Supporting Information for the Manuscript:

Entangled Zn(II)/Cd(II) Coordination Complexes Based on a Flexible Bis(methylbenzimidazole) Ligand and Different Dicarboxylates

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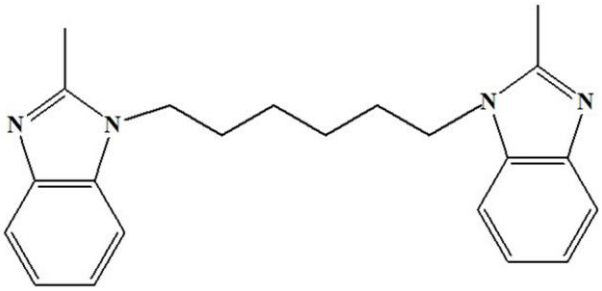

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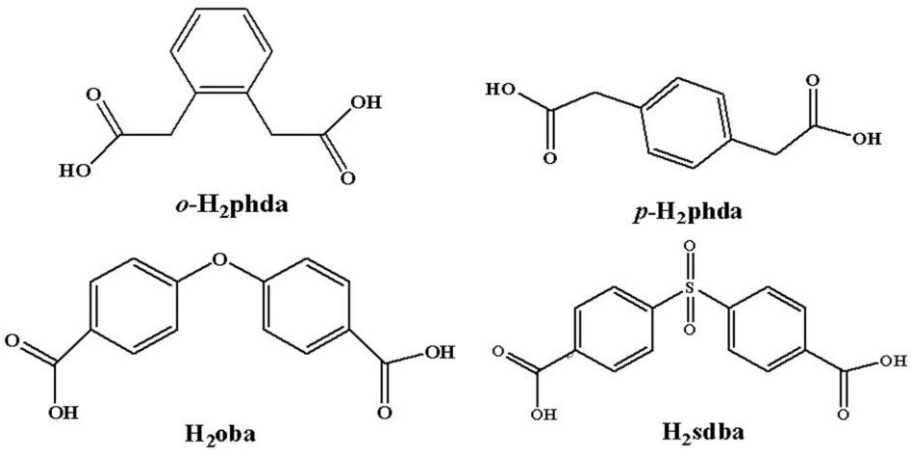
Scheme S1. The N-heterocyclic ligand adopted in this paper.



Scheme S**2.** Structures of the carboxylate ligands used in this paper

Table S1. Crystallographic data and structure refinement details for parts of complexes[a,b] under specific conditions

Complex	**1**-DMF	**3**-MeCN	**4**-MeCN	**5**-MeOH	**6**-MeOH
formula	$C_{21}H_{21}N_2O_4Zn$	$C_{32}H_{36}N_4O_5Zn$	$C_{32}H_{36}CdN_4O_5$	$C_{25}H_{21}N_2O_5Zn$	$C_{25}H_{21}Cd\ N_2O_5$
fw	430.77	622.02	669.05	494.81	541.84
T/K	293(2)	293(2)	293(2)	293(2)	293(2)
λ (Mo K), Å	0.71073	0.71073	0.71073	0.71073	0.71073
Cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*P2(1)/c*	*P 2/c*	*P2/c*	*P2(1)/c*	*P2(1)/c*
a (Å)	10.981(2)	9.2122(18)	9.0575(18)	11.936(2)	12.241(2)
b (Å)	10.867(2)	10.310(2)	10.338(2)	14.277(3)	14.012(3)
c (Å)	16.101(3)	17.092(5)	17.427(5)	13.726(3)	14.167(3)
α(°)	90	90	90	90	90
β(°)	104.41(3)	117.59(2)	115.35(2)	99.86(3)	99.53(3)
γ(°)	90	90	90	90	90
V ($Å^3$)	1860.7(6)	1438.8(6)	1474.7(6)	2304.6(8)	2396.5(8)
Z	4	2	2	4	4
$D_{calcd.}$($g\cdot cm^{-3}$)	1.538	1.436	1.507	1.426	1.502
Reflections collected /unique	22798 / 4462	10240 / 2682	15114 / 2752	28368 / 5503	19590 / 5702
R(int)	0.0443	0.0588	0.0543	0.0485	0.0455
abs. coeff/mm^{-1}	1.351	0.902	0.788	1.104	0.948
F(000)	892	652	688	1020	1092
θ (°)	1.91-27.95	2.39-25.50	1.97-25.50	1.73-27.93	2.06-27.92
GOF	1.066	1.164	1.132	1.006	0.991
R_1(I>2sigma(I))[a]	0.0495	0.0718	0.0514	0.0625	0.0539
wR_2(I>2sigma(I))[b]	0.1018	0.1624	0.1109	0.1386	0.1002

[a] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$. [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Notes:

1-DMF is the structure of complex 1 after boiling in DMF；

3-MeCN is the structure of complex 3 after boiling in MeCN；

4-MeCN is the structure of complex 4 after boiling in MeCN；

5-MeOH is the structure of complex 5 after boiling in MeOH；

6-MeOH is the structure of complex 6 after boiling in MeOH.

Table S2. The unit-cell parameters of complexes 1–8 under specific conditions

		H_2O	MeOH	EtOH	MeCN	DMF
Complex **1**	a (Å)	11.00	11.04	11.00	11.01	10.99
	b (Å)	10.89	10.90	10.88	10.90	10.86
	c (Å)	16.14	16.15	16.13	16.13	16.11
	α (°)	90	90	90	90	90
	β (°)	104.30	104.43	104.39	104.42	104.47
	γ (°)	90	90	90	90	90
	V ($Å^3$)	1874	1882	1869	1874	1860
Complex **2**	a (Å)	11.19	11.14	11.15	11.18	11.16
	b (Å)	11.07	11.02	11.03	11.02	11.05
	c (Å)	16.31	16.22	16.23	16.26	16.28
	α (°)	90	90	90	90	90
	β (°)	104.88	104.92	104.88	104.77	104.78
	γ (°)	90	90	90	90	90
	V ($Å^3$)	1952	1924	1929	1937	1940
Complex **3**	a (Å)	9.24	9.25	9.22	9.23	9.23
	b (Å)	10.30	10.35	10.34	10.32	10.27
	c (Å)	15.34	15.18	15.21	15.20	15.14
	α (°)	90	90	90	90	90
	β (°)	95.58	94.63	94.80	94.75	94.17
	γ (°)	90	90	90	90	90
	V ($Å^3$)	1452	1449	1445	1443	1431
Complex **4**	a (Å)	9.07	9.08	9.08	9.06	9.04
	b (Å)	10.32	10.34	10.35	10.36	10.36
	c (Å)	15.89	15.87	15.84	15.83	15.69

	α (°)	90	90	90	90	90
	β (°)	95.72	95.73	95.83	95.67	95.70
	γ (°)	90	90	90	90	90
	V (Å^3)	1480	1483	1481	1479	1463
Complex **5**	a (Å)	11.94	11.94	11.97	11.92	11.97
	b (Å)	14.43	14.29	14.34	14.26	14.29
	c (Å)	13.75	13.73	13.75	13.71	13.75
	α (°)	90	90	90	90	90
	β (°)	100.00	99.89	99.94	99.93	99.96
	γ (°)	90	90	90	90	90
	V (Å^3)	2332	2306	2324	2297	2316
Complex **6**	a (Å)	12.22	12.27	12.25	12.25	12.23
	b (Å)	14.00	14.02	13.97	13.99	13.95
	c (Å)	14.15	14.21	14.17	14.20	14.14
	α (°)	90	90	90	90	90
	β (°)	99.44	99.48	99.61	99.47	99.58
	γ (°)	90	90	90	90	90
	V (Å^3)	2388	2411	2389	2400	2379
Complex **7**	a (Å)	14.04	14.08	14.11	14.14	14.06
	b (Å)	14.89	14.90	14.95	14.91	14.93
	c (Å)	16.33	16.30	16.34	16.36	16.36
	α (°)	98.01	97.94	97.83	97.89	97.88
	β (°)	95.16	95.27	95.32	95.37	95.21
	γ (°)	95.47	95.65	95.68	95.71	95.57
	V (Å^3)	3348	3350	3379	3379	3365
Complex **8**	a (Å)	19.50	19.48	19.42	19.47	19.47

	b (Å)	22.02	22.02	21.93	22.00	22.04
	c (Å)	16.13	16.12	16.08	16.10	16.12
	α (°)	90	90	90	90	90
	β (°)	100.04	99.96	99.96	99.85	100.01
	γ (°)	90	90	90	90	90
	V ($Å^3$)	6819	6812	6744	6796	6812

Table S3. Selected Bond Lengths (Å) and Bond Angles (deg) for 1−8[a]

Complex **1**					
Zn(1)-N(1)	2.021(4)	Zn(1)-O(2)#1	2.055(3)	Zn(1)-O(1)	2.049(3)
Zn(1)-O(3)#2	2.070(3)	Zn(1)-O(4)#3	2.077(3)	N(1)-Zn(1)-O(2)#1	104.83(14)
N(1)-Zn(1)-O(1)	97.04(14)	O(2)#1-Zn(1)-O(1)	158.12(13)	N(1)-Zn(1)-O(3)#2	101.04(15)
O(2)#1-Zn(1)-O(3)#2	86.57(13)	O(1)-Zn(1)-O(3)#2	89.03(13)	N(1)-Zn(1)-O(4)#3	100.84(15)
O(2)#1-Zn(1)-O(4)#3	88.70(14)	O(1)-Zn(1)-O(4)#3	87.45(13)	O(3)#2-Zn(1)-O(4)#3	158.09(14)
Complex **2**					
O(4)-Cd(1)#5	2.267(2)	Cd(1)-N(1)	2.220(2)	Cd(1)-O(3)#2	2.240(2)
Cd(1)-O(1)	2.226(2)	Cd(1)-O(2)#1	2.232(2)	Cd(1)-O(4)#3	2.267(2)
N(1)-Cd(1)-O(3)#2	101.12(8)	N(1)-Cd(1)-O(1)	106.01(8)	O(3)#2-Cd(1)-O(4)#3	157.88(7)
N(1)-Cd(1)-O(2)#1	95.59(8)	N(1)-Cd(1)-O(4)#3	100.87(8)	O(1)-Cd(1)-O(2)#1	158.26(7)
N(1)-Cd(1)-O(4)#3	100.87(8)	O(1)-Cd(1)-O(4)#3	85.57(9)	O(1)-Cd(1)-O(3)#2	90.73(9)
O(2)#1-Cd(1)-O(4)#3	87.96(9)				
Complex **3**					
Zn(1)-O(1)#1	1.9537(19)	Zn(1)-O(1)	1.9537(19)	Zn(1)-N(1)	2.046(2)
Zn(1)-N(1)#1	2.046(2)	O(1)#1-Zn(1)-O(1)	124.90(11)	O(1)#1-Zn(1)-N(1)	103.38(8)
O(1)-Zn(1)-N(1)	110.31(8)	O(1)#1-Zn(1)-N(1)#1	110.31(8)	O(1)-Zn(1)-N(1)#1	103.38(8)
N(1)-Zn(1)-N(1)#1	102.59(12)				
Complex **4**					
Cd(1)-O(1)	2.2420(19)	Cd(1)-O(1)#1	2.2420(19)	Cd(1)-N(1)	2.271(2)
Cd(1)-N(1)#1	2.271(2)	Cd(1)-O(2)	2.5654(19)	Cd(1)-O(2)#1	2.5654(19)
O(1)-Cd(1)-O(1)#1	139.44(10)	O(1)-Cd(1)-N(1)	97.14(7)	O(1)#1-Cd(1)-N(1)	109.99(8)
O(1)-Cd(1)-N(1)#1	109.99(8)	O(1)#1-Cd(1)-N(1)#1	97.14(7)	N(1)-Cd(1)-N(1)#1	95.50(10)
O(1)-Cd(1)-O(2)	53.49(6)	O(1)#1-Cd(1)-O(2)	93.38(7)	N(1)-Cd(1)-O(2)	150.08(7)
N(1)#1-Cd(1)-O(2)	99.96(7)	O(1)-Cd(1)-O(2)#1	93.38(7)	O(1)#1-Cd(1)-O(2)#1	53.49(6)
N(1)-Cd(1)-O(2)#1	99.96(7)	N(1)#1-Cd(1)-O(2)#1	150.08(7)	O(2)-Cd(1)-O(2)#1	78.73(10)
Complex **5**					
Zn(1)-O(1)	2.021(3)	Zn(1)-N(1)	2.029(3)	Zn(1)-O(2)	2.040(3)
Zn(1)-O(4)	2.062(3)	Zn(1)-O(3)	2.083(3)	O(1)-Zn(1)-N(1)	103.77(14)
O(1)-Zn(1)-O(2)	91.93(14)	N(1)-Zn(1)-O(2)	105.45(14)	O(1)-Zn(1)-O(4)	156.39(13)
N(1)-Zn(1)-O(4)	99.67(14)	O(2)-Zn(1)-O(4)	84.55(13)	O(1)-Zn(1)-O(3)	86.22(14)
N(1)-Zn(1)-O(3)	97.85(14)	O(2)-Zn(1)-O(3)	156.37(13)	O(4)-Zn(1)-O(3)	87.78(14)
Complex **6**					
Cd(1)-O(4)	2.205(2)	Cd(1)-N(1)	2.217(2)	Cd(1)-O(1)	2.227(2)
Cd(1)-O(2)	2.2528(19)	Cd(1)-O(3)	2.266(2)	O(4)-Cd(1)-N(1)	103.80(8)
O(4)-Cd(1)-O(1)	95.60(9)	N(1)-Cd(1)-O(1)	105.08(9)	O(4)-Cd(1)-O(2)	155.83(8)
N(1)-Cd(1)-O(2)	99.91(8)	O(1)-Cd(1)-O(2)	82.65(8)	O(4)-Cd(1)-O(3)	85.27(9)

N(1)-Cd(1)-O(3)	98.95(10)	O(1)-Cd(1)-O(3)	154.97(10)	O(2)-Cd(1)-O(3)	86.45(9)
Complex **7**					
Zn(1)-O(5)	1.953(5)	Zn(1)-O(3)	1.997(5)	Zn(1)-N(3)	2.038(6)
Zn(1)-N(1)	2.054(6)	Zn(2)-O(11)	1.965(6)	Zn(2)-O(9)#1	1.968(6)
Zn(2)-N(7)#2	2.009(6)	Zn(2)-N(6)#3	2.044(6)	O(5)-Zn(1)-O(3)	128.1(2)
O(5)-Zn(1)-N(3)	98.5(2)	O(3)-Zn(1)-N(3)	112.6(2)	O(5)-Zn(1)-N(1)	101.8(2)
O(3)-Zn(1)-N(1)	105.0(2)	N(3)-Zn(1)-N(1)	109.6(2)	O(11)-Zn(2)-O(9)#1	105.2(3)
O(11)-Zn(2)-N(7)#2	106.7(3)	O(9)#1-Zn(2)-N(7)#2	125.9(3)	O(11)-Zn(2)-N(6)#3	98.3(2)
O(9)#1-Zn(2)-N(6)#3	105.8(3)	N(7)#2-Zn(2)-N(6)#3	111.3(2)		
Complex **8**					
Cd(1)-N(1)	2.244(7)	Cd(1)-N(3)#1	2.276(7)	Cd(1)-O(1)	2.304(6)
Cd(1)-O(4)#2	2.359(7)	Cd(1)-O(3)#2	2.370(7)	Cd(1)-O(2)	2.485(7)
N(1)-Cd(1)-N(3)#1	106.5(2)	N(1)-Cd(1)-O(1)	98.0(2)	N(3)#1-Cd(1)-O(1)	85.9(2)
N(1)-Cd(1)-O(4)#2	153.5(3)	N(3)#1-Cd(1)-O(4)#2	87.0(3)	O(1)-Cd(1)-O(4)#2	105.8(3)
N(1)-Cd(1)-O(3)#2	99.3(3)	N(3)#1-Cd(1)-O(3)#2	112.6(3)	O(1)-Cd(1)-O(3)#2	149.7(3)
O(4)#2-Cd(1)-O(3)#2	54.3(2)	N(1)-Cd(1)-O(2)	100.0(2)	N(3)#1-Cd(1)-O(2)	135.1(2)
O(1)-Cd(1)-O(2)	54.6(2)	O(4)#2-Cd(1)-O(2)	84.9(2)	O(3)#2-Cd(1)-O(2)	97.7(3)

[a] Symmetry transformations used to generate equivalent atoms in complex (**1**): #1 -x,-y+1,-z+1; #2 x,-y+1/2,z+1/2; #3 -x,y+1/2,-z+1/2. (**2**): #1 -x+1,-y+1,-z+1; #2 x,-y+1/2,z-1/2; #3 -x+1,y+1/2,-z+3/2; #5 -x+1,y-1/2,-z+3/2. (**3**) #1 -x+2,y,-z+3/2. (**4**): #1 -x,y,-z+1/2. (**7**): #1 x+1,y-1,z; #2 -x,-y,-z+1; #3 -x+1,-y+1,-z+2. (**8**): #1 x+1/2,-y+1/2,z+1/2 ; #2 -x+1/2,y+1/2,-z+1/2.

Table S4. Selected Bond Lengths (Å) and Bond Angles (deg) for parts of complexes[a] under specific conditions

Complex **1**-DMF					
Zn(1)-N(1)	2.027(2)	Zn(1)-O(2)#1	2.047(2)	Zn(1)-O(1)	2.054(2)
Zn(1)-O(3)#3	2.062(2)	Zn(1)-O(4)#2	2.066(2)	N(1)-Zn(1)-O(2)#1	97.33 (9)
N(1)-Zn(1)-O(1)	104.52(9)	O(2)#1-Zn(1)-O(1)	158.14(8)	N(1)-Zn(1)-O(3)#3	100.88(9)
O(2)#1-Zn(1)-O(3)#3	87.17(9)	O(1)-Zn(1)-O(3)#3	88.94(9)	N(1)-Zn(1)-O(4)#2	101.00(9)
O(2)#1-Zn(1)-O(4)#2	88.96(9)	O(1)-Zn(1)-O(4)#2	86.66(9)	O(3)#3-Zn(1)-O(4)#2	158.09(8)
Complex **3**-MeCN					
Zn(1)-O(1)#1	1.9514(18)	Zn(1)-O(1)	1.9514(18)	Zn(1)-N(1)	2.051(2)
Zn(1)-N(1)#1	2.051(2)	O(1)#1-Zn(1)-O(1)	124.34(11)	O(1)#1-Zn(1)-N(1)	102.62(8)
O(1)-Zn(1)-N(1)	111.52(7)	O(1)#1-Zn(1)-N(1)#1	111.52(7)	O(1)-Zn(1)-N(1)#1	102.62(8)
N(1)-Zn(1)-N(1)#1	102.36(12)				
Complex **4**-MeCN					
Cd(1)-O(1)	2.243(3)	Cd(1)-O(1)#1	2.243(3)	Cd(1)-N(1)	2.280(3)
Cd(1)-N(1)#1	2.280(3)	Cd(1)-O(2)	2.557(3)	Cd(1)-O(2)#1	2.557(3)
O(1)-Cd(1)-O(1)#1	138.29(18)	O(1)-Cd(1)-N(1)	111.01(13)	O(1)#1-Cd(1)-N(1)	96.95(12)
O(1)-Cd(1)-N(1)#1	96.95(12)	O(1)#1-Cd(1)-N(1)#1	111.01(13)	N(1)#1-Cd(1)-N(1)	95.32(17)
O(1)-Cd(1)-O(2)	53.57(11)	O(1)#1-Cd(1)-O(2)	92.93(12)	N(1)-Cd(1)-O(2)	99.12(12)
N(1)#1-Cd(1)-O(2)	150.26(12)	O(1)-Cd(1)-O(2)#1	92.93(12)	O(1)#1-Cd(1)-O(2)#1	53.57(11)
N(1)-Cd(1)-O(2)#1	150.26(12)	N(1)#1-Cd(1)-O(2)#1	99.12(12)	O(2)-Cd(1)-O(2)#1	80.67(17)
Complex **5**-MeOH					
Zn(1)-O(1)#2	2.064(3)	Zn(1)-N(1)	2.029(3)	Zn(1)-O(2)	2.026(3)
Zn(1)-O(4)#3	2.075(3)	Zn(1)-O(5)#1	2.036(3)	O(2)-Zn(1)-N(1)	103.49(12)
O(1)#2-Zn(1)-O(2)	156.45(11)	N(1)-Zn(1)-O(5)#1	105.30(12)	O(1)#2-Zn(1)-O(4)#3	88.03(12)
N(1)-Zn(1)-O(4)#3	97.96(12)	O(2)-Zn(1)-O(4)#3	86.27(12)	O(5)#1-Zn(1)-O(4)#3	156.42(12)
N(1)-Zn(1)-O(1)#2	99.93(12)	O(2)-Zn(1)-O(5)#1	91.97(11)	O(5)#1-Zn(1)-O(1)#2	84.24(11)
Complex **6**-MeOH					
Cd(1)-O(4)#3	2.271(3)	Cd(1)-N(1)	2.222(3)	Cd(1)-O(1)#1	2.203(3)
Cd(1)-O(2)	2.252 (3)	Cd(1)-O(5)#2	2.229(3)	O(1)#1-Cd(1)-N(1)	103.67(13)
O(1)#1-Cd(1)-O(5)#2	95.54(13)	N(1)-Cd(1)-O(5)#2	105.20(14)	O(1)#1-Cd(1)-O(2)	155.85(12)
N(1)-Cd(1)-O(2)	100.03(13)	O(5)#2-Cd(1)-O(2)	82.56(12)	O(1)#1-Cd(1)-O(4)#3	85.24(13)
N(1)-Cd(1)-O(4)#3	99.05(14)	O(5)#2-Cd(1)-O(4)#3	154.77(14)	O(2)-Cd(1)-O(4)#3	86.55(13)

[a] Symmetry transformations used to generate equivalent atoms in complex (**1**): #1 -x+2,-y,-z+2 ; #2 -x+2,y+1/2,-z+3/2 ; #3 x,-y-1/2,z+1/2. (**3**): #1 -x,y,-z+1/2. (**4**): #1 -x+1,y,-z+1/2. (**5**): #1 x-1,-y+1/2,z-1/2 ; #2 -x+1,-y,-z+1 ; #3 -x+2,y-1/2,-z+3/2. (**6**): #1 -x+1,-y,-z+1 ; #2 -x,y-1/2,-z+1/2 ; #3 x+1,-y+1/2,z+1/2.

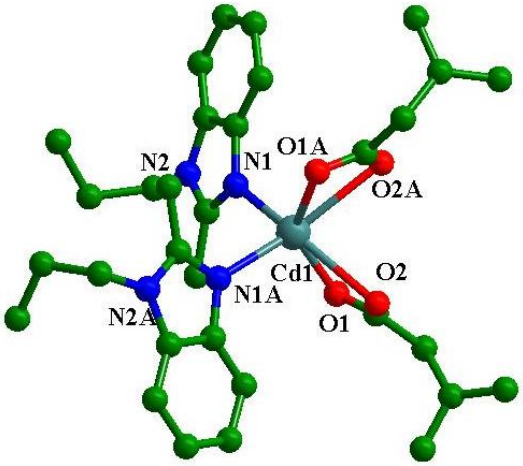
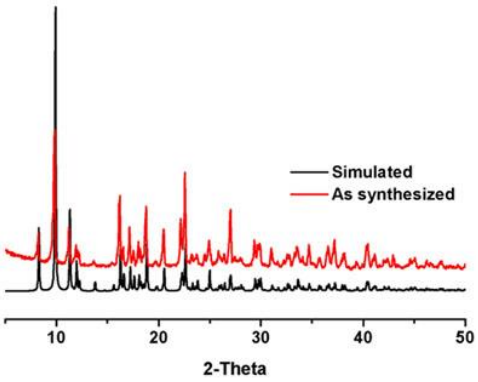
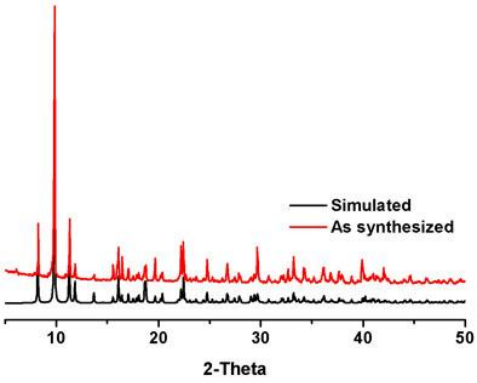


Figure. S1. Coordination environment of Cd(II) ion in **4** with hydrogen atoms omitted for clarity. Symmetry code: A = − x, y, 0.5 − z.

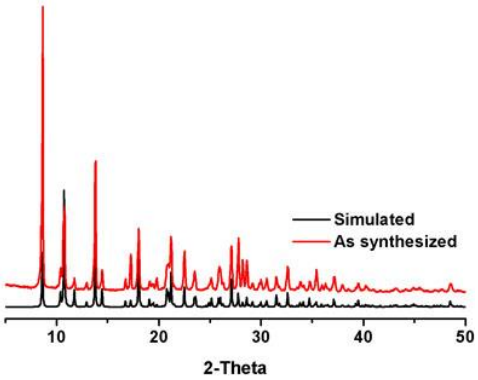
XRD Patterns. To confirm the phase purity of these polymers, the PXRD patterns were recorded for complexes **1**−**8**, and they were comparable to the corresponding simulated ones calculated from the single-crystal diffraction data (Figure. S2, Supporting Information), indicating a pure phase of each bulky sample.



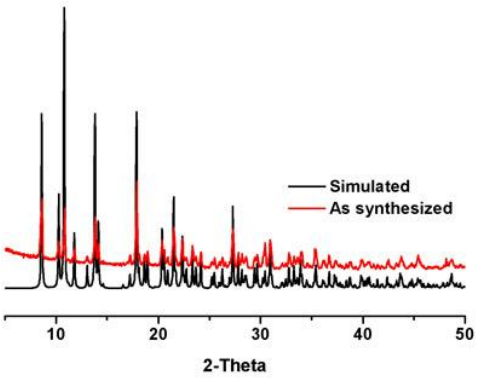
Complex **1**



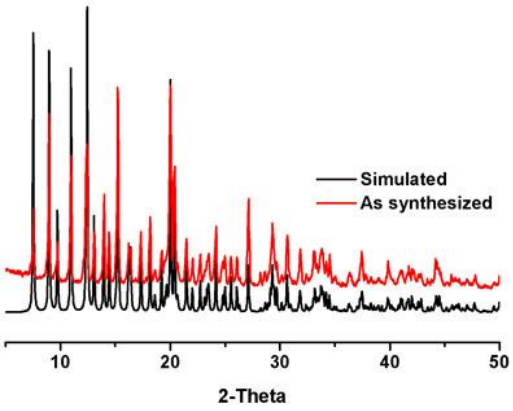
Complex **2**



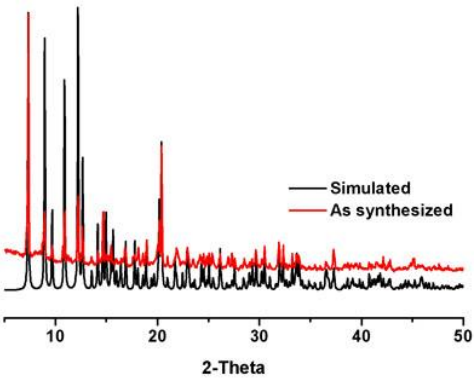
Complex **3**



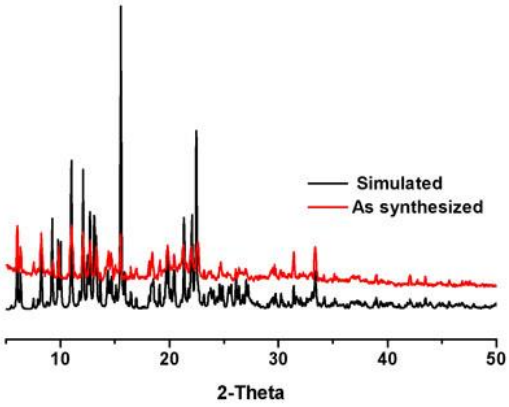
Complex **4**



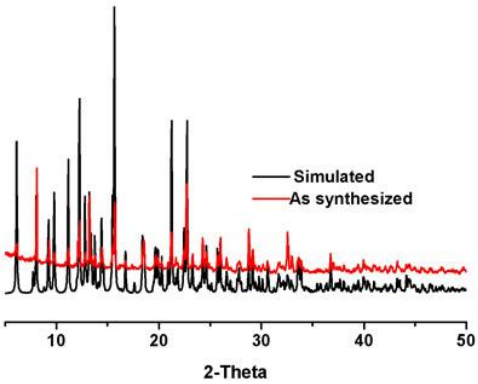
Complex **5**



Complex **6**

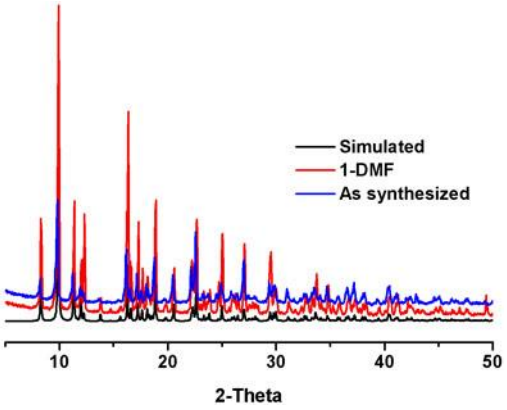


Complex **7**

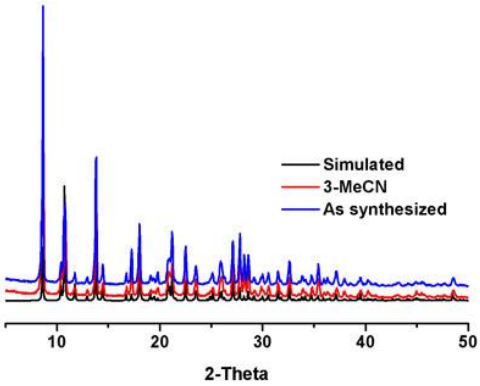


Complex **8**

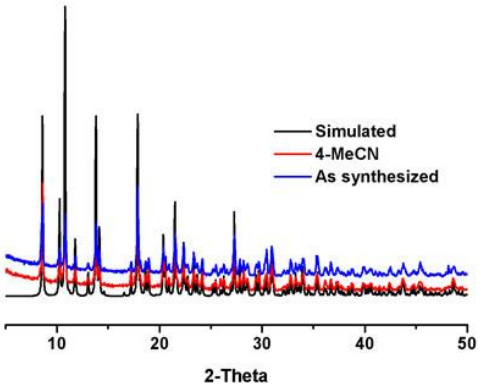
Figure. S2. Experimental (red) and simulated (black) PXRD patterns of **1**−**8**.



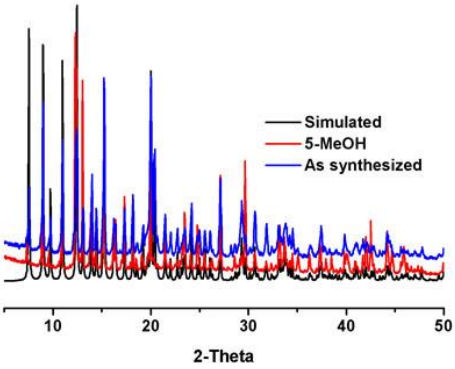
Complex **1-DMF**



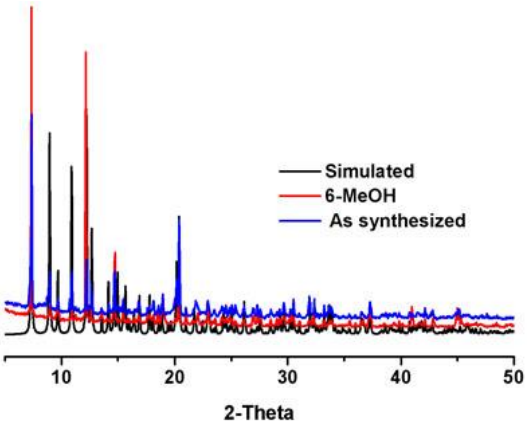
Complex **3-MeCN**



Complex **4-MeCN**



Complex **5-MeOH**



Complex **6-MeOH**

Figure. S3. Experimental (blue), simulated (black) and refluxed (red) PXRD patterns of parts of complexes under specific conditions.

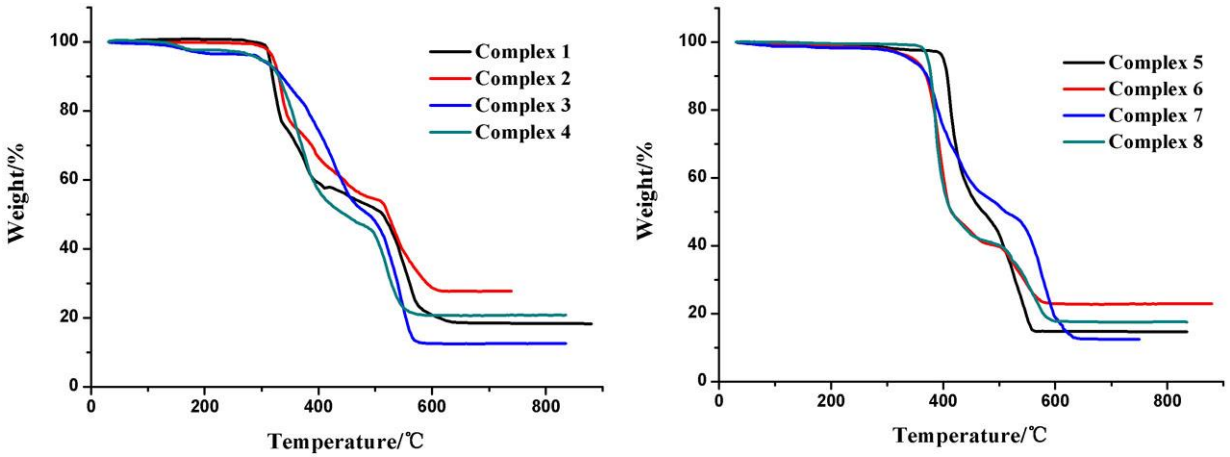
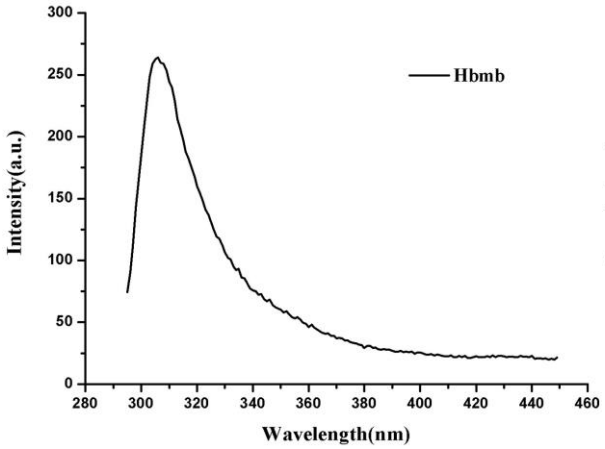
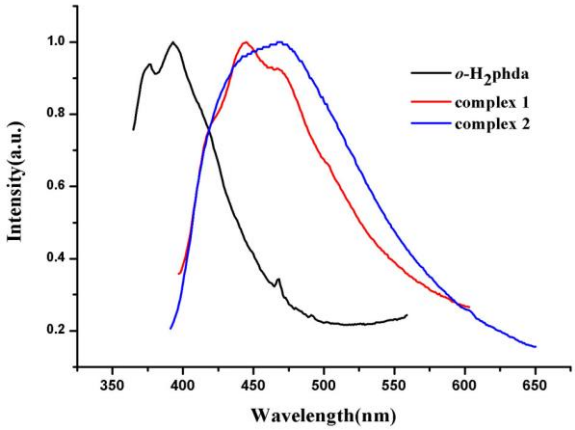


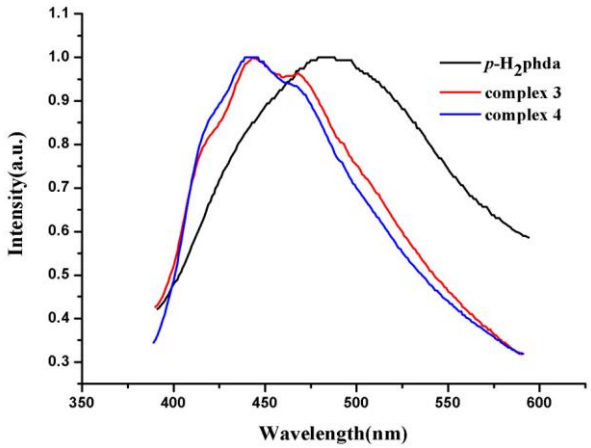
Figure. S4 Thermogravimetric curve of complexes **1**−**8**.



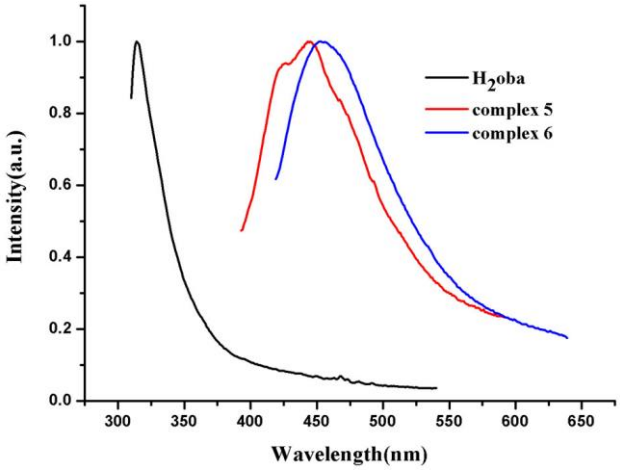
(a)



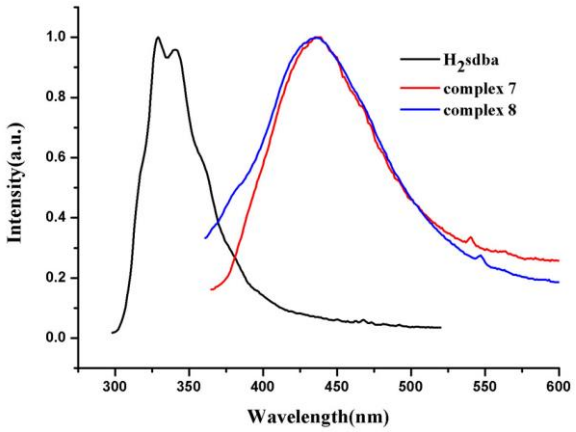
(b)



(c)



(d)



(e)

Figure. S5. (a) Solid-state emission spectra of the ligand hbmb. (b) Solid-state emission spectra of *o*-H_2phda, complex **1** and complex **2**. (c) Solid-state emission spectra of *p*-H_2phda, complex **3** and complex **4**. (d) Solid-state emission spectra of H_2oba, complex **5** and complex **6**. (e) Solid-state emission spectra of H_2sdba, complex **7** and complex **8**.