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Electronic Supplementary Information (ESI)

Syntheses, structures and luminescent properties of lithium(I)-sulfonate complexes constructed from *ortho*-hydroxyl arenedisulfonic acids: structral evolutions tuned by pH value, coordination geometry and modes

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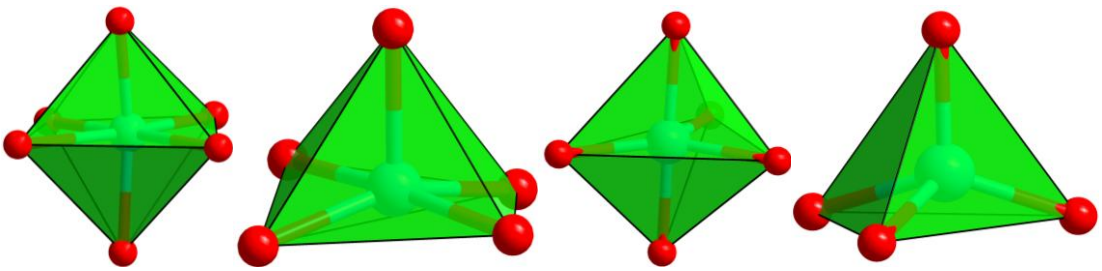

A **B** **C** **D**

Scheme S1. Observed polyhedra in complexes **1** (**A**), **2** (**B**), **3** (**A**, **B**, **C**, **D**), **4** (**D**), **5** (**A**, **D**), **6** (**C**, **D**).

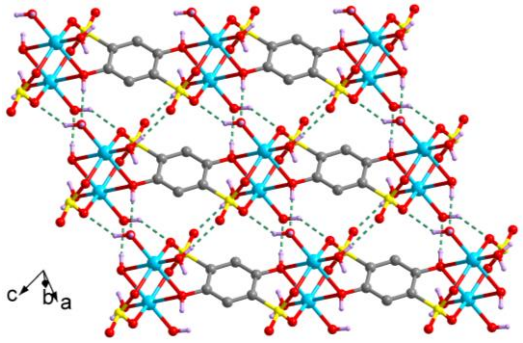

Figure S1. 2-D hydrogen-bonding layer of complex **1** in the *ac* plane.

The regular 3-D supramolecular network of complex **1** can be understood in the following manners. Firstly, the O2, O3 and O4 atoms of $\mathbf{H_2L1^{2-}}$ dianions form hydrogen bonds with H1w1, H2w2 and O2w of coordinated water molecules to generate 2-D hydrogen-bonding layer in the *ac* plane (Fig. S1, Table S2). Subsequently, the H1w2 and H2w1 of coordinated water molecules form hydrogen bonds with the O2, O3 and O4 atoms of $\mathbf{H_2L1^{2-}}$ dianions in the adjacent layers, thus giving rise to the 3-D supramolecular network (Fig. 1c, Table S2).

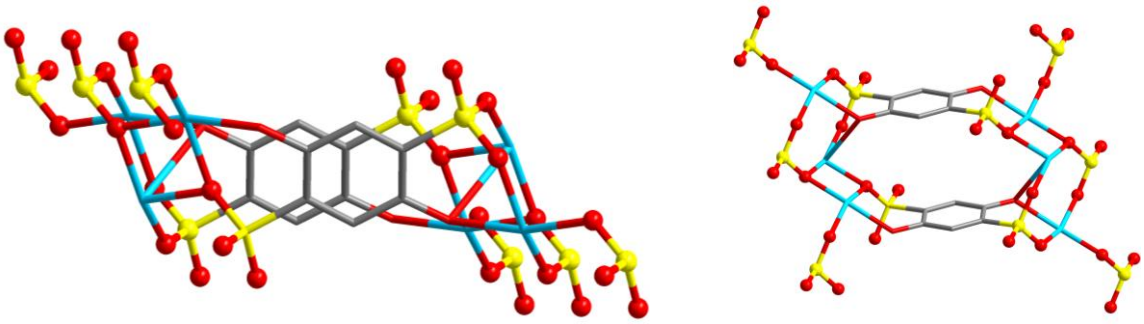

Figure S2. Side view (left) and planform (right) of the pseudo-sulfocalixarene motif in the layer of complex **2**.

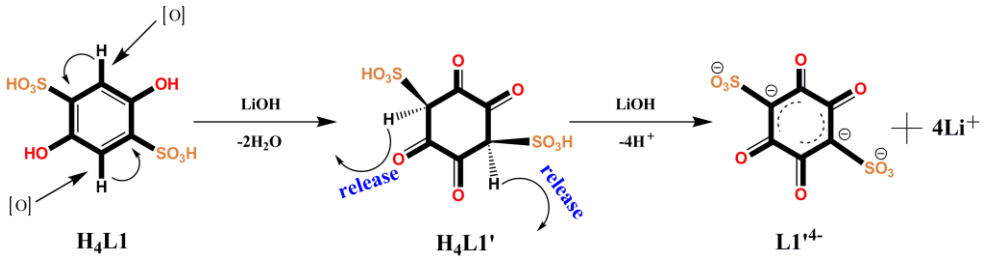

Figure S3. *In situ* formation of **H_4L1'**.

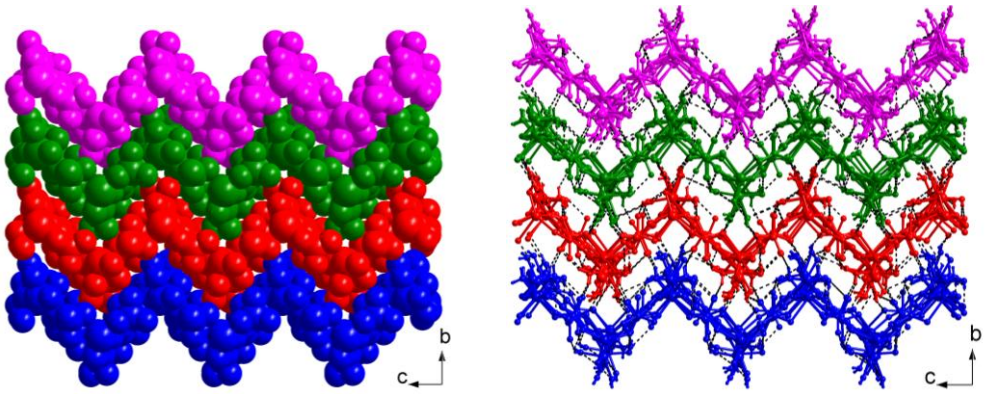

Figure S4. Representation of the 3-D supramolecular network of complex **3** extended by the hydrogen bonds (denoted as black dashed lines). Different layer was denoted as different color.

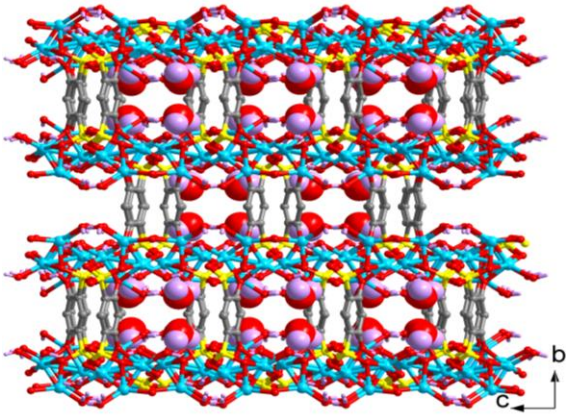

Figure S5. Illustration of the 3-D pillared layered structure along the *a*-axis with channels filled by free water molecules.

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Powder X-ray diffraction (PXRD)

Powder X-ray diffraction (PXRD) patterns for solid samples of **1**, **2** and **4-6** are measured at room temperature as illustrated in Figure S6. 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.

Thermogravimetric analysis

To examine the thermal stability of the complexes, in this study, their stabilities were analyzed on crystalline samples by thermogravimetric analyses (TGA) from room temperature to 800 °C at a rate of 10 °C min^{-1}, under N_2 atmosphere. As shown in Figure S7, the TGA curve indicates that complex **1** loses the coordinated water molecules from 50 to 126 °C with the observed weight loss of 20.64% (calcd 20.35%). Then, one sharp step corresponding to the loss of the organic components occurs in the temperature range 360 - 465 °C. Complex **2** loses the coordinated water molecules from 60 to 140 °C with the observed weight loss of 11.58% (calcd 11.33%). The organic components are then removed progressively from 365 to 760 °C. The sharp weight loss in complex **4** between 37 and 70 °C corresponds to the removal of the free NH_4^+ cations (obsd 6.57%, calcd 6.15%). Then, the organic components are removed progressively from 306 to 555 °C. Complex **5** can stable up to 103 ^oC, at which one free and one coordinated water molecules begin to gradually decompose and complete at 155 ^oC (obsd 11.68%, calcd 11.33%). The following gradually weight loss from 380 °C corresponds to the loss of the organic components. For complex **6**, the first sharp step between 35 and 150 °C corresponds to the release of one free and two coordinated water molecules with the observed weight loss of 26.56% (calcd 26.89%). Then, the following weight loss with the decomposing of organic components occurs in the temperature range 350 - 545 °C.

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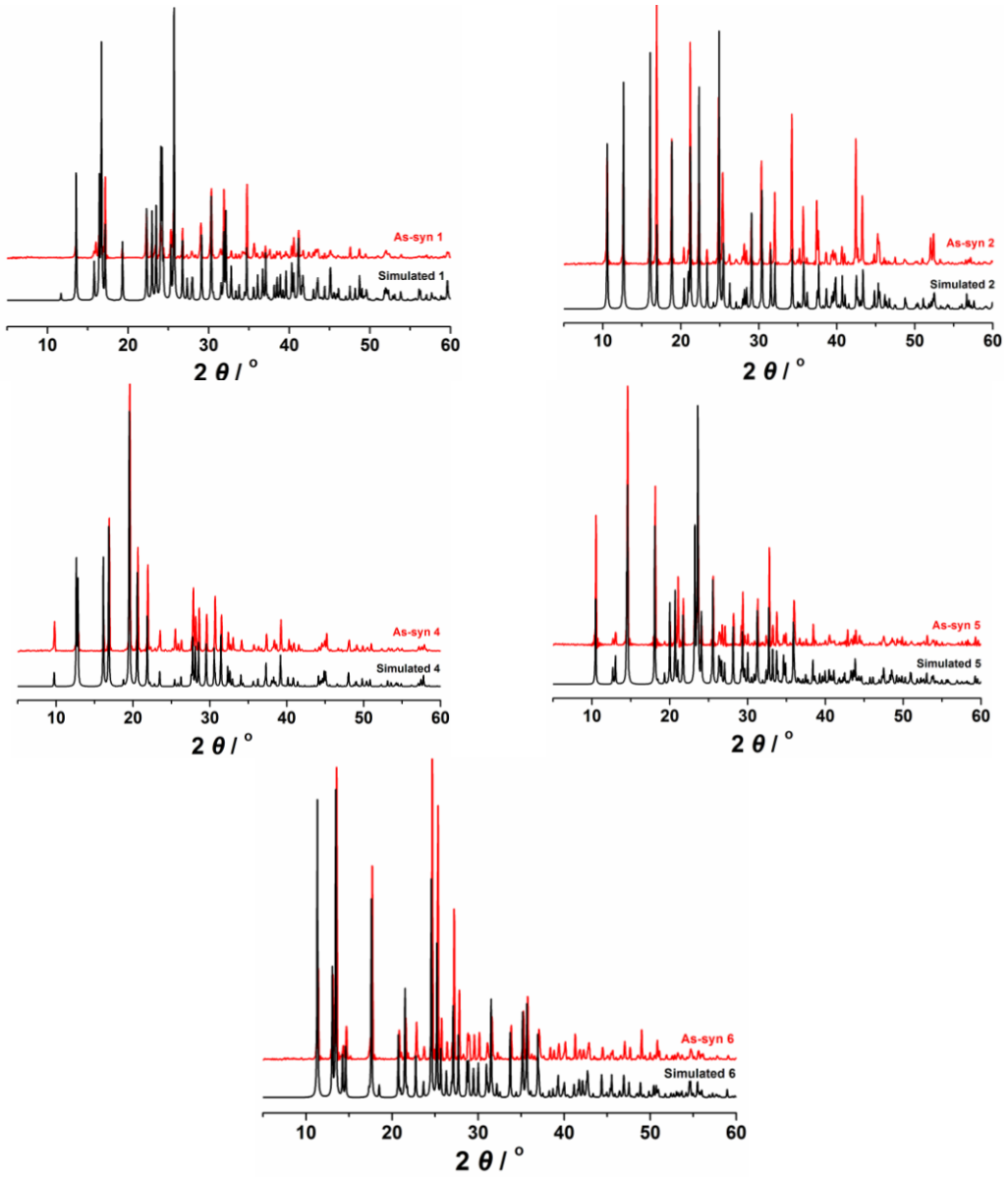

Figure S6. PXRD patterns for complexes **1**, **2** and **4-6**.

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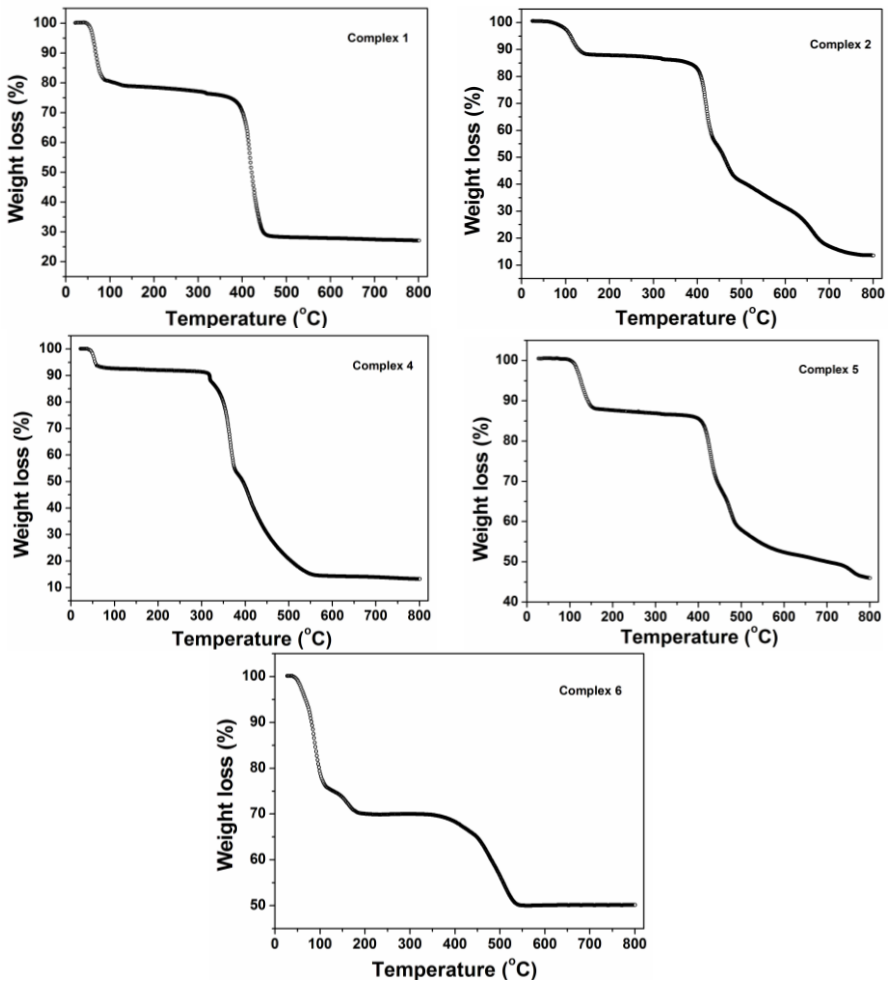

Figure S7. TG curves of complexes **1**, **2** and **4-6**.

Table S1 Selected Bond Distances (Å) and Angles (°) for Complexes **1-6**[a]

Complex **1**			
Li(1)-O(1W)	1.979(5)	Li(1)-O(2)^{i}	2.095(5)
Li(1)-O(1)	2.070(5)	Li(1)-O(4)^{ii}	2.394(5)
Li(1)-O(2W)	2.077(5)	Li(1)-O(4)^{iii}	2.479(5)
O(1W)-Li(1)-O(1)	97.7(2)	O(2W)-Li(1)-O(4)^{ii}	178.5(2)
O(1W)-Li(1)-O(2W)	92.8(2)	O(2)^{i}-Li(1)-O(4)^{ii}	81.63(17)
O(1)-Li(1)-O(2W)	97.0(2)	O(1W)-Li(1)-O(4)^{iii}	176.1(2)
O(1W)-Li(1)-O(2)^{i}	103.7(2)	O(1)-Li(1)-O(4)^{iii}	78.99(16)
O(1)-Li(1)-O(2)^{i}	153.6(3)	O(2W)-Li(1)-O(4)^{iii}	85.66(18)
O(2W)-Li(1)-O(2)^{i}	97.2(2)	O(2)^{i}-Li(1)-O(4)^{iii}	80.04(16)
O(1W)-Li(1)-O(4)^{ii}	88.39(19)	O(4)^{ii}-Li(1)-O(4)^{iii}	93.22(17)
O(1)-Li(1)-O(4)^{ii}	83.69(17)		
Complex **2**			
Li(1)-O(2)^{i}	2.000(5)	Li(1)-O(1)	2.099(5)
Li(1)-O(1W)	2.019(5)	Li(1)-O(4)	2.203(5)
Li(1)-O(1)^{ii}	2.045(5)		
O(2)^{i}-Li(1)-O(1W)	102.8(2)	O(1)^{ii}-Li(1)-O(1)	86.27(19)
O(2)^{i}-Li(1)-O(1)^{ii}	103.2(2)	O(2)^{i}-Li(1)-O(4)	83.76(18)
O(1W)-Li(1)-O(1)^{ii}	95.9(2)	O(1W)-Li(1)-O(4)	92.9(2)
O(2)^{i}-Li(1)-O(1)	153.0(3)	O(1)^{ii}-Li(1)-O(4)	167.3(3)
O(1W)-Li(1)-O(1)	101.2(2)	O(1)-Li(1)-O(4)	82.99(19)
Complex **3**			

Li(1)-O(1W)	1.965(12)	Li(4)-C(7)^{ii}	2.750(12)
Li(1)-O(4)	1.981(9)	Li(4)-C(7)	2.750(12)
Li(1)-O(1)	2.041(13)	Li(5)-O(8W)	1.829(15)
Li(1)-O(10)^{i}	2.070(9)	Li(5)-O(7W)	2.085(10)
Li(1)-O(3)^{i}	2.508(13)	Li(5)-O(7W)^{ii}	2.085(10)
Li(1)-Li(2)	3.133(14)	Li(5)-O(15)^{ii}	2.113(9)
Li(1)-Li(7)^{i}	3.364(13)	Li(5)-O(15)	2.113(9)
Li(2)-O(2W)	1.892(9)	Li(5)-Li(6)	3.152(8)
Li(2)-O(3W)	1.914(10)	Li(6)-O(15)	1.976(7)
Li(2)-O(4)	2.026(9)	Li(6)-O(9)^{iii}	2.063(7)
Li(2)-O(5)	2.181(9)	Li(6)-O(8)^{iii}	2.134(8)
Li(2)-O(1W)	2.337(11)	Li(6)-O(9W)	2.185(8)
Li(3)-O(4W)	1.902(6)	Li(6)-O(7W)	2.223(9)
Li(3)-O(5)	2.023(7)	Li(6)-O(13)	2.328(10)
Li(3)-O(11)	2.043(7)	Li(6)-Li(7)^{iii}	3.220(9)
Li(3)-O(6)	2.047(9)	Li(7)-O(11W)	2.012(10)
Li(3)-O(12)	2.105(8)	Li(7)-O(10W)	2.030(8)
Li(3)-Li(4)	3.334(8)	Li(7)-O(10)	2.067(8)
Li(4)-O(5W)	1.948(15)	Li(7)-O(9)	2.092(8)
Li(4)-O(6W)	1.973(13)	Li(7)-O(9W)^{iv}	2.154(9)
Li(4)-O(11)	2.002(9)		
Li(4)-O(11)^{ii}	2.002(9)		

O(1W)-Li(1)-O(4)	82.6(4)	O(5W)-Li(4)-C(7)	121.5(6)
O(1W)-Li(1)-O(1)	148.3(8)	O(6W)-Li(4)-C(7)	123.3(6)
O(4)-Li(1)-O(1)	86.4(4)	O(11)-Li(4)-C(7)	24.81(18)
O(1W)-Li(1)-O(10)^{i}	98.7(5)	O(11)^{ii}-Li(4)-C(7)	57.0(3)

O(4)-Li(1)-O(10)^{i}	177.7(7)	C(7)^{ii}-Li(4)-C(7)	32.81(18)
O(1)-Li(1)-O(10)^{i}	93.4(4)	O(8W)-Li(5)-O(7W)	105.0(4)
O(1W)-Li(1)-O(3)^{i}	118.8(7)	O(8W)-Li(5)-O(7W)^{ii}	105.0(4)
O(4)-Li(1)-O(3)^{i}	91.8(4)	O(7W)-Li(5)-O(7W)^{ii}	101.9(7)
O(1)-Li(1)-O(3)^{i}	91.1(5)	O(8W)-Li(5)-O(15)^{ii}	107.4(7)
O(10)^{i}-Li(1)-O(3)^{i}	85.9(4)	O(7W)-Li(5)-O(15)^{ii}	144.8(6)
O(2W)-Li(2)-O(3W)	116.6(5)	O(7W)^{ii}-Li(5)-O(15)^{ii}	82.7(2)
O(2W)-Li(2)-O(4)	120.3(5)	O(8W)-Li(5)-O(15)	107.4(7)
O(3W)-Li(2)-O(4)	122.2(4)	O(7W)-Li(5)-O(15)	82.7(2)
O(2W)-Li(2)-O(5)	96.5(4)	O(7W)^{ii}-Li(5)-O(15)	144.8(6)
O(3W)-Li(2)-O(5)	108.6(5)	O(15)^{ii}-Li(5)-O(15)	74.9(4)
O(4)-Li(2)-O(5)	74.8(3)	O(15)-Li(6)-O(9)^{iii}	175.4(5)
O(2W)-Li(2)-O(1W)	94.9(5)	O(15)-Li(6)-O(8)^{iii}	99.2(3)
O(3W)-Li(2)-O(1W)	93.2(4)	O(9)^{iii}-Li(6)-O(8)^{iii}	83.7(3)
O(4)-Li(2)-O(1W)	72.9(3)	O(15)-Li(6)-O(9W)	96.4(4)
O(5)-Li(2)-O(1W)	147.3(5)	O(9)^{iii}-Li(6)-O(9W)	80.5(2)
O(4W)-Li(3)-O(5)	97.9(3)	O(8)^{iii}-Li(6)-O(9W)	164.0(3)
O(4W)-Li(3)-O(11)	92.2(3)	O(15)-Li(6)-O(7W)	82.4(2)
O(5)-Li(3)-O(11)	169.4(3)	O(9)^{iii}-Li(6)-O(7W)	101.2(4)
O(4W)-Li(3)-O(6)	107.7(4)	O(8)^{iii}-Li(6)-O(7W)	88.6(4)
O(5)-Li(3)-O(6)	85.2(3)	O(9W)-Li(6)-O(7W)	97.0(3)
O(11)-Li(3)-O(6)	95.0(3)	O(15)-Li(6)-O(13)	83.4(4)
O(4W)-Li(3)-O(12)	111.0(4)	O(9)^{iii}-Li(6)-O(13)	93.1(3)
O(5)-Li(3)-O(12)	91.0(3)	O(8)^{iii}-Li(6)-O(13)	89.6(3)
O(11)-Li(3)-O(12)	82.2(3)	O(9W)-Li(6)-O(13)	88.7(4)
O(6)-Li(3)-O(12)	141.2(3)	O(7W)-Li(6)-O(13)	165.2(3)
O(5W)-Li(4)-O(6W)	112.1(6)	O(11W)-Li(7)-O(10W)	102.8(4)

O(5W)-Li(4)-O(11)	108.3(5)	O(11W)-Li(7)-O(10)	89.5(4)
O(6W)-Li(4)-O(11)	121.9(6)	O(10W)-Li(7)-O(10)	108.9(4)
O(5W)-Li(4)-O(11)^{ii}	108.3(5)	O(11W)-Li(7)-O(9)	146.8(4)
O(6W)-Li(4)-O(11)^{ii}	121.9(6)	O(10W)-Li(7)-O(9)	110.2(4)
O(11)-Li(4)-O(11)^{ii}	80.0(5)	O(10)-Li(7)-O(9)	76.7(3)
O(5W)-Li(4)-C(7)^{ii}	121.5(6)	O(11W)-Li(7)-O(9W)^{iv}	99.1(5)
O(6W)-Li(4)-C(7)^{ii}	123.3(6)	O(10W)-Li(7)-O(9W)^{iv}	97.4(4)
O(11)-Li(4)-C(7)^{ii}	57.0(3)	O(10)-Li(7)-O(9W)^{iv}	149.7(3)
O(11)^{ii}-Li(4)-C(7)^{ii}	24.81(18)	O(9)-Li(7)-O(9W)^{iv}	80.5(3)

Complex **4**

Li(1)-O(2)^{ii}	1.9291(19)	Li(1)-O(1)	1.9359(19)
O(2)^{i}-Li(1)-O(2)^{ii}	113.12(16)	O(2)^{ii}-Li(1)-O(1)	110.30(5)
O(2)^{i}-Li(1)-O(1)	105.55(5)	O(1)^{iii}-Li(1)-O(1)	112.15(15)

Complex **5**

Li(1)-O(1)	2.018(4)	Li(1)-O(8)^{ii}	2.468(5)
Li(1)-O(3)^{i}	2.026(4)	Li(2)-O(2)	1.902(4)
Li(1)-O(1W)	2.079(4)	Li(2)-O(6)^{iv}	1.961(4)
Li(1)-O(4)	2.155(4)	Li(2)-O(7)^{v}	1.964(4)
Li(1)-O(7)^{ii}	2.278(5)	Li(2)-O(3)^{vi}	1.993(4)
O(1)-Li(1)-O(3)^{i}	122.1(2)	O(3)^{i}-Li(1)-O(8)^{ii}	155.7(2)
O(1)-Li(1)-O(1W)	92.01(18)	O(1W)-Li(1)-O(8)^{ii}	81.01(15)
O(3)^{i}-Li(1)-O(1W)	96.55(18)	O(4)-Li(1)-O(8)^{ii}	96.44(16)
O(1)-Li(1)-O(4)	83.68(16)	O(7)^{ii}-Li(1)-O(8)^{ii}	76.28(14)
O(3)^{i}-Li(1)-O(4)	87.41(17)	O(2)-Li(2)-O(6)^{iv}	105.38(19)
O(1W)-Li(1)-O(4)	175.3(2)	O(2)-Li(2)-O(7)^{v}	109.7(2)

O(1)-Li(1)-O(7)^{ii}	157.3(2)	O(6)^{iv}-Li(2)-O(7)^{v}	119.5(2)
O(3)^{i}-Li(1)-O(7)^{ii}	79.62(15)	O(2)-Li(2)-O(3)^{vi}	131.9(2)
O(1W)-Li(1)-O(7)^{ii}	91.75(17)	O(6)^{iv}-Li(2)-O(3)^{vi}	102.68(18)
O(4)-Li(1)-O(7)^{ii}	91.50(17)	O(7)^{v}-Li(2)-O(3)^{vi}	88.53(16)
O(1)-Li(1)-O(8)^{ii}	82.25(15)		

Complex **6**

Li(1)-O(4)^{i}	1.926(3)	Li(2)-O(4)	2.027(4)
Li(1)-O(2)^{ii}	1.931(4)	Li(2)-O(4)^{i}	2.056(4)
Li(1)-O(1)	1.953(3)	Li(2)-O(3)^{i}	2.083(4)
Li(1)-O(1W)	1.995(4)	Li(2)-O(1)	2.532(4)
Li(2)-O(2W)	1.944(4)	Li(2)-Li(2)^{i}	2.554(7)
O(4)^{i}-Li(1)-O(2)^{ii}	112.61(17)	O(4)-Li(2)-O(4)^{i}	102.54(15)
O(4)^{i}-Li(1)-O(1)	96.13(14)	O(2W)-Li(2)-O(3)^{i}	96.42(16)
O(2)^{ii}-Li(1)-O(1)	98.01(15)	O(4)-Li(2)-O(3)^{i}	102.61(17)
O(4)^{i}-Li(1)-O(1W)	115.79(17)	O(4)^{i}-Li(2)-O(3)^{i}	92.14(14)
O(2)^{ii}-Li(1)-O(1W)	114.35(16)	O(2W)-Li(2)-O(1)	89.32(14)
O(1)-Li(1)-O(1W)	117.38(17)	O(4)-Li(2)-O(1)	84.27(13)
O(2W)-Li(2)-O(4)	112.76(17)	O(4)^{i}-Li(2)-O(1)	77.16(13)
O(2W)-Li(2)-O(4)^{i}	140.7(2)	O(3)^{i}-Li(2)-O(1)	168.42(17)

[a] Symmetry transformations used to generate equivalent atoms: (i) -x+2,-y,-z+2; (ii) x+1,y,z-1; (iii) -x+1,-y,-z+3 for **1**; (i) -x+1,-y+1,-z+2; (ii) -x,-y+1,-z+2 for **2**; (i) -x+1/2,-y+1/2,z+1/2; (ii) -x,y,z; (iii) x,y,z+1; (iv) x,y,z-1 for **3**; (i) -x+1/2,y-1/2,z; (ii) x,y-1/2,-z+3/2; (iii) -x+1/2,y+0,-z+3/2 for **4**; (i) -x,-y,-z+2; (ii) -x+1,-y,-z+1; (iv) x,y,z+1; (v) -x+1,-y+1,-z+1; (vi) -x,-y+1,-z+2 for **5**; (i) -x+1,-y,-z-1; (ii) -x+1/2,-y,z+1/2 for **6**.

Table S2 Selected Hydrogen Bond Parameters for Complexes **1-6**[a]

D-H...A	d(H...A) /Å	d(D...A) /Å	<(DHA)/^{o}
	Complex **1**		
O(1W)-H(1W1)...O(3)^{v}	2.09(3)	2.934(3)	175(4)
O(1W)-H(1W2)...O(3)^{vi}	2.05(3)	2.895(3)	172(3)
O(2W)-H(2W1)...O(1)^{vii}	1.92(3)	2.764(3)	172(3)
O(2W)-H(2W2)...O(2)^{viii}	2.16(2)	2.883(3)	143(3)
O(4)-H(4O)...O(2W)^{ix}	1.89(3)	2.730(3)	168(3)
	Complex **2**		
O(1W)-H(1W1)...O(2)^{iv}	1.94(3)	2.755(3)	161(3)
O(1W)-H(1W2)...O(3)^{v}	2.03(2)	2.794(3)	149(3)
O(4)-H(4O)...O(1W)^{vi}	1.93(3)	2.762(3)	168(4)
	Complex **3**		
O(1W)-H(1W1)...O(3W)	2.33(8)	3.101(6)	152(15)
O(1W)-H(1W1)...O(2W)	2.57(12)	3.130(10)	125(12)
O(1W)-H(1W2)...O(3)^{vi}	2.34(16)	2.869(7)	121(15)
O(2W)-H(2W1)...O(2)^{i}	2.24(3)	2.990(5)	149(5)
O(2W)-H(2W2)...O(12)	2.27(4)	2.852(4)	126(4)
O(2W)-H(2W2)...O(3W)^{vi}	2.65(4)	3.134(5)	118(3)
O(3W)-H(3W1)...O(1)^{vii}	2.26(3)	3.061(6)	156(5)
O(3W)-H(3W2)...O(13)^{viii}	2.17(3)	2.942(4)	150(6)
O(4W)-H(4W1)...O(8)^{vi}	2.089(12)	2.935(5)	175(6)
O(4W)-H(4W2)...O(5)	2.37(5)	2.961(5)	128(5)
O(5W)-H(5W)...O(6)	2.062(7)	2.916(3)	174.5(17)
O(6W)-H(6W)...O(8)^{ix}	1.98	2.832(3)	175.9

O(7W)-H(7W1)...O(14)^{x}	2.11(3)	2.847(4)	145(5)
O(7W)-H(7W2)...O(7)^{iii}	2.39(3)	3.123(6)	144(4)
O(8W)-H(8W)...O(7)^{xi}	2.12(5)	2.722(4)	128(6)
O(9W)-H(9W1)...O(7)^{x}	1.97(3)	2.734(5)	150(5)
O(9W)-H(9W2)...O(14)	2.13(3)	2.902(5)	151(6)
O(10W)-HAW2...O(3)^{xii}	2.36(7)	2.935(5)	125(7)
O(10W)-HAW1...O(14)^{xiii}	2.04(4)	2.839(4)	155(8)
O(11W)-HBW2...O(9W)^{iv}	2.58(11)	3.172(11)	127(12)
O(11W)-HBW1...O(1)^{v}	2.06(8)	2.822(8)	147(12)
Complex **4**			
O(4)-H(4O)...O(3)^{vi}	1.88(2)	2.704(2)	166(2)
N(1)-H(1N1)...O(1)	2.00(2)	2.834(2)	160.8(19)
N(1)-H(1N2)...O(2)^{vii}	2.20(2)	2.868(2)	135.3(18)
N(1)-H(1N2)...O(4)^{vii}	2.44(2)	3.171(2)	144.6(17)
Complex **5**			
O(1W)-H(1W2)...O(5)^{ix}	2.06(2)	2.883(2)	166(2)
O(1W)-H(1W1)...O(1)^{x}	2.25(2)	2.981(2)	144(3)
O(2W)-H(2W2)...O(5)^{iii}	2.05(3)	2.886(3)	173(3)
O(2W)-H(2W1)...O(6)^{xi}	2.09(2)	2.933(3)	172(3)
O(4)-H(4O)...O(2W)	1.76(2)	2.611(2)	177(3)
O(8)-H(8O)...O(1W)^{viii}	1.90(2)	2.732(2)	169(3)
Complex **6**			
O(1W)-H(1W1)...O(2W)^{iii}	2.02	2.818(2)	164.5
O(1W)-H(1W2)...O(3W)^{v}	2.06	2.861(2)	164.6
O(2W)-H(2W1)...O(3)^{vi}	1.97	2.789(2)	174.4
O(2W)-H(2W2)...O(3)^{i}	2.19	3.0033(19)	174.6
O(3W)-H(3W1)...O(2)^{ii}	2.08	2.897(2)	170.5

O(3W)-H(3W2)...O(2W)[vii]	2.05	2.866(2)	170.5

[a] Symmetry transformations used to generate equivalent atoms: (v) x,y,z-1; (vi) -x+2,-y+1,-z+2; (vii) -x+1,-y+1,-z+2; (viii) x-1,y,z; (ix) x,y,z+1 for **1**; (iv) x-1,y-1,z; (v) x,y-1,z; (vi) x+1,y,z for **2**; (i) -x+1/2,-y+1/2,z+1/2; (iv) x,y,z-1; (v) -x+1/2,-y+1/2,z-1/2; (vi) x,-y,z+1/2; (vii) -x+1/2,y-1/2,z; (viii) x,-y,z-1/2; (ix) -x,-y,z+1/2; (x) x,-y+1,z+1/2; (xi) -x,-y+1,z+1/2; (xii) -x+1/2,y+1/2,z; (xiii) x,-y+1,z-1/2 for **3**; (vi) x,-y+3/2,z-1/2; (vii) -x+1/2,-y+3/2,-z+1 for **4**; (iii) x,y-1,z; (viii) x,y,z-1; (ix) x,y-1,z+1; (x) -x+1,-y,-z+2; (xi) -x,-y,-z+1 for **5**; (i) -x+1,-y,-z-1; (ii) -x+1/2,-y,z+1/2; (iii) -x+1/2,-y,z-1/2; (v) x,y,z-1; (vi) x,y,z+1; (vii) -x+1,-y,-z for **6**.