## **ELECTRONIC SUPPORTING INFORMATION**

## A variety of metal-organic and supramolecular networks constructed from a new flexible multifunctional building block bearing picolinate and terephthalate functionalities: hydrothermal self-assembly, structural features, magnetic and luminescent properties

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1					
Co(1)-O(1)	2.033(2)	Co(1)-O(1)#1	2.033(2)	Co(1)-O(7)	2.189(2)
Co(1)-O(7)#1	2.189(2)	Co(1)-N(1)	2.071(3)	Co(1)-N(1)#1	2.071(3)
O(1) -Co(1)-N(1)	79.63(10)	O(1)-Co(1)-N(1)#1	100.37(10)	O(1)-Co(1)-O(7)	86.62(9)
O(1)-Co(1)-O(7)#1	93.38(9)	N(1)-Co(1)-O(7)	89.03(10)	N(1)-Co(1)-O(7)#1	90.97(10)
2					
Cd(1)-O(1)	2.288(2)	Cd(1)-O(1)#3	2.288(2)	Cd(1)-O(5)#1	2.277(2)
Cd(1)-O(5)#2	2.277(2)	Cd(1)-N(1)#1	2.324(2)	Cd(1)-N(1)#2	2.324(2)
Cd(2)-O(2)	2.218(2)	Cd(2)-O(2)#4	2.218(2)	Cd(2)-O(5)#2	2.282(2)
Cd(2)-O(5)#5	2.282 (2)	Cd(2)-O(7)	2.423(2)	Cd(2)-O(7)#4	2.423(2)
O(5)#1-Cd(1)-O(5)#2	171.73(9)	O(5)#1-Cd(1)-O(1)#3	89.98(7)	O(5)#2-Cd(1)-O(1)#3	96.29(7)
O(5)#1-Cd(1)-O(1)	96.29(7)	O(5)#2-Cd(1)-O(1)	89.98(7)	O(1)#3-Cd(1)-O(1)	81.55(10)
O(5)#1-Cd(1)-N(1)#1	71.57(6)	O(5)#2-Cd(1)-N(1)#1	103.06(7)	O(1)#3-Cd(1)-N(1)#1	159.16(7)
O(1)-Cd(1)-N(1)#1	90.70(8)	O(5)#1-Cd(1)-N(1)#2	103.06(7)	O(1)-Cd(1)-N(1)#2	159.16(7)
N(1)#1-Cd(1)-N(1)#2	102.62(11)	O(2)-Cd(2)-O(2)#4	141.28(11)	O(2)-Cd(2)-O(5)#2	95.95(7)
O(2)-Cd(2)-O(5)#5	110.06(7)	O(2)#4-Cd(2)-O(5)#5	95.95(7)	O(5)#2-Cd(2)-O(5)#5	95.29(10)
O(2)-Cd(2)-O(7)	86.31(9)	O(2)#4-Cd(2)-O(7)	72.35(8)	O(5)#2-Cd(2)-O(7)	77.93(8)
O(5)#5-Cd(2)-O(7)	163.01(9)	O(2)-Cd(2)-O(7)#4	72.35(8)	O(2)#4-Cd(2)-O(7)#4	86.31(9)
O(5)#2-Cd(2)-O(7)#4	163.00(9)	O(5)#5-Cd(2)-O(7)#4	77.93(8)	O(7)-Cd(2)-O(7)#4	112.63(14)
3					
Mn(1)-O(2)	2.132(2)	Mn(1)-O(2)#1	2.132(2)	Mn(1)-O(5)#2	2.227(2)
Mn(1)-O(5)#3	2.227(2)	Mn(1)-O(7)	2.313(3)	Mn(1)-O(7)#1	2.313(3)
Mn(2)-O(1)#4	2.149(2)	Mn(2)-O(1)#5	2.149(2)	Mn(2)-O(5)	2.203(2)
Mn(2)-O(5)#1	2.203(2)	Mn(2)-N(1)	2.280(3)	Mn(2)-N(1)#1	2.280(3)
O(2)#1-Mn(1)-O(2)	139.72(14)	O(2)#1-Mn(1)-O(5)#2	92.71(9)	O(2)-Mn(1)-O(5)#2	113.84(9)
O(5)#2-Mn(1)-O(5)#3	98.07(11)	O(2)#1-Mn(1)-O(7)	73.28(10)	O(2)-Mn(1)-O(7)	83.80(11)
O(5)#2-Mn(1)-O(7)	162.28(11)	O(5)#3-Mn(1)-O(7)	78.51(9)	O(5)#3-Mn(1)-O(7)#1	162.27(11)
O(7)-Mn(1)-O(7)#1	109.87(16)	O(1)#4-Mn(2)-O(1)#5	84.82(13)	O(1)#4-Mn(2)-O(5)#1	90.03(9)
O(1)#4-Mn(2)-O(5)	95.60(9)	O(1)#5-Mn(2)-O(5)	90.03(9)	O(5)#1-Mn(2)-O(5)	172.38(11)
O(1)#4-Mn(2)-N(1)#1	162.69(10)	O(1)#5-Mn(2)-N(1)#1	91.27(9)	N(1)#1-Mn(2)-N(1)	97.15(13)
O(5)-Mn(2)-N(1)#1	101.27(9)	O(5)#1-Mn(2)-N(1)	101.27(9)	O(5)-Mn(2)-N(1)	73.54(9)
4					
Mn(1)-O(1)	2.154(3)	Mn(1)-O(3)#1	2.103(3)	Mn(1)-O(7)	2.130(3)
Mn(1)-N(1)	2.243(3)	Mn(1)-N(2)	2.280(3)	Mn(1)-N(3)	2.336(3)
Mn(2)-O(4)	2.210(3)	Mn(2)-O(4)#4	2.210(3)	Mn(2)-O(5)#2	2.157(3)
Mn(2)-O(5)#3	2.157(3)	Mn(2)-O(8)	2.209(3)	Mn(2)-O(8)#4	2.209(3)
O(3)#1-Mn(1)-O(7)	94.19(9)	O(3)#1-Mn(1)-O(1)	92.97(9)	O(7)-Mn(1)-O(1)	167.41(9)
O(3)#1-Mn(1)-N(1)	107.75(11)	O(7)-Mn(1)-N(1)	93.05(9)	O(1)-Mn(1)-N(1)	74.89(9)
O(3)#1-Mn(1)-N(2)	88.23(13)	O(7)-Mn(1)-N(2)	97.51(9)	O(1)-Mn(1)-N(2)	93.05(9)
N(1)-Mn(1)-N(2)	160.18(9)	O(3)#1-Mn(1)-N(3)	159.49(10)	O(7)-Mn(1)-N(3)	83.96(10)
O(1)-Mn(1)-N(3)	92.88(10)	N(1)-Mn(1)-N(3)	92.76(10)	N(2)-Mn(1)-N(3)	71.84(11)

## **Table S1** Selected bond lengths [Å] and angles [°] for 1–6.<sup>*a*</sup>

O(5)#2-Mn(2)-O(8)	85.70(10)	O(5)#3-Mn(2)-O(8)	94.30(10)	O(5)#3-Mn(2)-O(8)#4	85.70(10)
O(5)#2-Mn(2)-O(4)	84.04(12)	O(5)#3-Mn(2)-O(4)	95.96(12)	O(8)-Mn(2)-O(4)	90.12(10)
O(8)#4-Mn(2)-O(4)	89.88(10)	O(5)#2-Mn(2)-O(4)#4	95.96(12)	O(5)#3-Mn(2)-O(4)#4	84.04(12)
O(8)-Mn(2)-O(4)#4	89.88(10)				
5					
Zn1-O1	1.954(3)	Zn1-O3#1	1.935(2)	Zn-O7	1.969(3)
Zn1-O8	1.977(3)	Zn2-N1	2.127(3)	Zn2-N1#2	2.127(3)
Zn2-O6	2.118(3)	Zn2-O6#2	2.118(3)	Zn2-O9	2.046(3)
Zn2-O9#2	2.046(3)				
O1-Zn1-O7	116.94(11)	O1-Zn1-O8	101.18(12)	O7-Zn1-O8	99.39(12)
O3#1-Zn1-O1	123.40(11)	O3#1-Zn1-O7	104.75(12)	O3#1-Zn1-O8	108.16(11)
N1-Zn2-N1#2	169.96(19)	O9#2-Zn2-N1	95.64(12)	O9-Zn2-N1	91.24(12)
O9-Zn2-O9#2	93.46(18)	O9-Zn2-O6	169.17(10)	O9-Zn2-O6#2	90.26(12)
O6#2-Zn2-N1	94.44(12)	O6-Zn2-N1	78.26(12)	O6-Zn2-O6#2	87.93(17)
6					
Zn(1)-O(1)	2.109(3)	Zn(1)-O(3)#2	2.022(3)	Zn(1)-O(6)#1	1.957(3)
Zn(1)-O(7)	2.147(4)	Zn(1)-N(1)	2.065(4)	Zn(2)-O(4)	1.978(3)
Zn(2)-O(4)#3	1.978(3)	Zn(2)-O(8)	2.135(3)	Zn(2)-O(8)#3	2.135(3)
Zn(2)-N(2)	2.053(6)				
O(6)#1-Zn(1)-O(3)#2	117.38(14)	O(6)#1-Zn(1)-N(1)	114.05(15)	O(3)#2-Zn(1)-N(1)	128.38(14)
O(6)#1-Zn(1)-O(1)	106.13(14)	O(3)#2-Zn(1)-O(1)	91.71(13)	N(1)-Zn(1)-O(1)	78.16(14)
O(6)#1-Zn(1)-O(7)	88.47(15)	O(3)#2-Zn(1)-O(7)	83.96(14)	N(1)-Zn(1)-O(7)	93.34(15)
O(1)-Zn(1)-O(7)	165.10(14)	O(4)-Zn(2)-O(4)#3	131.0(2)	O(4)-Zn(2)-N(2)	114.52(10)
O(4)#3-Zn(2)-N(2)	114.52(10)	O(4)-Zn(2)-O(8)#3	91.04(13)	N(2)-Zn(2)-O(8)#3	85.04(10)
O(4)-Zn(2)-O(8)	93.07(13)	O(4)#3-Zn(2)-O(8)	91.04(13)	N(2)-Zn(2)-O(8)	85.04(10)
O(8)#3-Zn(2)-O(8)	170.1(2)				

<sup>*a*</sup> Symmetry transformations used to generate equivalent atoms: #1 -*x*+2, -*y*+1, -*z*+1 for 1; #1 *x*+1/2, *y*, -*z*+2; #2 *x*+1/2, -*y*+1/2, *z*+1/2; #3 *x*, -*y*+1/2, -*z*+5/2; #4 *x*, -*y*+1/2, -*z*+3/2; #5 *x*+1/2, *y*, -*z*+1 for 2; #1 *x*, -*y*+1/2, -*z*+3/2; #2 *x*-1/2, *y*, -*z*+1; #3 *x*-1/2, -*y*+1/2, *z*+1/2; #4 *x*+1/2, *y*, -*z*+2; #5 *x*+1/2, -*y*+1/2, *z*-1/2 for 3; #1 *x*, *y*-1, *z*; #2 -*x*+1, -*y*+2, -*z*+1; #3 *x*, *y*+1, *z*; #4 -*x*+1, -*y*+3, -*z*+1 for 4; #1 *x*, -*y*+1, *z*-1/2; #2 - *x*+1, *y*, -*z*+3/2 for 5; #1 *x*, -*y*+1, *z*+1/2; #2 -*x*+1/2, *y*+1/2, *z*; #3 -*x*+1, *y*, -*z*+1/2 for 6.

Table S2 Conventional hydrogen bonds in crystal packing [Å, °] of 1–6.

Complexes	D-H…A	<i>d</i> (D-H)	<i>d</i> (H···A)	<i>d</i> (D···A)	∠DHA	Symmetry code
1	O(4)-H(4)···O(7)	0.82	1.94	2.636(3)	142.4	<i>x</i> , - <i>y</i> +1/2, <i>z</i> +1/2
	O(6)-H(6)···O(5)	0.85	1.80	2.645(4)	171	- <i>x</i> +1, - <i>y</i> +2, - <i>z</i> +1
	O(7)-H(1W)···O(2)	0.85	1.93	2.772(3)	171.3	- <i>x</i> +2, <i>y</i> +1/2, - <i>z</i> +1
	O(7)-H(2W)···O(2)	0.85	1.79	2.643(4)	175.5	- <i>x</i> +1, - <i>y</i> +2, <i>z</i> +1/2
2	O(7)-H(1W)…O(1)	0.82	2.09	2.906(3)	170.3	<i>x</i> , - <i>y</i> +1/2, - <i>z</i> +5/2
	O(4)-H(4)···O(6)	0.82	1.84	2.655(3)	171.8	- <i>x</i> +3/2, - <i>y</i> +1, <i>z</i> +1
3	O(7)-H(1W)···O(1)	0.82	2.14	2.930(4)	162.6	<i>x</i> , - <i>y</i> +1/2, - <i>z</i> +5/2

	O(4)-H(4)···O(6)	0.82	1.86	2.675(3)	176.9	- <i>x</i> +1/2, - <i>y</i> +1, <i>z</i> +1
4	O(9)-H(5W)···O(6)	0.86	2.13	2.938(5)	156.7	- <i>x</i> +1, - <i>y</i> +1, - <i>z</i> +1
	O(8)-H(4W)…O(6)	0.85	2.16	2.881(4)	143.6	<i>x</i> +1, <i>y</i> +1, <i>z</i>
	O(7)-H(1W)···O(2)	0.82	1.93	2.727(4)	165.4	<i>x</i> -1, <i>y</i> , <i>z</i>
	O(7)-H(2W)…O(9)	0.82	1.91	2.726(4)	167.9	<i>x</i> -1, <i>y</i> , <i>z</i>
5	O(7)-H(7A)···O(6)	0.88	1.82	2.649(4)	156.0	- <i>x</i> +1, - <i>y</i> +1, - <i>z</i> +1
	O(7)-H7B)···O(2)	0.88	1.93	2.7664(4)	156.2	<i>x</i> , <i>y</i> +1, <i>z</i>
	O(8)-H(8A)…O(4)	0.86	1.94	2.682(4)	143.7	- <i>x</i> +1/2, - <i>y</i> +3/2, - <i>z</i> +1
	O(8)-H(7B)···O(4)	0.86	2.10	2.723(4)	129.0	<i>x</i> , - <i>y</i> +2, <i>z</i> -1/2
	O(9)-H(9A)···O(2)	0.87	1.89	2.672(4)	149.6	<i>x</i> , - <i>y</i> +1, <i>z</i> +1/2
6	O(7)-H(1W)···O(9)	0.85	2.00	2.679(9)	135.3	x-1/2, y+1/2, -z+1/2
	O(7)-H(2W)…O(1)	0.85	2.07	2.799(5)	142.8	- <i>x</i> +1/2, <i>y</i> -1/2, <i>z</i>
	O(8)-H(3W)…O(6)	0.86	2.04	2.787(5)	145.3	<i>x</i> , - <i>y</i> +1, <i>z</i> +1/2
	O(8)-H(4W)…O(5)	0.86	2.00	2.735(5)	142.6	- <i>x</i> +1/2, - <i>y</i> +1/2, <i>z</i> +1/2
	O(9)-H(5W)···O(10)	0.66	2.28	2.779(14)	133.8	X+1/2, -y+1/2, -z+1
	O(10)-H(7W)···O(9)	0.87	2.45	2.779(13)	102.8	<i>x</i> -1/2, - <i>y</i> +1/2, - <i>z</i> +1



Figure S1 Thermogravimetric analysis (TGA) curves of compounds 1–6.



Figure S2 The PXRD patterns of compounds 1–6 at room temperature.