# **Supporting Information**

## A series of coordination complexes based on unsymmetrical multicarboxylate ligands: syntheses, structures and properties

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Fig. S1 The TG curves of 1.



Fig. S2 The TG curves of 2.



Fig. S3 The TG curves of 3.



Fig. S4 The TG curves of 4.



Fig. S5 The TG curves of 5.



Fig. S6 The TG curves of 6.



Fig. S7 Emission spectra of  $H_2L^1$  and  $H_3L^2$  in the solid state at room temperature.



Fig. S8 Emission spectra of compound 1 and 5 in the solid state at room temperature.



Fig. S9 Emission spectra of compound 2, 4 and 6 in the solid state at room temperature.

Complex 1				
Zn(1)-O(1)	2.028(3)	C(17)-O(3)	1.376(5)	
Zn(1)-O(1W)	2.061(3)	C(20)-O(3)	1.444(5)	
Zn(1)-N(2)	2.097(3)	Zn(1)-O(4)#1	2.323(3)	
Zn(1)-O(5)	2.127(3)	O(4)-Zn(1)#1	2.323(3)	
Zn(1)-N(1)	2.206(3)	O(5)-Zn(1)#1	2.127(3)	
O(1)-Zn(1)-O(1W)	89.73(11)	O(1)-Zn(1)-N(2)	93.47(12)	
O(1W)-Zn(1)-N(2)	106.76(12)	O(1W)-Zn(1)-C(21)#1	135.33(12)	
O(5)#1-Zn(1)-C(21)#1	29.93(11)	O(1)-Zn(1)-C(21)#1	100.50(12)	
O(1W)-Zn(1)-O(5)#1	105.72(11)	N(2)-Zn(1)-O(5)#1	145.05(12)	
O(1)-Zn(1)-O(5)#1	99.24(11)	N(2)-Zn(1)-C(21)#1	115.73(13)	
O(1)-Zn(1)-N(1)	170.81(12)	N(1)-Zn(1)-C(21)#1	84.95(12)	
O(1W)-Zn(1)-N(1)	91.52(12)	N(1)-Zn(1)-O(4)#1	84.57(12)	
O(5)#1-Zn(1)-O(4)#1	58.56(10)	N(2)-Zn(1)-O(4)#1	87.82(11)	
O(1W)-Zn(1)-O(4)#1	163.75(10)	O(1)-Zn(1)-O(4)#1	96.64(12)	
O(5)#1-Zn(1)-N(1)	89.19(11)	N(2)-Zn(1)-N(1)	77.46(12)	

Table S1 Selected bond lengths (Å) and angles (°) for complexes 1-6.

Table S2 Selected bond lengths (A	(°) and angles (°)	for complexes 2.
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Complex 2			
Cd(2)-O(6)#4	2.310(3)	Cd(1)-O(6)#5	2.267(3)
Cd(1)-O(1)#6	2.317(3)	Cd(1)-O(1)#2	2.317(3)
Cd(1)-O(4)#5	2.352(3)	Cd(2)-O(2)#6	2.303(4)
O(1W)-Cd(2)	2.290(4)	O(6)-Cd(2)#4	2.310(3)
O(6)-Cd(1)	2.267(3)	O(6)-Cd(2)	2.261(3)
O(5)-Cd(2)	2.271(4)	O(4)-Cd(1)	2.352(3)
O(2)-Cd(2)#3	2.303(4)	O(1)-Cd(1)#2	2.317(3)
C(7)-O(1)-Cd(1)#2	130.5(3)	C(7)-O(2)-Cd(2)#3	128.1(3)
C(10)-O(4)-Cd(1)	127.8(3)	C(10)-O(5)-Cd(2)	136.6(3)
Cd(2)-O(6)-Cd(1)	108.55(12)	Cd(2)-O(6)-Cd(2)#4	93.97(11)
Cd(1)-O(6)-Cd(2)#4	134.67(14)	Cd(2)-O(6)-H(5)	102.0
Cd(1)-O(6)-H(5)	96.1	Cd(2)#4-O(6)-H(5)	117.5
Cd(2)-O(1W)-H(1)	120.3	Cd(2)-O(1W)-H(2)	83.3
O(6)#5-Cd(1)-O(6)	180.00(17)	O(6)#5-Cd(1)-O(1)#6	80.34(12)
O(6)-Cd(1)-O(1)#6	99.66(12)	O(6)#5-Cd(1)-O(1)#2	99.66(12)
O(6)-Cd(1)-O(1)#2	80.34(12)	O(1)#6-Cd(1)-O(1)#2	180.00(13)
O(6)#5-Cd(1)-O(4)	87.65(12)	O(6)-Cd(1)-O(4)	92.35(12)
O(1)#6-Cd(1)-O(4)	94.53(13)	O(1)#2-Cd(1)-O(4)	85.47(13)
O(6)#5-Cd(1)-O(4)#5	92.35(12)	O(6)-Cd(1)-O(4)#5	87.65(12)
O(6)-Cd(2)-O(1W)	91.28(13)	O(6)-Cd(2)-O(2)#6	88.69(12)
O(5)-Cd(2)-O(2)#6	98.27(16)	O(1W)-Cd(2)-O(2)#6	173.48(16)

### Complex 3 Co(1)-O(2)#2 2.111(3) Co(1)-O(2)#3 2.111(3) Co(1)-O(4) 2.124(3) 2.124(3)Co(1)-O(4)#4 Co(1)-O(6) Co(1)-O(6)#4 2.145(3) 2.145(3) Co(2)-O(1)#3 2.076(3) Co(2)-O(5) 2.087(3)Co(2)-O(1W) 2.101(3) Co(2)-O(6)2.106(2)Co(2)-O(6)#5 2.134(3)O(1)-Co(2)#6 2.076(3)O(2)-Co(1)#2 2.111(3) O(6)-Co(2)#5 2.134(3) O(2)#2-Co(1)-O(2)#3 180.000(1) O(2)#2-Co(1)-O(4) 83.23(11) O(2)#3-Co(1)-O(4) 96.77(11) O(2)#2-Co(1)-O(4)#4 96.77(11) O(2)#3-Co(1)-O(4)#4 83.23(11) O(4)-Co(1)-O(4)#4 180.000(1) O(2)#2-Co(1)-O(6) 83.67(10) O(2)#3-Co(1)-O(6) 96.33(10) O(4)-Co(1)-O(6)91.83(10) O(4)#4-Co(1)-O(6) 88.17(10) O(2)#2-Co(1)-O(6)#4 96.33(10) O(2)#3-Co(1)-O(6)#4 83.67(10) O(4)-Co(1)-O(6)#4 88.17(10) O(4)#4-Co(1)-O(6)#4 91.83(10) 180.000(1) O(1)#3-Co(2)-O(5) O(6)-Co(1)-O(6)#4 99.51(13) O(1)#3-Co(2)-O(1W) O(5)-Co(2)-O(1W) 174.33(12) 85.13(13) O(1)#3-Co(2)-O(6) 90.70(11) O(5)-Co(2)-O(6) 92.77(11) O(1W)-Co(2)-O(6) 92.34(11) O(1)#3-Co(2)-O(6)#5 88.34(11) O(5)-Co(2)-O(6)#5 172.12(12) O(1W)-Co(2)-O(6)#5 87.00(11) O(6)-Co(2)-O(6)#5 87.76(10) O(1)#3-Co(2)-N(1) 82.18(13) O(5)-Co(2)-N(1) 83.32(12) O(1W)-Co(2)-N(1)95.20(13) O(6)-Co(2)-N(1) O(6)#5-Co(2)-N(1) 97.20(12) 171.17(12)

Table S3 Selected bond lengths (Å) and angles (°) for complexes 3.

## Table S4 Selected bond lengths (Å) and angles (°) for complexes 4.

Complex 4			
Cd(1)-O(6)	2.293(5)	Cd(1)-O(1)	2.335(5)
Cd(1)-O(5)#3	2.338(5)	Cd(2)-O(6)	2.325(4)
Cd(2)-O(6)#4	2.325(4)	O(2)-Cd(3)	2.307(5)
O(4)-Cd(3)#6	2.430(7)	O(5)-Cd(1)#6	2.338(5)
O(5)-Cd(3)#6	2.521(6)	N(4)-Cd(1)-O(6)	92.33(19)
N(4)-Cd(1)-N(9)#2	102.2(2)	O(6)-Cd(1)-N(9)#2	103.73(19)
N(4)-Cd(1)-O(1)	167.9(2)	O(6)-Cd(1)-O(1)	96.28(17)
N(9)#2-Cd(1)-O(1)	84.05(19)	N(4)-Cd(1)-O(5)#3	89.2(2)
O(6)-Cd(1)-O(5)#3	77.26(18)	N(9)#2-Cd(1)-O(5)#3	168.4(2)
O(1)-Cd(1)-O(5)#3	84.4(2)	O(6)-Cd(1)-N(3)	164.80(19)
O(1)-Cd(1)-N(3)	77.9(2)	O(5)#3-Cd(1)-N(3)	88.1(2)
O(6)-Cd(2)-O(6)#4	180.0(2)	O(6)-Cd(2)-N(7)#4	90.40(18)
O(6)#4-Cd(2)-N(7)#4	89.60(18)	O(6)-Cd(2)-N(7)	89.60(18)
O(6)#4-Cd(2)-N(7)	90.40(18)	O(6)-Cd(2)-N(5)	92.26(18)
O(6)#4-Cd(2)-N(5)	87.74(18)	O(6)#4-Cd(2)-N(5)#4	92.26(18)
C(10)-O(4)-Cd(3)#6	94.5(5)	C(10)-O(5)-Cd(1)#6	146.9(5)
O(6)-Cd(3)-N(6)#7	132.6(2)	O(6)-Cd(3)-O(2)	88.55(19)
N(8)-Cd(3)-O(2)	173.4(2)	N(6)#7-Cd(3)-O(2)	81.78(19)
O(6)-Cd(3)-O(4)#3	126.82(19)	N(8)-Cd(3)-O(4)#3	89.3(2)
O(4)#3-Cd(3)-O(5)#3	52.80(19)	O(2)-Cd(3)-O(4)#3	96.8(2)
O(6)-Cd(3)-O(5)#3	74.08(17)	N(8)-Cd(3)-O(5)#3	86.4(2)
N(6)#7-Cd(3)-O(5)#3	153.3(2)	O(2)-Cd(3)-O(5)#3	99.24(18)

#### Complex 5 O(2)-Zn(1) 1.950(4) O(7B)-Zn(1)#1 2.025(11) O(6B)-Zn(1)#1 Zn(1)-O(6B)#3 2.017(11) 2.017(11) Zn(1)-O(7B)#3 2.025(11) C(17)-N(1) 1.2582(18) C(1)-C(6) 1.370(6) C(1)-C(2)1.390(6) 1.497(6) C(1)-C(7)C(2)-C(3)1.374(7) C(5)-O(5) 1.363(6) C(7)-O(2) 1.256(6) C(7)-O(1) 1.259(6) C(8)-O(4) 1.196(7) C(8)-O(3) 1.308(7) C(9)-O(5) 1.442(6) O(7B)-C(11)-Zn(1)#1 47.5(7) O(6B)-C(11)-Zn(1)#1 48.6(7) O(7A)-C(11)-Zn(1)#1 73.8(6) O(6A)-C(11)-Zn(1)#1 70.5(8) C(17)-N(1)-Zn(1) C(21)-N(1)-Zn(1)125.09(15) 120.92(15) C(7)-O(2)-Zn(1)C(11)-O(7B)-Zn(1)#1 115.0(3) 110.4(10) O(6B)-O(7B)-Zn(1)#1 C(11)-O(6B)-Zn(1)#1 106.8(9) 67.7(6) O(7B)-O(6B)-Zn(1)#1 68.3(6) O(2)-Zn(1)-O(6B)#3 140.0(4) 99.1(4) O(2)-Zn(1)-N(1) 105.99(14) O(2)-Zn(1)-O(7B)#3 O(6B)#3-Zn(1)-N(1) O(7B)#3-Zn(1)-N(1) 142.1(4) 101.6(4) O(2)-Zn(1)-N(2) 100.01(16) O(6B)#3-Zn(1)-N(2) 103.0(3) 121.1(3) O(7B)#3-Zn(1)-N(2) 103.2(4) O(2)-Zn(1)-C(11)#3 O(6B)#3-Zn(1)-C(11)#3 24.6(3) O(7B)#3-Zn(1)-C(11)#3 22.1(3)

### Table S5 Selected bond lengths (Å) and angles (°) for complexes 5.

Table S6 Selected bond lengths (A	Å) and angles (°)	) for complexes 6.
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Complex 6			
Cd(1)-O(2)	2.327(7)	Cd(1)-O(2W)	2.338(7)
Cd(1)-O(1W)	2.374(11)	Cd(1)-O(3W)	2.390(18)
Cd(1)-O(1)	2.515(13)	Cd(2)-O(6)#2	2.248(7)
Cd(2)-O(6)#3	2.248(7)	Cd(2)-O(3)#4	2.336(7)
Cd(2)-O(3)	2.336(6)	Cd(2)-O(4)#4	2.441(8)
Cd(2)-O(4)	2.441(8)	O(6)-Cd(2)#3	2.248(7)
C(11)-O(6)-Cd(2)#3	108.9(6)	C(8)-O(4)-Cd(2)	89.9(6)
C(7)-O(1)-Cd(1)	88.4(11)	O(4)#4-Cd(2)-O(4)	87.9(4)
O(3)-Cd(2)-O(4)	54.5(2)	O(3)#4-Cd(2)-O(4)	86.3(3)
O(6)#3-Cd(2)-O(4)	98.5(3)	O(6)#2-Cd(2)-O(4)	142.9(2)
O(3)-Cd(2)-O(4)#4	86.3(3)	O(3)#4-Cd(2)-O(4)#4	54.5(2)
O(6)#3-Cd(2)-O(4)#4	142.9(3)	O(6)#2-Cd(2)-O(4)#4	98.5(3)
O(3)#4-Cd(2)-O(3)	126.8(3)	O(6)#3-Cd(2)-O(3)	127.0(3)
O(6)#2-Cd(2)-O(3)	89.3(3)	O(6)#3-Cd(2)-O(3)#4	89.3(3)
O(6)#2-Cd(2)-O(3)#4	127.0(3)	O(6)#2-Cd(2)-O(6)#3	97.9(5)
O(3W)-Cd(1)-O(1)	63.5(6)	O(1W)-Cd(1)-O(1)	106.6(4)
O(2W)-Cd(1)-O(1)	129.4(3)	O(2)-Cd(1)-O(1)	53.3(3)

D-H···A	d (H···A)	d (D…A)	∠D-H… A
1			
O(1w)-H(1)···O(5)	1.89	2.725	169
O(1w)-H(2)···O(1)	2.52	2.884	107
O(1w)-H(2)···O(2)	1.84	2.620	151
C(5)-H(5A)···O(5)	2.59	3.391	144
C(9)-H(9A)····O(4)	2.38	3.106	134
2			
O(1w)-H(1)···O(3)	2.44	3.050(6)	129
O(1w)-H(1)···O(4)	2.01	2.772(6)	149
O(1w)-H(2)···O(2)	2.33	3.167(8)	168
O(1w)-H(2)…O(2W)	2.45	2.862(8)	112
O(2w)-H(3)…O(2)	1.94	2.706(7)	149
O(2w)-H(4)…O(2W)	2.12	2.871(8)	148
O(6)-H(5)····O(1)	2.59	2.957(5)	107
O(6)-H(5)…O(2W)	2.43	3.198(7)	150
C(11)-H(11A)····O(5)	2.44	3.078(9)	126
C(15)-H(15A)····O(1)	2.38	3.254(8)	157
3			
O(1W)-H(1)…O(2W)	2.08	2.813(9)	144
O(1W)-H(2)···O(3)	2.55	3.006(5)	115
O(6)-H(5)…O(2W)	2.51	3.296(8)	154
C(11)-H(11A)····O(2)	2.22	3.121(7)	163
C(15)-H(15A)····O(5)	2.27	2.873(8)	122
4			
O(1W)-H(2)…O(1W)	1.81	2.61(2)	157
C(11)-H(11A)····O(1)	2.48	2.961(11)	112
C(14)-H(14A)····O(2)	2.34	2.913(10)	119
C(16)-H(16A)…O(1w)	2.50	3.366(18)	156
C(17)-H(17A)····O(1)	2.45	3.037(10)	121
5			
O(3)-H(1)···O(1)	1.81	2.681(5)	165
C(2)-H(2A)····O(3)	2.42	2.736(6)	100
C(18)-H(18A)····O(7A)	2.20	3.103(12)	165
C(18)-H(18A)····O(7B)	2.46	3.282(14)	147
6			
C(10)-H(10A)···O(2)	2.55	3.402(18)	147
C(12)-H(12A)····O(7)	2.32	3.158(14)	150
C(13)-H(13A)····O(1W)	2.32	3.234(16)	165
C(15)-H(15A)····O(4W)	2.24	3.044(14)	145
C(15)-H(15A)····O(1)	2.52	3.099(18)	121
C(17)-H(17A)···O(4)	2.55	3.221(14)	126

Table S7 Distances (Å) and Angles (°) of Hydrogen bonds for complexes 1-6.