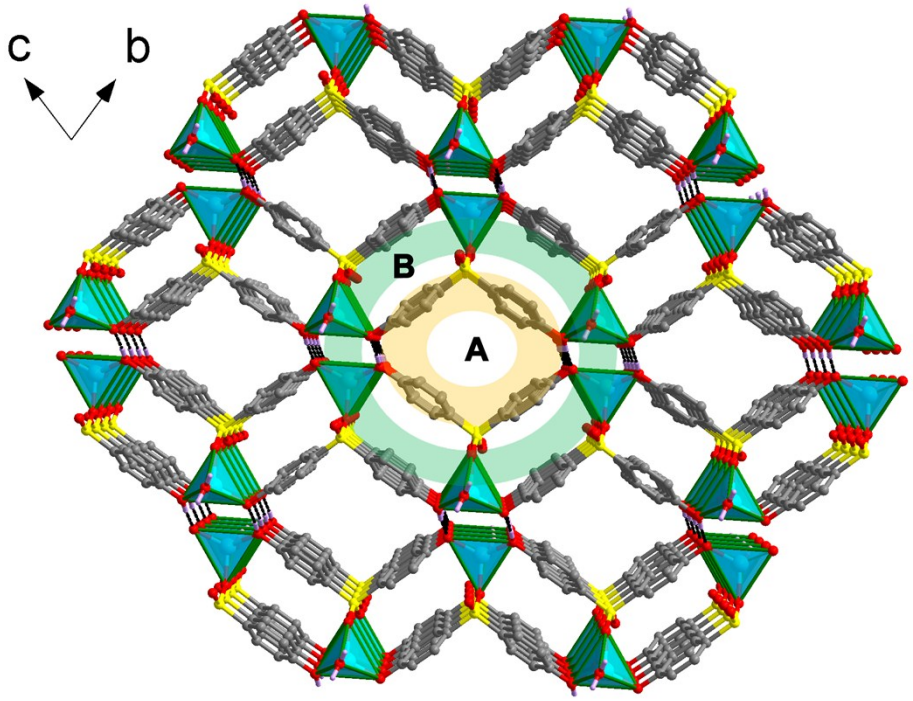


Fig. S2 3-D supramolecular network of complex **1**.

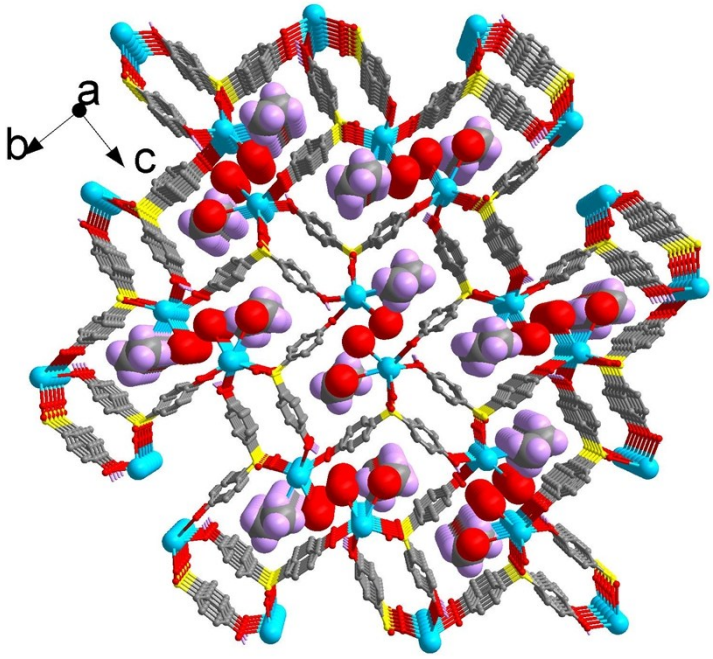


Fig. S3 3-D hybrid supramolecular network of complexes **4** and **5** with the guest solvent molecules being denoted as space-filling mode.

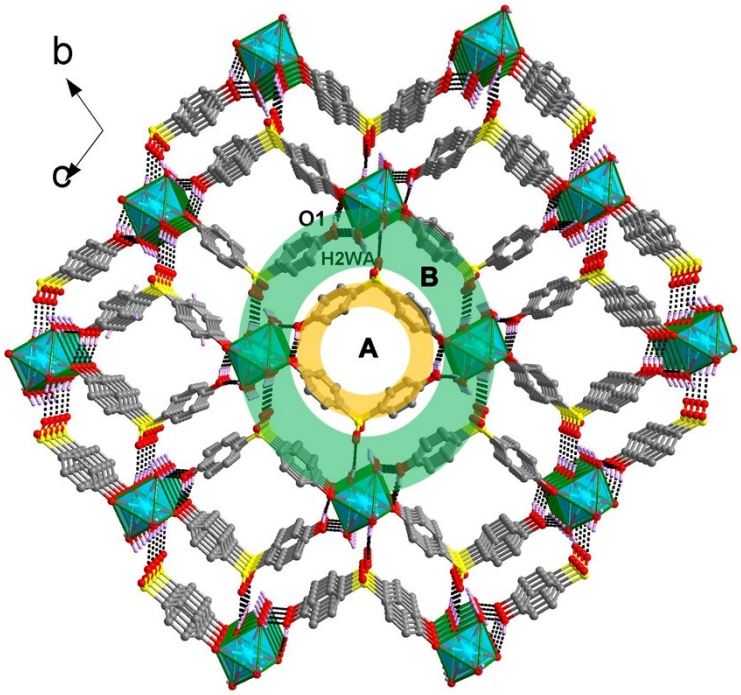


Fig. S4 3-D hybrid supramolecular network of complex **7**.

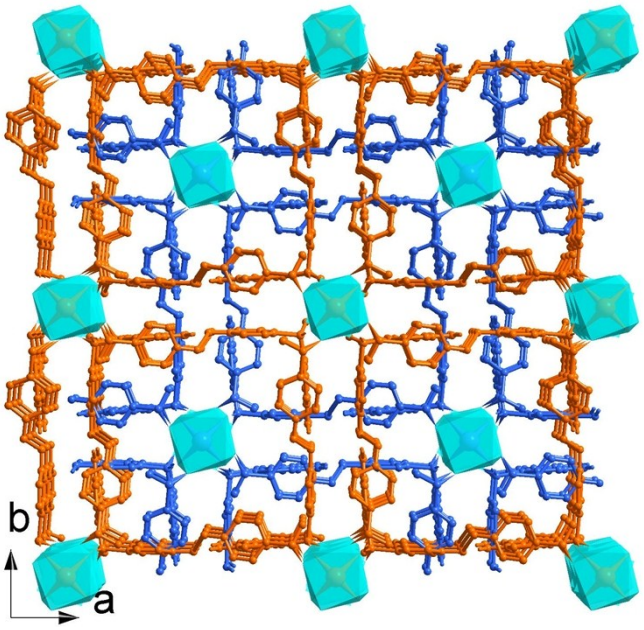
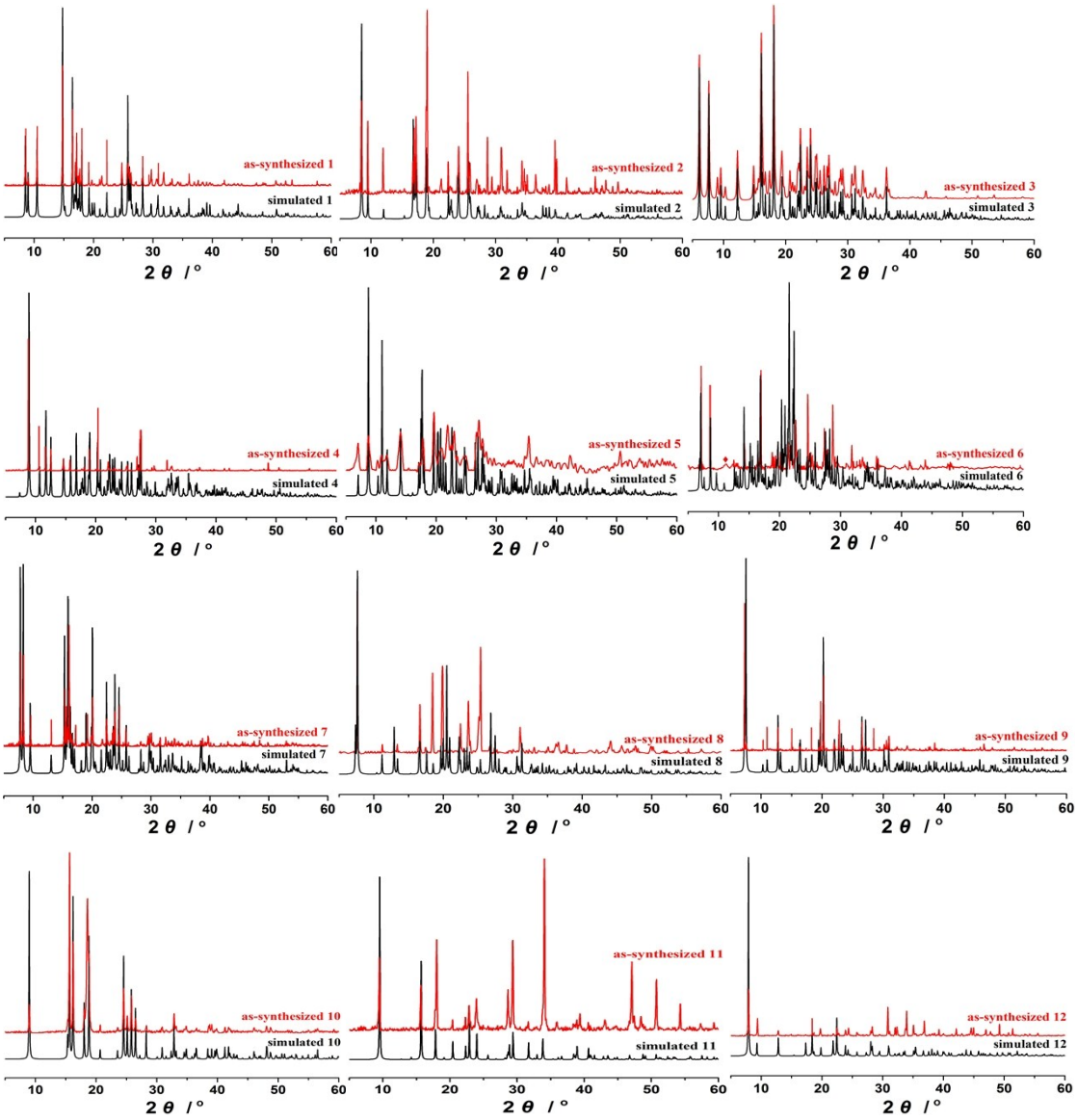


Fig. S5 3-D supramolecular network of complex **8**.

Powder X-ray diffraction (PXRD)

Powder X-ray diffraction (PXRD) patterns for solid samples of **1-13** were measured at room temperature as illustrated in Fig. S6. Most of the patterns are highly similar to their simulated ones (based on the single-crystal X-ray diffraction data), indicating that the single-crystal structures are really representative of the bulk of the corresponding samples. For complexes **6** and **13**, few very weak peaks in PXRD patterns of as-synthesized solid samples are observed, which may ascribe to either the micro stress between different particles that can cause both broadening and shifting of diffraction peaks or the trace amount of impurities in these two complexes.



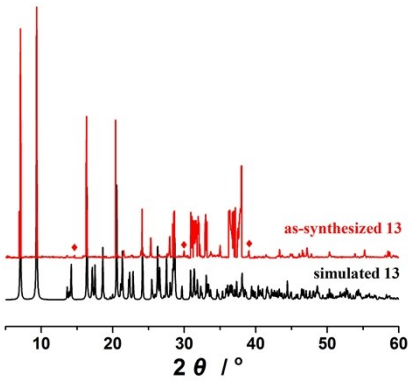


Fig. S6 PXRD patterns of complexes **1-13** at room temperature.

Thermogravimetric analysis

To examine the thermal stability of these complexes, in this study, their stabilities were analyzed on crystalline samples by thermogravimetric analyses (TGA) from room temperature to 850 °C at a rate of 10 °C min^{-1}, under N_2 atmosphere. As shown in Fig. S7, except for complexes **8**, **9** and **11**, the other ten complexes exhibit two (three for complex **4**) obvious loss steps . The first one corresponding to the loss of coordinated/free solvent molecules occurs in the range of 112-183 °C (**1**), 75-151 °C (**2**), 75-110 °C (**3**), 60-140 °C and 140-215 °C (**4**), 52-280 °C (**5**), 55-122 °C (**6**), 50-155°C (**7**), 100-177 °C (**10**), 96-166 °C (**12**) and 63-107 °C (**13**), respectively. Their observed weight loss is reasonably close to the calculated value (for **1**, obsd 6.22%, calcd 6.57%; for **2**, obsd 6.46%, calcd 6.21%; for **3**, obsd 3.65%, calcd 3.24%; for **4**, obsd 10.30%, calcd 10.32% for EtOH and obsd 4.55%, calcd 4.04% for H_2O; for **5**, obsd 16.90%, calcd 16.97%; for **6**, obsd 18.40%, calcd 18.90%; for **7**, obsd 11.31%, calcd 11.80%; for **10**, obsd 6.53%, calcd 6.20%; for **12**, obsd 9.13%, calcd 9.69%; for **13**, obsd 11.87%, calcd 11.73%). Then, the second weight losses begin from 277 °C for **1**, 213 °C for **2**, 300 °C for **3**, 230 °C for **4**, 380 °C for **5**, 270 °C for **6**, 255 °C for **7**, 275 °C for **10**, 370 °C for **12**, 223 °C for **13** with the decomposing of organic components, leaving the residue of A_2SO_4 or $AESO_4$ (A = Li, Na, K and Cs, AE = Mg, Ca, Sr and Ba) for these ten complexes (for **1**, obsd 19.97%, calcd 20.05%; for **2**, obsd 24.61%, calcd 24.47%; for **3**, obsd 15.95%, calcd 15.65%; for **4**, obsd 41.29%, calcd 40.55%; for **5**, obsd 40.75%, calcd 39.31%; for **6**, obsd 12.03%, calcd 12.63%; for **7**, obsd 22.50%, calcd 22.29%; for **10**, obsd 41.88%, calcd 41.42%; for **12**, obsd 49.26%, calcd 49.39%; for **13**, obsd 54.01%, calcd 54.70%). The decomposing of organic components in complexes **8**, **9** and **11** begin from 314 °C for **8**, 265 °C for **9**, 340 °C for **11**, leaving the residue of $SrSO_4$, $BaSO_4$ and $CaSO_4$ for these three complexes (for **8**, obsd 16.64%, calcd 16.90%; for **9**, obsd 20.91%, calcd 20.54%; for **11**, obsd 47.09%, calcd 47.22%).

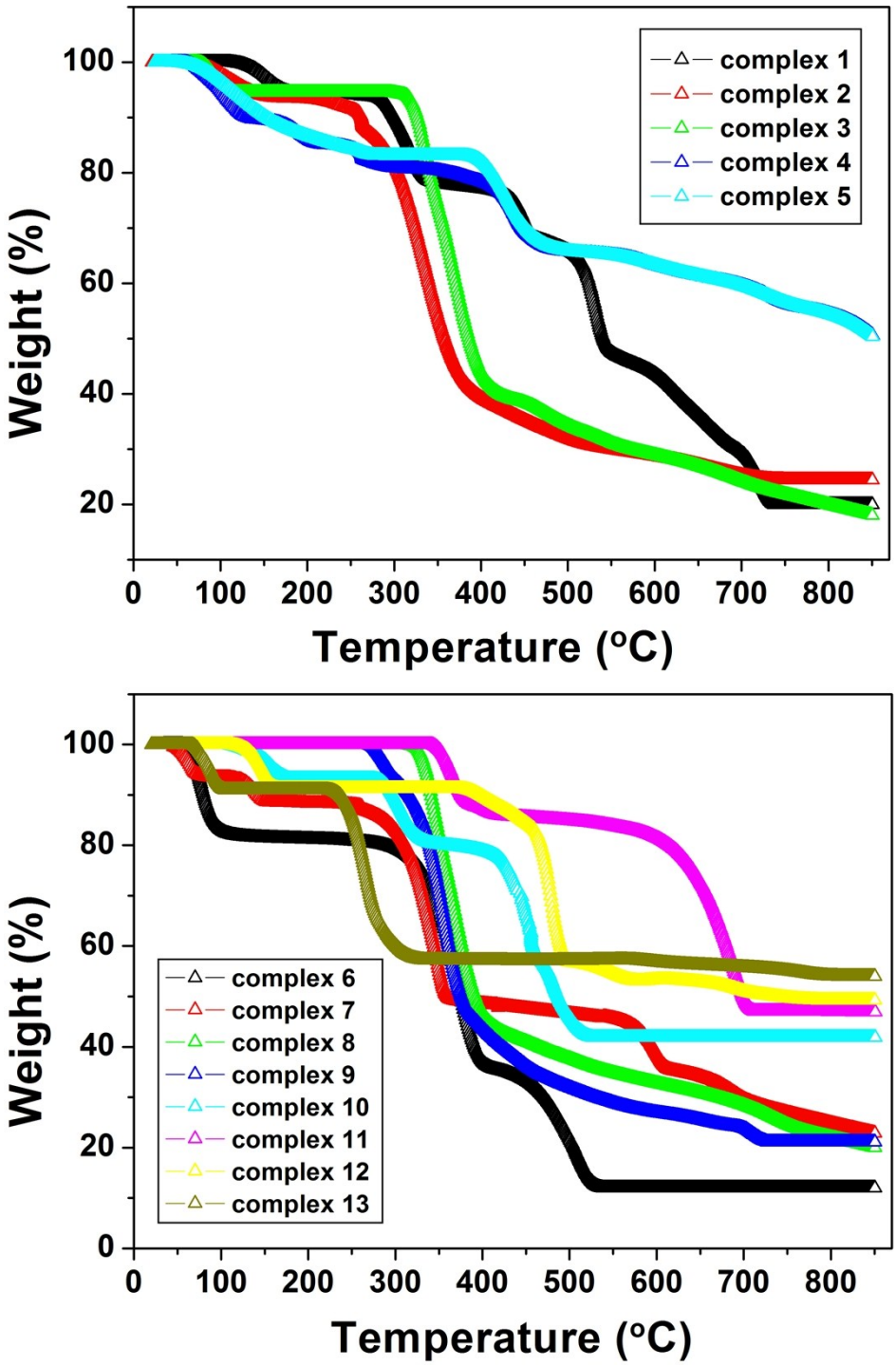


Fig. S7 TG curves of complexes **1-13**.

Table S1 Selected bond lengths (Å) of complexes **1-13**[a]

1			
Li(1)-O(1W)	1.882(6)	Li(1)-O(4)^{i}	1.943(6)
Li(1)-O(1)	1.940(6)	Li(1)-O(2)^{ii}	1.966(5)
2			
Na(1)-O(1W)	2.302(3)	Na(1)-O(4)	2.459(4)
Na(1)-O(1W)^{i}	2.364(3)	Na(1)-O(2)^{iii}	2.476(4)
Na(1)-O(3)^{ii}	2.382(3)	Na(1)-O(4)^{iv}	2.715(4)
3			
K(1)-O(4)^{i}	2.688(4)	K(1)-O(7)	2.785(4)
K(1)-O(6)^{ii}	2.714(3)	K(1)-O(1)^{iv}	2.883(3)
K(1)-O(2)^{iii}	2.742(3)	K(1)-O(1W)	3.056(4)
K(1)-O(3)	2.765(3)		
4			
Cs(1)-O(2)	3.032(5)	Cs(1)-O(1W')	3.217(18)
Cs(1)-O(4)^{i}	3.050(5)	Cs(1)-O(1W)	3.40(4)
Cs(1)-O(1)^{ii}	3.114(5)	Cs(1)-O(1W')^{iv}	3.41(2)
Cs(1)-O(3)^{iii}	3.163(5)	Cs(1)-O(5)	3.65(3)
5			
Cs(1)-O(2)^{i}	3.063(5)	Cs(1)-O(3)^{iii}	3.107(5)
Cs(1)-O(4)	3.088(5)	Cs(1)-O(5)	3.284(13)
Cs(1)-O(1)^{ii}	3.104(5)	Cs(1)-O(1W)	3.385(14)
6			
Mg(1)-O(6W)	2.022(2)	Mg(1)-O(3W)	2.070(3)
Mg(1)-O(2W)	2.038(2)	Mg(1)-O(4W)	2.082(3)
Mg(1)-O(1W)	2.056(2)	Mg(1)-O(5W)	2.093(3)
7			
Ca(1)-O(4)	2.329(2)	Ca(1)-O(1W)	2.331(2)
Ca(1)-O(4)^{i}	2.329(2)	Ca(1)-O(2W)^{i}	2.340(2)
Ca(1)-O(1W)^{i}	2.331(2)	Ca(1)-O(2W)	2.340(2)
8			
Sr(1)-O(2)^{i}	2.529(6)	Sr(2)-O(6)^{ii}	2.667(7)
Sr(1)-O(2)^{ii}	2.529(6)	Sr(2)-O(6)^{i}	2.667(7)

Sr(1)-O(2)	2.529(6)	Sr(2)-O(3)	2.698(6)
Sr(1)-O(2)^{iii}	2.529(6)	Sr(2)-O(3)^{i}	2.698(6)
Sr(2)-O(6)	2.667(7)	Sr(2)-O(3)^{ii}	2.698(6)
Sr(2)-O(6)^{iii}	2.667(7)	Sr(2)-O(3)^{iii}	2.698(6)
9			
Ba(1)-O(6)^{i}	2.764(14)	Ba(1)-O(2)^{i}	2.786(10)
Ba(1)-O(6)	2.764(14)	Ba(1)-O(2)	2.786(10)
Ba(1)-O(6)^{ii}	2.764(14)	Ba(2)-O(3)	2.746(12)
Ba(1)-O(6)^{iii}	2.764(14)	Ba(2)-O(3)^{ii}	2.746(12)
Ba(1)-O(2)^{iii}	2.786(10)	Ba(2)-O(3)^{iii}	2.746(12)
Ba(1)-O(2)^{ii}	2.786(10)	Ba(2)-O(3)^{i}	2.746(12)
10			
Mg(1)-O(1)^{i}	1.9920(14)	Mg(1)-O(1)	2.0522(13)
Mg(1)-O(1)^{ii}	1.9920(14)	Mg(1)-O(1)^{iii}	2.0522(13)
Mg(1)-O(1W)	2.004(2)		
11			
Ca(1)-O(1)^{i}	2.3439(18)	Ca(1)-O(1)^{iv}	2.3439(18)
Ca(1)-O(1)^{ii}	2.3439(18)	Ca(1)-O(2)^{v}	2.396(3)
Ca(1)-O(1)^{iii}	2.3439(18)	Ca(1)-O(2)	2.396(3)
12			
Sr(1)-O(4)^{i}	2.534(4)	Sr(1)-O(3)^{ii}	2.566(6)
Sr(1)-O(1W)	2.538(5)	Sr(1)-O(2)^{iii}	2.569(5)
Sr(1)-O(1)	2.538(4)	Sr(1)-O(1W)^{iv}	2.925(6)
Sr(1)-O(2W)	2.540(5)	Sr(1)-O(2W)^{v}	2.966(6)
13			
Ba(1)-O(4)^{i}	2.627(3)	Ba(1)-O(1)^{iii}	2.713(2)
Ba(1)-O(1)	2.660(3)	Ba(1)-O(2)^{iv}	2.747(3)
Ba(1)-O(5)	2.692(3)	Ba(1)-O(1W)	3.078(3)
Ba(1)-O(3)^{ii}	2.709(3)		

[a] Symmetry operations: **For 1**, i -x,-y,-z+1; ii x,y-1,z+1. **For 2**, i x,-y+3/2,z+1/2; ii x,y,z-1; iii -x+1,-y+1,-z; iv x,-y+3/2,z-1/2. **For 3**, i -x+1/2,y-1/2,z-1/2; ii x,y,z+1; iii x,y,z-1; iv -x+1,-y,z-1/2. **For 4**, i -x+1,-y,-z+1; ii -x+1/2,y-1/2,-z+3/2; iii x+1,y,z; iv -x+1,-y,-z+2. **For 5**, i -x+1,y-1/2,-z+3/2; ii x+1,-y+3/2,z+1/2; iii -x+2,y-1/2,-z+3/2. **For 7**, i -x,-y+1,-z+1. **For 8**, i y,-x,z; ii -x,-y,z; iii -y,x,z. **For 9**, i -

y+1,x,z; ii y,-x+1,z; iii -x+1,-y+1,z. **For 10**, i -x+1/2,-y+3/2,-z+1/2; ii x-1/2,-y+3/2,z; iii -x,y,-z+1/2. **For 11**, i -x+1/2,y+1/2,z; ii x-1/2,-y+1/2,-z+1; iii x-1/2,y+1/2,z; iv -x+1/2,-y+1/2,-z+1; v -x,-y+1,-z+1. **For 12**, i x,y,z-1; ii x-1/2,-y+1/2,z-1/2; iii x+1/2,-y+1/2,z-1/2; iv -x,-y+1,-z-1; v -x+1,-y+1,-z-1. **For 13**, i -x+1/2,-y+3/2,-z+1; ii x-1/2,y-1/2,z; iii -x,y,-z+1/2; iv x-1/2,y+1/2,z.

Table S2 Hydrogen bond parameters of complexes **1-13**[a]

D-H...A	d(D-H) / Å	d(H...A) / Å	d(D...A) / Å	<(DHA) / °
1				
O(1W)-H(1W1)...O(3)^{iv}	0.85(3)	1.986(11)	2.826(3)	170(4)
O(1W)-H(1W2)...O(1)^{v}	0.85(3)	1.890(12)	2.736(3)	172(4)
O(2)-H(2O)...O(1)^{vi}	0.85(3)	1.664(11)	2.509(3)	176(4)
2				
O(1)-H(1O)...O(2)^{vi}	0.85 (4)	1.661(14)	2.510(4)	172(6)
O(1W)-H(1W1)...O(1)^{vii}	0.85 (4)	1.842(14)	2.680(4)	169(4)
O(1W)-H(1W2)...O(1)^{viii}	0.85 (4)	2.027(15)	2.844(4)	162(4)
3				
O(1W)-H(1W1)...O(3)	0.85(5)	2.46(5)	3.073(5)	130(6)
O(1W)-H(1W2)...O(8)^{vii}	0.85(5)	1.849(13)	2.695(5)	172(6)
O(1)-H(1O)...O(8)^{viii}	0.85(5)	1.770(15)	2.611(5)	169(5)
O(5)-H(5O)...O(8)^{ix}	0.85(5)	1.803(13)	2.652(5)	175(6)
O(4)-H(4O)...O(1W)^{x}	0.85(5)	1.85(2)	2.671(5)	162(6)
4				
O(4)-H(4)...O(1)^{vii}	0.85(7)	1.675(16)	2.523(7)	174(10)
5				
O(1)-H(1O)...O(4)^{vii}	0.85 (7)	1.670(14)	2.524(7)	177(10)
O(1W)-H(1W1)...O(4)^{viii}	0.85	1.79	2.634(11)	173.1
O(1W)-H(1W2)...O(5)^{ix}	0.85	1.87	2.718(17)	173.2
6				
O(1W)-H(1WA)...O(8W)^{i}	0.85(4)	2.09(2)	2.819(5)	144(4)
O(1W)-H(1WB)...O(5)	0.85(4)	1.974(14)	2.805(4)	168(4)
O(2W)-H(2WA)...O(10)^{ii}	0.85(4)	2.05(2)	2.813(3)	150(3)
O(2W)-H(2WB)...O(1)	0.85(4)	1.850(15)	2.677(3)	164(4)
O(3W)-H(3WA)...O(8)^{iii}	0.85(4)	1.998(15)	2.827(3)	166(3)

O(3W)-H(3WB)...O(10W)^{iv}	0.85(4)	1.936(14)	2.775(4)	168(3)
O(4)-H(4O)...O(12)^{v}	0.85(4)	1.722(15)	2.554(3)	165(4)
O(4W)-H(4WB)...O(8W)^{i}	0.85	2.19	3.012(5)	161.4
O(4W)-H(4WA)...O(3)^{vi}	0.85	2.19	3.010(3)	161.5
O(5W)-H(5WA)...O(10)^{vii}	0.85(4)	2.058(13)	2.899(3)	168(3)
O(5W)-H(5WB)...O(1)	0.85(4)	1.837(11)	2.685(3)	170(4)
O(5)-H(5O)...O(7W)^{ii}	0.85(4)	1.801(17)	2.629(4)	166(5)
O(6W)-H(6WA)...O(2)^{vi}	0.85(4)	1.989(13)	2.821(3)	168(4)
O(6W)-H(6WB)...O(1)^{viii}	0.85(4)	1.791(12)	2.638(3)	172(3)
O(7W)-H(7WA)...O(10W)^{ix}	0.85(4)	1.977(16)	2.785(5)	158(4)
O(7W)-H(7WB)...O(9W)	0.85(4)	2.031(16)	2.861(5)	165(5)
O(8)-H(8O)...O(12)^{x}	0.85(4)	1.741(14)	2.568(3)	166(4)
O(8W)-H(8WA)...O(4)^{iv}	0.85	1.96	2.796(4)	168.5
O(8W)-H(8WB)...O(6)	0.85	2.09	2.928(5)	168.8
O(9)-H(9O)...O(7)^{i}	0.85(4)	1.85(2)	2.649(3)	156(5)
O(9W)-H(9WA)...O(3)^{ix}	0.85(4)	2.353(19)	3.158(4)	159(4)
O(9W)-H(9WB)...O(12)	0.85(4)	1.986(13)	2.825(4)	168(5)
O(10W)-H(10A)...O(9W)^{xi}	0.85(4)	2.32(2)	3.103(6)	154(5)
O(10W)-H(10B)...O(9)	0.85(4)	1.993(17)	2.820(5)	164(5)
7				
O(1W)-H(1WA)...O(4)^{ii}	0.85 (4)	2.041(19)	2.851(3)	159(4)
O(1W)-H(1WA)...O(1W)^{ii}	0.851(4)	2.64(4)	3.140(5)	119(4)
O(1W)-H(1WB)...O(3)^{iii}	0.850(4)	1.957(17)	2.748(3)	154(3)
O(1)-H(1O)...O(4)^{iv}	0.858(4)	1.765(15)	2.610(4)	168(5)
O(2W)-H(2WA)...O(1)^{v}	0.85	1.96	2.766(4)	155.8
O(2W)-H(2WB)...O(2)^{vi}	0.85	2.07	2.860(4)	154.8
8				
O(1)-H(1O)...O(5)^{iv}	0.85	1.73	2.576(11)	177.0
O(4)-H(4O)...O(1)^{v}	0.85	1.94	2.793(12)	177.7
O(8)-H(8O)...O(5)^{vi}	0.85	1.60	2.454(11)	176.3
9				
O(1)-H(1O)...O(8)^{iv}	0.85	1.69	2.54(3)	173.3
O(4)-H(4O)...O(1)^{v}	0.85	2.03	2.87(2)	177.5

O(8)-H(8O)...O(5)[vi]	0.85	1.77	2.58(3)	158.0
10				
O(1W)-H(1W1)...O(2)[vi]	0.85(2)	1.907(14)	2.710(2)	158(3)
12				
O(1W)-H(1W1)...O(1)[iv]	0.85 (7)	1.92(4)	2.647(8)	143(6)
O(1W)-H(1W2)...O(4)[ix]	0.85 (7)	2.02(5)	2.658(7)	132(6)
O(2W)-H(2W1)...O(1)[x]	0.85 (7)	1.84(3)	2.663(7)	162(7)
O(2W)-H(2W2)...O(4)[xi]	0.85 (7)	2.04(6)	2.641(9)	127(6)
13				
O(1W)-H(1W)...O(1)[vii]	0.85(5)	2.13(3)	2.914(5)	153(6)
O(5)-H(5O)...O(4)[viii]	0.85 (5)	1.762(15)	2.607(5)	172(8)

[a] Symmetry operations: **For 1**, iv -x+1,-y,-z+1; v -x+1,-y-1,-z+1; vi -x,-y,-z. **For 2**, vi -x+2,-y+1,-z; vii x-1,y,z-1; viii x-1,-y+3/2,z-1/2. **For 3**, vii -x+1/2,y-1/2,z+1/2; viii x+1/2,-y+1/2,z+1; ix -x,-y,z-1/2; x -x+1/2,y+1/2,z-1/2. **For 4**, vii x-1/2,-y+1/2,z-1/2. **For 5**, vii x,-y+3/2,z-1/2; viii x+1,y,z; ix -x+2,-y+1,-z+1. **For 6**, i x-1,y,z; ii x+1,-y+3/2,z+1/2; iii -x+3,-y+1,-z+1; iv -x+2,y-1/2,-z+1/2; v x,-y+3/2,z+1/2; vi x,y-1,z; vii -x+1,y-1/2,-z+1/2; viii -x+2,-y+1,-z+1; ix x-1,-y+3/2,z-1/2; x -x+2,y+1/2,-z+1/2; xi -x+1,-y+1,-z. **For 7**, ii -x+1,-y+1,-z+1; iii x,y-1,z; iv -x+1,-y+2,-z+2; v x,y-1,z-1; vi -x+1,-y+2,-z+1. **For 8**, iv y-1,-x,z; v y,-x-1,z; vi y-1/2,-x+1/2,z+1/2. **For 9**, iv x,y+1,z; v -y+2,x,z; vi y+1/2,-x+1/2,z-1/2. **For 10**, vi x,-y+1,z-1/2. **For 12**, iv -x,-y+1,-z-1; ix x-1,y,z-1; x x+1,y,z; xi -x+1,-y+1,-z; **For 13**, vii -x,y-1,-z+1/2; viii -x+1/2,-y+1/2,-z+1.