Electronic Supplementary Information (ESI)

for

Constructing novel Cd(II) metal-organic frameworks based on different highly connected secondary building units *via* reaction condition alteration

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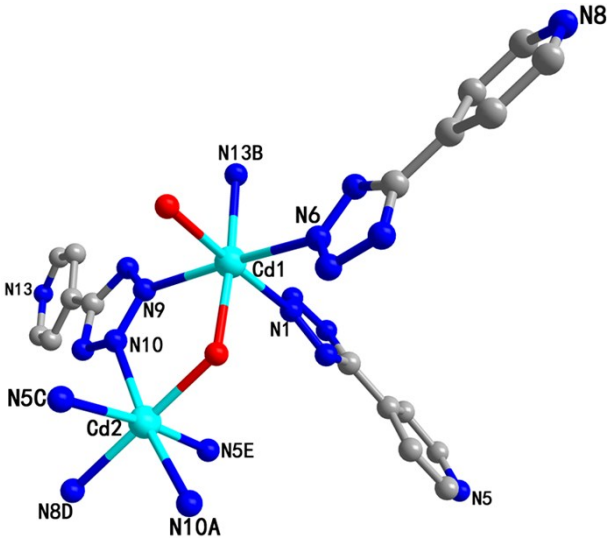


Fig. S1 Coordination environments of Cd1 and Cd2 in **1**. Symmetry code: A: x, 3/2-y, 3/2-z; B: 3/2+x, y, 2-z; C: 3/2-x, -1/2+y, 3/2-z; D: -1+x, y, z; E: 3/2-x, 2-y, z.

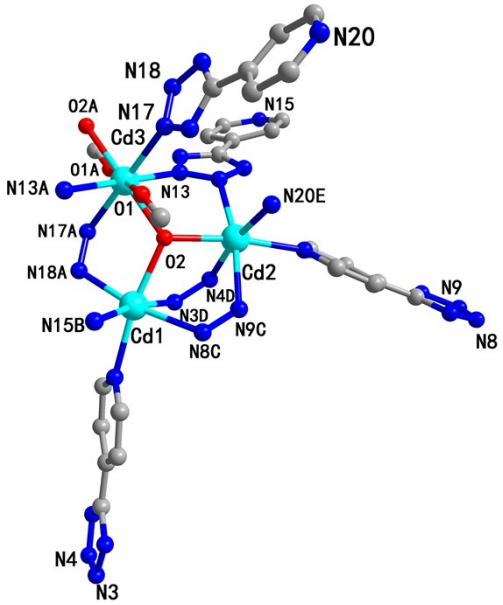


Fig. S2 Coordination environments of Cd1, Cd2 and Cd3 in **2**. Symmetry code: A: 1-x, 1-y, 1-z; B: x, -1+y, z; C: 1/2-x, -1/2+y, 3/2-z; D:3/2-x, -1/2+y, 3/2-z; E: -x, 1-y, 1-z.

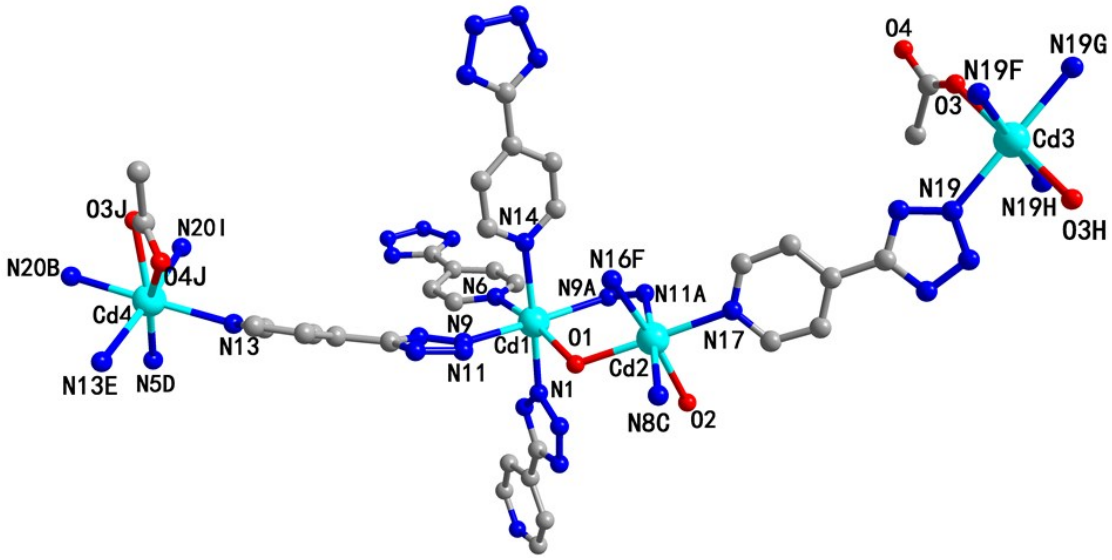


Fig. S3 Coordination environments of Cd1-4 in **3**. Symmetry code: A: x, 1-y, z; B: x, 1+y, 1+z; C: x, 1-y, -1+z; D: 1/2-x, 1/2+y, 2-z; E: x, 2-y, z; F: -x, y, -z; G: -x, -y, -z; H: x, -y, z; I: x, 1-y, 1+z; J: -x, 1+y, 1-z.

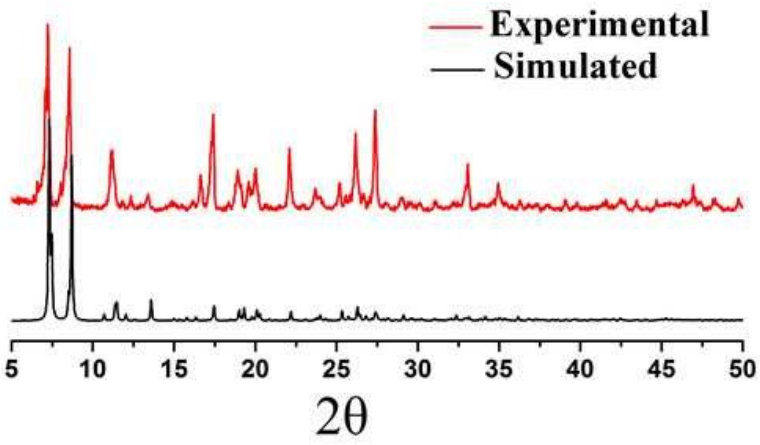


Fig. S4 Simulated and experimental PXRD patterns of compound **1**.

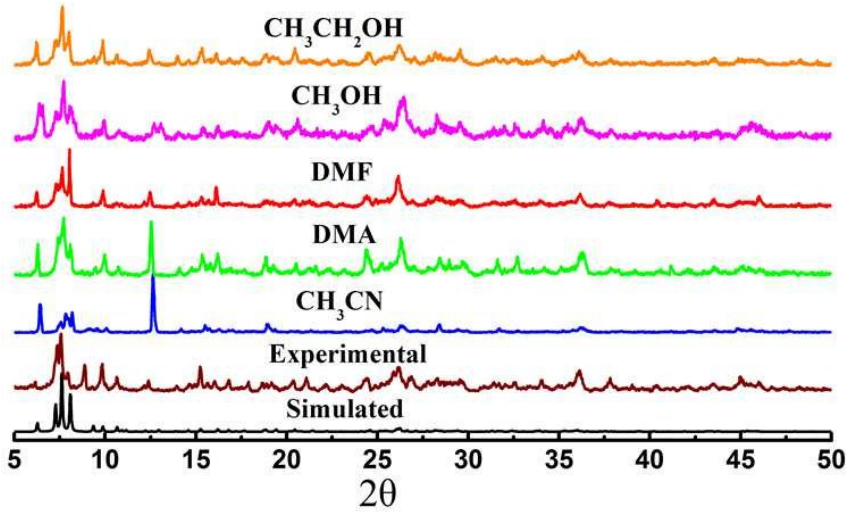


Fig. S5 Simulated and experimental PXRD patterns of as-synthesized **2** and samples soak in common organic solvents for three days.

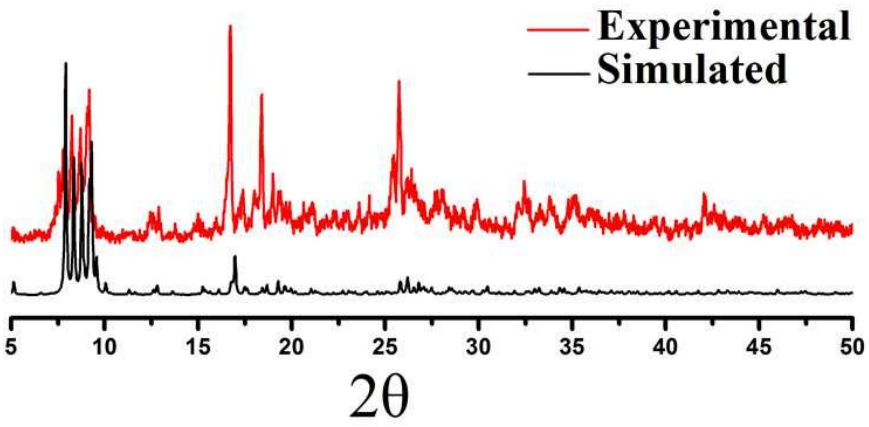


Fig. S6 Simulated and experimental PXRD patterns of compound **3**.

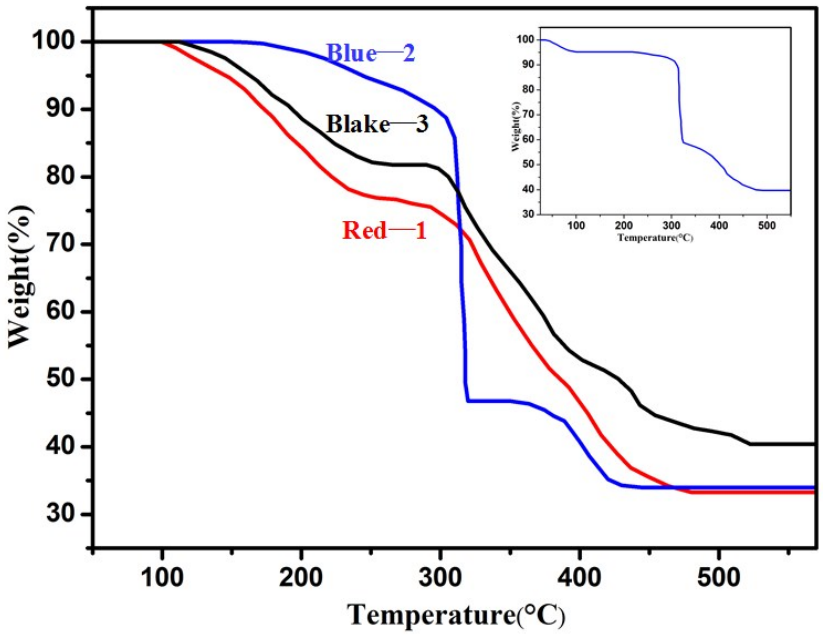


Fig. S7 Thermagravimetric profiles for **1**-**3**. Red line: **1**; Blue line: **2**; Black line: **3**; The insert figure: activated compound **2**.

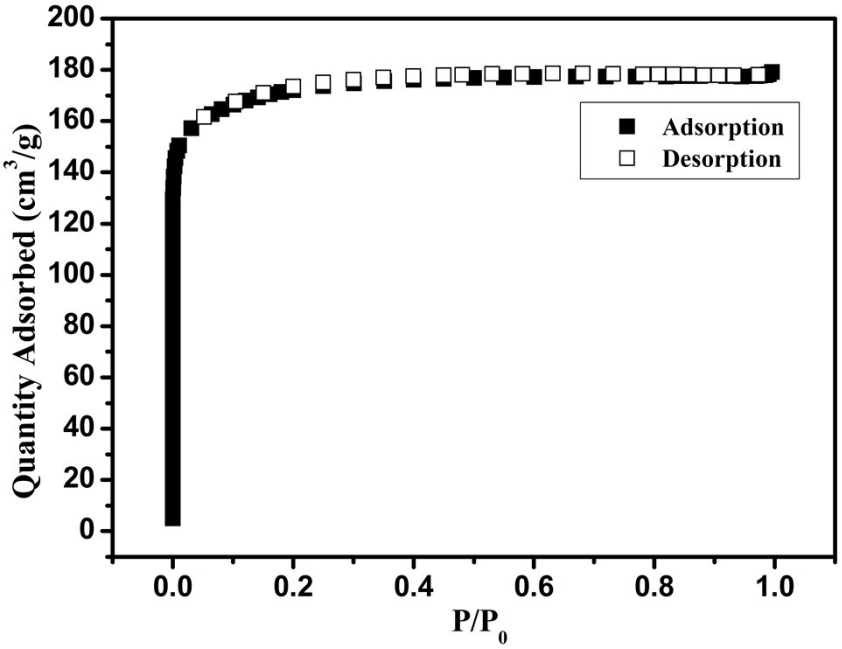


Fig. S8 The N_2 adsorption isotherms of **2**.

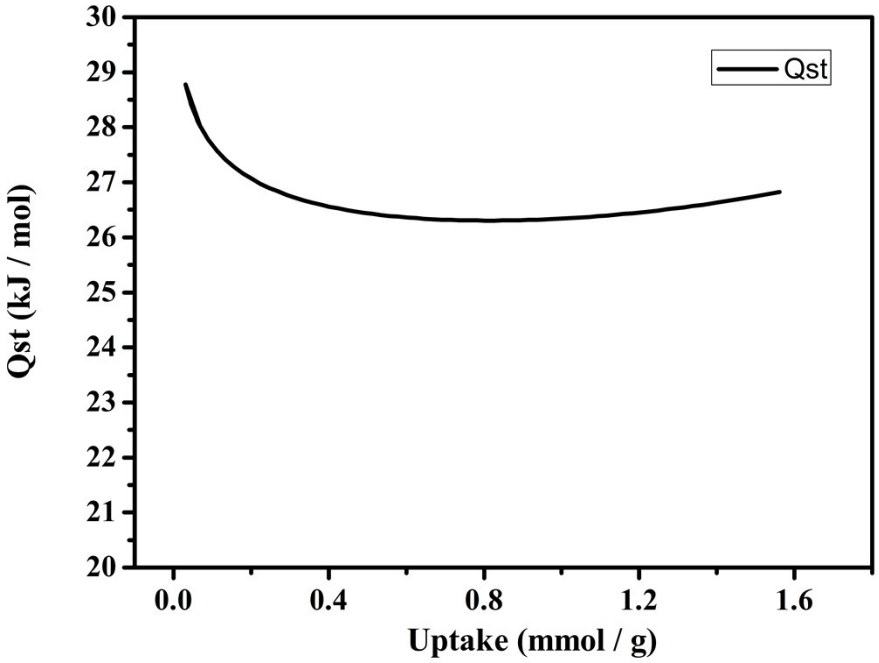


Fig. S9 The isoteric heat of adsorption (Qst) for the CO_2 adsorption of **2**.

Table S1 The summarization of the coordination modes of 4-ptz ligand in literatures. Color scheme: metal centers (green) and the others are the same with compound **1**.

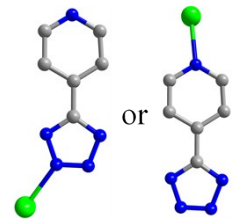
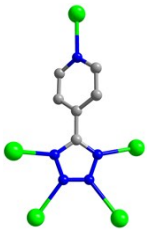
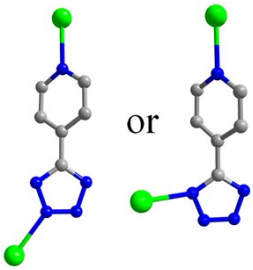
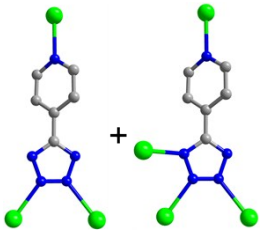
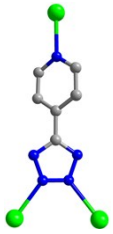
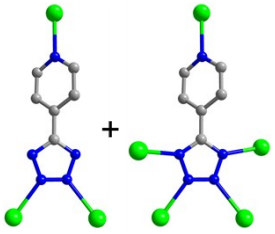
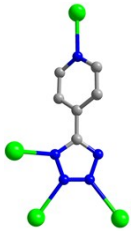
Bridging mode	Ref	Bridging mode	Ref
	1		5
μ_1-bridging mode		μ_5-bridging mode	
	1,2		3a
μ_2-bridging mode		μ_3-, μ_4- bridging mode	
	2d,3		3a
μ_3-bridging mode		μ_3-, μ_5- bridging mode	
	2a,4		
μ_4-bridging mode			

Table S2 Crystal Data and Structure Refinements for MOFs **1-3**.

Compounds	**1**	**2**	**3**
Empirical formula	$C_{43}H_{66}Cd_3N_{28}O_{12}$	$C_{61}H_{80}Cd_5N_{42}O_{13}$	$C_{123}H_{158}Cd_9N_{78}O_{22}$
Formula weight	1504.40	2171.65	4092.86
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	Pnna	P21/n	C2/m
Temperature	293k	113k	293k
a [Å]	14.044(3)	12.6177(19)	39.073(8)
b [Å]	20.297(4)	12.5869(18)	19.229(4)
c [Å]	23.635(5)	28.561(4)	13.798(3)
α [°]	90	90	90
β [°]	90	96.843(2)	103.60(3)
γ [°]	90	90	90
V [Å^3]	6737(2)	4503.6(11)	10076(4)
Z	4	2	2
Dc[g/cm^{-3}]	1.478	1.598	1.346
μ *[mm^{-1}]*	1.010	1.239	1.000
F(000)	3020.0	2160.0	4080.0
unique reflns	5939	7926	9205
GOF on F^2	0.975	1.366	1.033
$R_1(I>2\sigma(I))^a$	0.0818(3758)	0.1205(7846)	0.0583(6762)
$wR_2(I>2\sigma(I))^b$	0.2257(5939)	0.3212(7926)	0.1502(9205)

$^aR_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. $^b wR_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2\}^{1/2}$

Table S3 Bond lengths (Å) and angles (°) for MOFs **1-3**.

1

N(13)-Cd(1)#1	2.372(7)	N(6)-Cd(1)-N(13)#2	95.6(3)
Cd(1)-O(1)	2.292(7)	O(1)-Cd(1)-N(9)	85.6(3)
Cd(1)-N(1)	2.355(8)	N(1)-Cd(1)-N(9)	93.6(3)
Cd(1)-O(2)	2.358(7)	O(2)-Cd(1)-N(9)	90.3(3)
Cd(1)-N(6)	2.353(8)	N(6)-Cd(1)-N(9)	171.8(3)
Cd(1)-N(13)#2	2.372(7)	N(13)#2-Cd(1)-N(9)	91.0(3)
Cd(1)-N(9)	2.379(8)	O(1)-Cd(2)-N(5)#3	93.77(19)
Cd(2)-O(1)	2.246(14)	O(1)-Cd(2)-N(5)#4	93.8(2)
Cd(2)-N(5)#3	2.357(7)	N(5)#3-Cd(2)-N(5)#4	172.5(4)
Cd(2)-N(5)#4	2.357(7)	O(1)-Cd(2)-N(8)#5	180.000(3)
Cd(2)-N(8)#5	2.383(10)	N(5)#3-Cd(2)-N(8)#5	86.2(2)
Cd(2)-N(10)	2.377(8)	N(5)#4-Cd(2)-N(8)#5	86.2(2)
Cd(2)-N(10)#6	2.377(8)	O(1)-Cd(2)-N(10)	85.92(19)
O(1)-Cd(1)#6	2.292(7)	N(5)#3-Cd(2)-N(10)	91.6(3)
N(5)-Cd(2)#4	2.357(7)	N(5)#4-Cd(2)-N(10)	88.9(3)
N(8)-Cd(2)#7	2.383(10)	N(8)#5-Cd(2)-N(10)	94.08(19)
O(1)-Cd(1)-N(1)	90.46(19)	O(1)-Cd(2)-N(10)#6	85.92(19)
O(1)-Cd(1)-O(2)	88.39(18)	N(5)#3-Cd(2)-N(10)#6	88.9(3)
N(1)-Cd(1)-O(2)	175.9(3)	N(5)#4-Cd(2)-N(10)#6	91.6(3)
O(1)-Cd(1)-N(6)	87.6(3)	N(8)#5-Cd(2)-N(10)#6	94.08(19)
N(1)-Cd(1)-N(6)	91.0(3)	N(10)-Cd(2)-N(10)#6	171.8(4)
O(2)-Cd(1)-N(6)	85.0(3)	Cd(2)-O(1)-Cd(1)	121.1(3)

O(1)-Cd(1)-N(13)#2	175.7(3)	Cd(2)-O(1)-Cd(1)#6	121.1(3)
N(1)-Cd(1)-N(13)#2	92.4(3)	Cd(1)-O(1)-Cd(1)#6	117.8(6)
O(2)-Cd(1)-N(13)#2	89.0(3)		

Symmetry codes: #1 x-1/2,y,-z+2; #2 x+1/2,y,-z+2; #3 -x+3/2,y-1/2,-z+3/2; #4 -x+3/2,-y+2,z; #5 x-1,y,z; #6 x,-y+3/2,-z+3/2; #7 x+1,y,z.

2

Cd(1)-O(2)	2.291(11)	Cd(3)-N(17)	2.397(13)
Cd(1)-N(18)#1	2.337(16)	N(4)-Cd(2)#6	2.382(15)
Cd(1)-N(1)	2.345(15)	N(3)-Cd(1)#6	2.385(15)
Cd(1)-N(15)#2	2.371(15)	N(8)-Cd(1)#8	2.405(15)
Cd(1)-N(3)#3	2.385(15)	N(9)-Cd(2)#8	2.382(14)
Cd(1)-N(8)#4	2.405(15)	N(18)-Cd(1)#1	2.337(16)
Cd(2)-O(2)	2.267(11)	N(20)-Cd(2)#5	2.331(17)
Cd(2)-N(20)#5	2.331(17)	O(2)-Cd(1)-N(18)#1	89.1(5)
Cd(2)-N(6)	2.347(15)	O(2)-Cd(1)-N(1)	170.4(5)
Cd(2)-N(12)	2.360(15)	N(18)#1-Cd(1)-N(1)	97.9(6)
Cd(2)-N(4)#3	2.382(15)	O(2)-Cd(1)-N(15)#2	99.7(5)
Cd(2)-N(9)#4	2.382(14)	N(18)#1-Cd(1)-N(15)#2	99.9(6)
Cd(3)-O(2)#1	2.227(11)	N(1)-Cd(1)-N(15)#2	85.7(6)
Cd(3)-O(2)	2.227(11)	O(2)-Cd(1)-N(3)#3	85.5(4)
Cd(3)-O(1)	2.360(10)	N(18)#1-Cd(1)-N(3)#3	87.9(6)
Cd(3)-O(1)#1	2.360(10)	N(1)-Cd(1)-N(3)#3	88.2(6)
Cd(3)-N(13)	2.383(14)	N(15)#2-Cd(1)-N(3)#3	170.7(5)
Cd(3)-N(13)#1	2.383(14)	O(2)-Cd(1)-N(8)#4	82.1(4)

Cd(3)-N(17)#1	2.397(14)	N(18)#1-Cd(1)-N(8)#4	168.5(5)
N(1)-Cd(1)-N(8)#4	90.2(5)	O(2)-Cd(3)-O(1)#1	125.3(4)
N(15)#2-Cd(1)-N(8)#4	88.8(5)	O(1)-Cd(3)-O(1)#1	180.000(1)
N(3)#3-Cd(1)-N(8)#4	84.2(5)	O(2)#1-Cd(3)-N(13)	93.8(4)
O(2)-Cd(2)-N(20)#5	98.8(5)	O(2)-Cd(3)-N(13)	86.2(4)
O(2)-Cd(2)-N(6)	171.7(5)	O(1)-Cd(3)-N(13)	120.7(4)
N(20)#5-Cd(2)-N(6)	86.0(6)	O(1)#1-Cd(3)-N(13)	59.3(4)
O(2)-Cd(2)-N(12)	88.8(5)	O(2)#1-Cd(3)-N(13)#1	86.2(4)
N(20)#5-Cd(2)-N(12)	101.1(6)	O(2)-Cd(3)-N(13)#1	93.8(4)
N(6)-Cd(2)-N(12)	96.9(6)	O(1)-Cd(3)-N(13)#1	59.3(4)
O(2)-Cd(2)-N(4)#3	86.5(4)	O(1)#1-Cd(3)-N(13)#1	120.7(4)
N(20)#5-Cd(2)-N(4)#3	170.4(6)	N(13)-Cd(3)-N(13)#1	180.000(2)
N(6)-Cd(2)-N(4)#3	87.8(5)	O(2)#1-Cd(3)-N(17)#1	93.2(4)
N(12)-Cd(2)-N(4)#3	86.9(5)	O(2)-Cd(3)-N(17)#1	86.8(4)
O(2)-Cd(2)-N(9)#4	83.7(4)	O(1)-Cd(3)-N(17)#1	121.8(4)
N(20)#5-Cd(2)-N(9)#4	89.2(6)	O(1)#1-Cd(3)-N(17)#1	58.2(4)
N(6)-Cd(2)-N(9)#4	89.7(5)	N(13)-Cd(3)-N(17)#1	94.1(5)
N(12)-Cd(2)-N(9)#4	168.1(5)	N(13)#1-Cd(3)-N(17)#1	85.9(5)
N(4)#3-Cd(2)-N(9)#4	83.4(5)	O(2)#1-Cd(3)-N(17)	86.8(4)
O(2)#1-Cd(3)-O(2)	180.000(2)	O(2)-Cd(3)-N(17)	93.2(4)
O(2)#1-Cd(3)-O(1)	125.3(4)	O(1)-Cd(3)-N(17)	58.2(4)
O(2)-Cd(3)-O(1)	54.7(4)	O(1)#1-Cd(3)-N(17)	121.8(4)
O(2)#1-Cd(3)-O(1)#1	54.7(4)	N(13)-Cd(3)-N(17)	85.9(5)
N(17)#1-Cd(3)-N(17)	180.000(2)	N(13)#1-Cd(3)-N(17)	94.1(5)

Cd(3)-O(2)-Cd(2)	116.3(5)	Cd(3)-O(2)-Cd(1)	115.7(5)
Cd(2)-O(2)-Cd(1)	109.6(4)		

Symmetry codes: #1 -x+1,-y+1,-z+1, #2 x,y-1,z, #3 -x+3/2,y+1/2,-z+3/2, #4 -x+1/2,y-1/2,-z+3/2, #5 -x,-y+1,-z+1, #6 -x+3/2,y-1/2,-z+3/2, #7 x,y+1,z, #8 -x+1/2,y+1/2,-z+3/2.

3

Cd(1)-O(1)	2.270(5)	O(3)-Cd(3)-N(19)#2	80.6(2)
Cd(1)-N(6)	2.287(8)	N(19)#3-Cd(3)-N(19)#2	94.5(3)
Cd(1)-N(1)	2.302(8)	N(19)-Cd(3)-N(19)#2	180.0(3)
Cd(1)-N(9)#1	2.340(5)	O(3)#2-Cd(3)-N(19)#4	99.4(2)
Cd(1)-N(9)	2.340(5)	O(3)-Cd(3)-N(19)#4	80.6(2)
Cd(1)-N(14)	2.379(8)	N(19)#3-Cd(3)-N(19)#4	180.0(2)
Cd(3)-O(3)#2	2.258(8)	N(19)-Cd(3)-N(19)#4	94.5(3)
Cd(3)-O(3)	2.258(8)	N(19)#2-Cd(3)-N(19)#4	85.5(3)
Cd(3)-N(19)#3	2.293(6)	O(1)-Cd(2)-N(17)	175.4(2)
Cd(3)-N(19)	2.293(6)	O(1)-Cd(2)-N(11)#1	88.08(18)
Cd(3)-N(19)#2	2.293(6)	N(17)-Cd(2)-N(11)#1	95.0(2)
Cd(3)-N(19)#4	2.293(6)	O(1)-Cd(2)-N(16)#5	81.80(19)
Cd(2)-O(1)	2.219(3)	N(17)-Cd(2)-N(16)#5	94.4(2)
Cd(2)-N(17)	2.271(6)	N(11)#1-Cd(2)-N(16)#5	95.9(2)
Cd(2)-N(11)#1	2.304(5)	O(1)-Cd(2)-N(8)#6	88.06(19)
Cd(2)-N(16)#5	2.331(5)	N(17)-Cd(2)-N(8)#6	89.1(2)
Cd(2)-N(8)#6	2.333(5)	N(11)#1-Cd(2)-N(8)#6	174.5(2)
Cd(2)-O(2)	2.450(9)	N(16)#5-Cd(2)-N(8)#6	87.4(2)

Cd(4)-O(3)#7	2.295(7)	O(1)-Cd(2)-O(2)	93.3(2)
Cd(4)-N(13)#8	2.330(5)	N(17)-Cd(2)-O(2)	90.3(2)
Cd(4)-N(13)	2.330(5)	N(11)#1-Cd(2)-O(2)	86.7(2)
Cd(4)-N(5)#9	2.363(7)	N(16)#5-Cd(2)-O(2)	174.4(2)
Cd(4)-N(20)#10	2.397(5)	N(8)#6-Cd(2)-O(2)	89.6(3)
Cd(4)-N(20)#11	2.397(6)	O(3)#7-Cd(4)-N(13)#8	108.7(2)
N(11)-Cd(2)#1	2.304(5)	O(3)#7-Cd(4)-N(13)	108.7(2)
N(8)-Cd(2)#11	2.333(5)	N(13)#8-Cd(4)-N(13)	100.3(3)
N(20)-Cd(4)#12	2.397(5)	O(3)#7-Cd(4)-N(5)#9	157.2(3)
N(16)-Cd(2)#5	2.331(5)	N(13)#8-Cd(4)-N(5)#9	85.4(2)
N(5)-Cd(4)#9	2.363(7)	N(13)-Cd(4)-N(5)#9	85.4(2)
O(1)-Cd(2)#1	2.219(3)	O(3)#7-Cd(4)-N(20)#10	77.7(2)
O(3)-Cd(4)#7	2.295(7)	N(13)#8-Cd(4)-N(20)#10	88.7(2)
O(1)-Cd(1)-N(6)	167.5(3)	N(13)-Cd(4)-N(20)#10	166.2(2)
O(1)-Cd(1)-N(1)	81.1(3)	N(5)#9-Cd(4)-N(20)#10	85.0(2)
N(6)-Cd(1)-N(1)	86.4(3)	O(3)#7-Cd(4)-N(20)#11	77.7(2)
O(1)-Cd(1)-N(9)#1	85.33(14)	N(13)#8-Cd(4)-N(20)#11	166.2(2)
N(6)-Cd(1)-N(9)#1	95.65(14)	N(13)-Cd(4)-N(20)#11	88.7(2)
N(1)-Cd(1)-N(9)#1	94.25(14)	N(5)#9-Cd(4)-N(20)#11	85.0(2)
O(1)-Cd(1)-N(9)	85.33(14)	N(20)#10-Cd(4)-N(20)#11	80.7(3)
N(6)-Cd(1)-N(9)	95.65(13)	Cd(2)-O(1)-Cd(2)#1	107.6(2)
N(1)-Cd(1)-N(9)	94.25(14)	Cd(2)-O(1)-Cd(1)	116.42(16)
N(9)#1-Cd(1)-N(9)	166.3(3)	Cd(2)#1-O(1)-Cd(1)	116.42(16)
O(1)-Cd(1)-N(14)	104.4(3)	Cd(3)-O(3)-Cd(4)#7	115.6(4)

N(6)-Cd(1)-N(14)	88.1(3)	O(3)#2-Cd(3)-N(19)#3	80.6(2)
N(1)-Cd(1)-N(14)	174.5(3)	O(3)-Cd(3)-N(19)#3	99.4(2)
N(9)#1-Cd(1)-N(14)	86.29(14)	O(3)#2-Cd(3)-N(19)	80.6(2)
N(9)-Cd(1)-N(14)	86.29(14)	O(3)-Cd(3)-N(19)	99.4(2)
O(3)#2-Cd(3)-O(3)	180.0(3)	N(19)#3-Cd(3)-N(19)	85.5(3)
O(3)#2-Cd(3)-N(19)#3	80.6(2)		

Symmetry codes: #1 x,-y+1,z; #2 -x,-y,-z; #3 x,-y,z; #4 -x,y,-z; #5 -x,y,-z+1; #6 x,-y+1,z-1; #7 -x,-y+1,-z+1; #8 x,-y+2,z; #9 -x+1/2,-y+3/2,-z+2; #10 x,y+1,z+1; #11 x,-y+1,z+1; #12 x,y-1,z-1.

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