Supporting Information

Two Schiff base ligands for distiguishing Zn^{II}/Cd^{II} sensing – effect of substituent on fluorecent sensing

Zhi-Peng Zheng,[a] Qin Wei,[a] Wen-Xia Yin,[a] Lin-Tao Wan,[a] Xia Huang,[a] Ying Yu*,[a] Yue-Peng Cai*,[a,b]

[a]School of Chemistry and Environment, South China Normal University; Guangzhou Key Laboratory of Materials for Energy Conversion and Storage, Guangzhou 510006, P.R. China
[b]State Key Laboratory of Structure Chemistry, Fujian, Fuzhou 350002, P.R. China

Contents

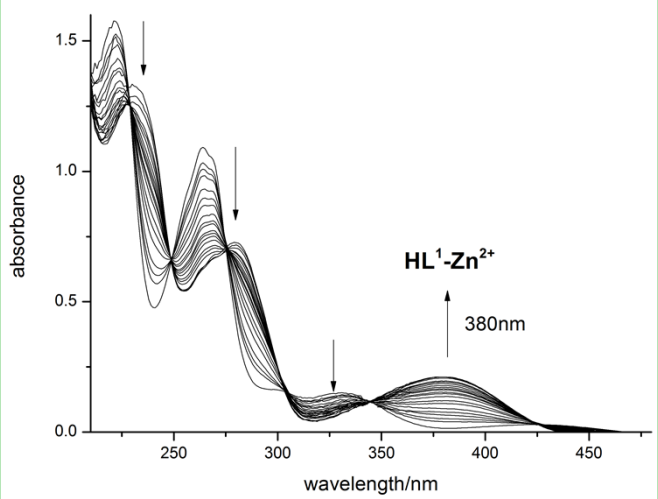


Figure S1. UV-vis spectral changes of **HL¹** upon addition of $ZnCl_2$ in ethanol at room temperature ([**HL¹**] = 0.1 mM, [Zn^{2+}] = 0, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09, 0.10, 0.11, 0.12, 0.13, 0.14, 0.15, 0.16, 0.17, 0.18, 0.19, 0.20 mM.

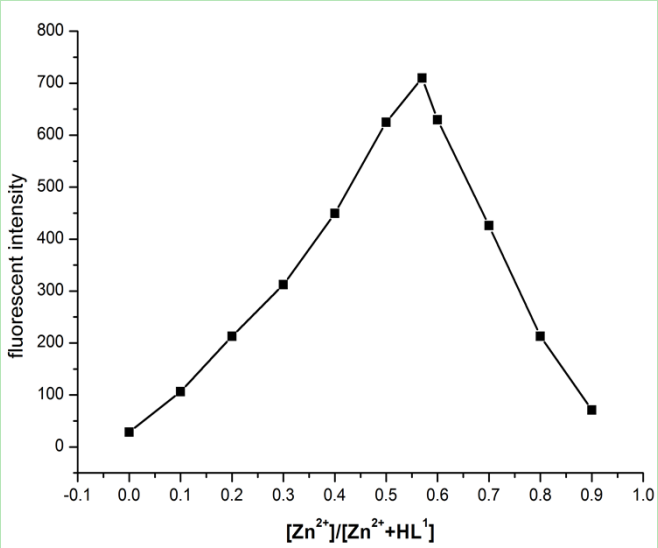


Figure S2. Job's plot showing the 4:3 binding ratio of Zn^{2+} to **HL¹**.

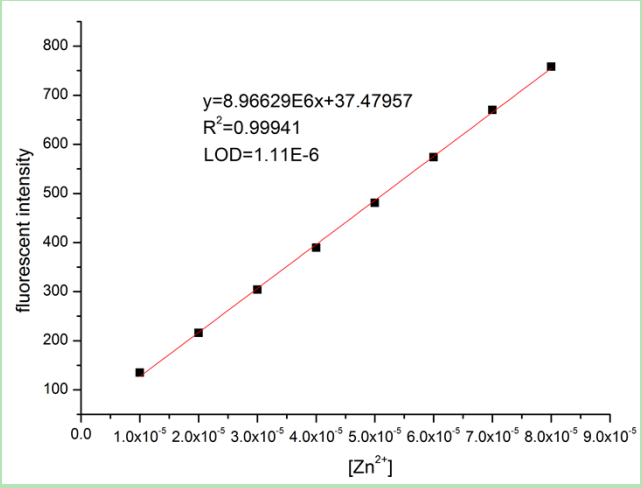


Figure S3. Limit of detection of **HL¹** (0.1mM) for $Zn^{2+}$with a linearity range of 1×10^{-5} to 9×10^{-5} M.

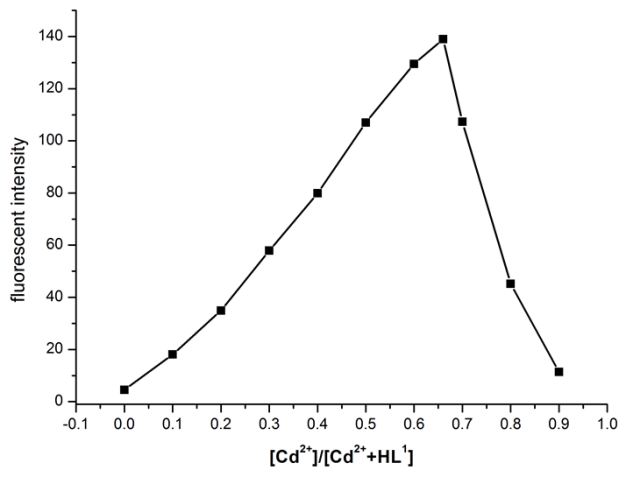


Figure S4. Job's plot showing the 2:1 binding ratio of Cd^{2+} to **HL**[1].

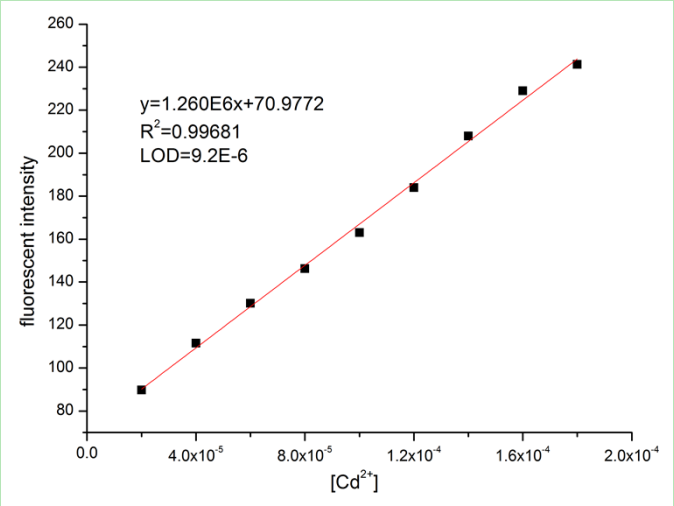


Figure S5. Limit of detection of **HL**[1] (0.1mM) for $Cd^{2+}$with a linearity range of 2×10^{-5} to 1.8×10^{-4} M

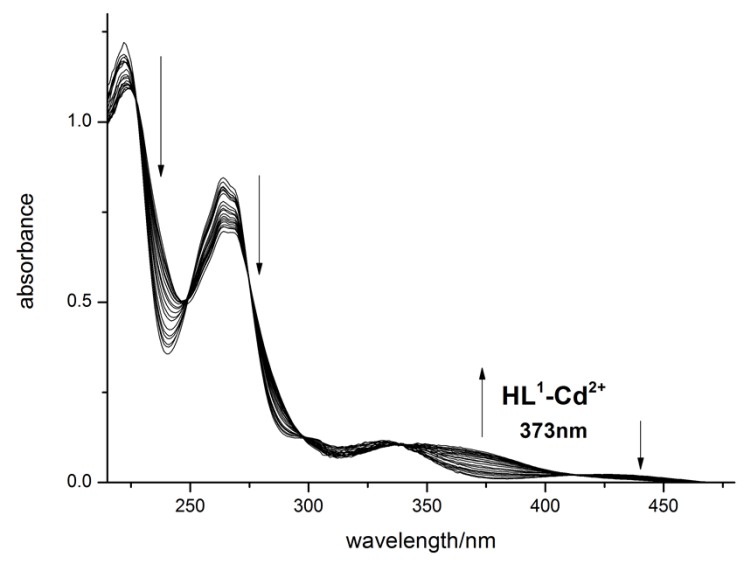
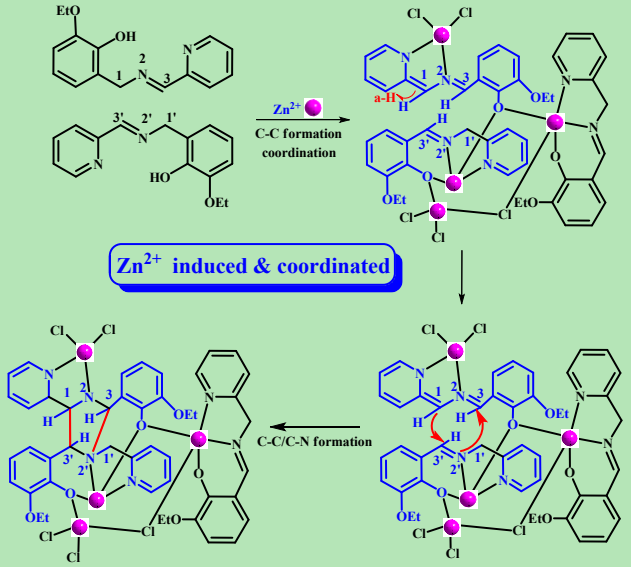


Figure S6. UV-vis spectral changes of **HL**[1] upon addition of $CdCl_2$ in ethanol at room temperature ([**HL**[1]] = 0.1 mM, [Cd^{2+}] = 0, 0.02, 0.04, 0.06, 0.08, 0.10, 0.12, 0.14, 0.16, 0.18, 0.20, 0.22, 0.24, 0.26, 0.28, 0.30, 0.32, 0.34, 0.36, 0.38, 0.40 mM.).



Scheme S1. Proposed mechanism for Zn-induced dimerization of **HL^1** to generate **L$^{1'}$** in compound **1**. Newly formed C-C, C-N bonds were highlighted as red and **L$^{1'}$** as blue.

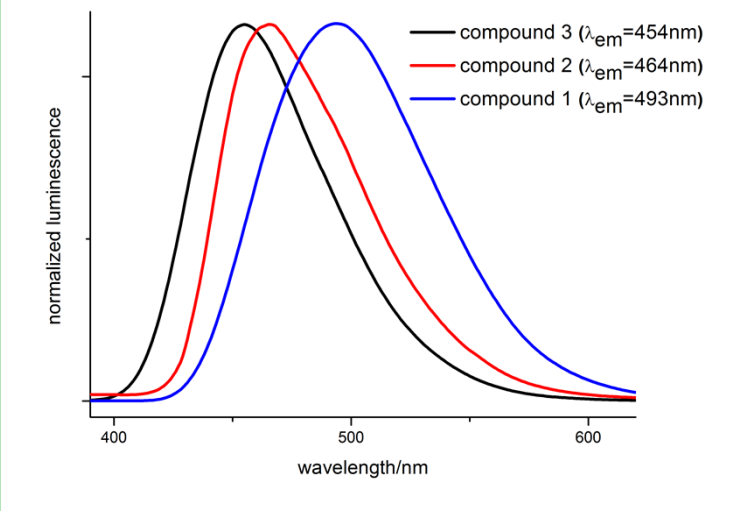


Figure S7. Emission spectra of compounds **1-3** in ethanol at room temperature. (λ_{ex} = 350 nm)

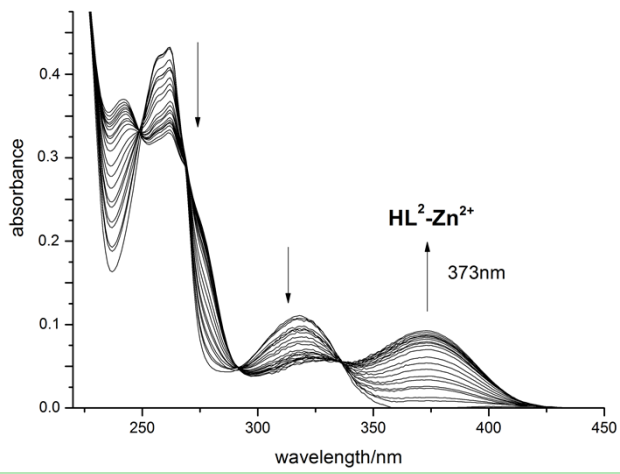


Figure S8. UV-vis spectral changes of **HL^2** upon addition of $ZnCl_2$ in ethanol at room temperature ([**HL^2**] = 10μM, [Zn^{2+}] =0, 1.0, 2.0, 3.0, 4.0 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 11.0, 12.0 13.0, 14.0, 15.0, 16.0, 17.0, 18.0, 19.0, 20.0 μM .).

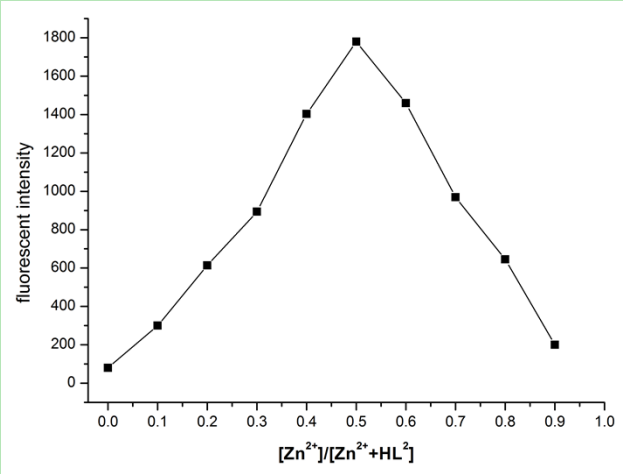


Figure S9. Job's plot showing the 1:1 binding ratio of **HL²** to Zn^{2+}.

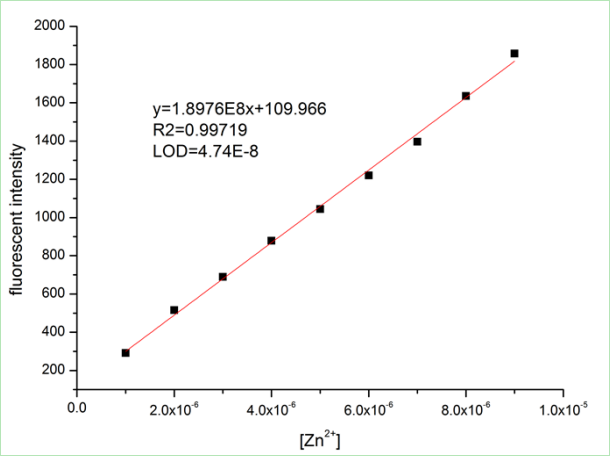


Figure S10. Limit of detection of **HL²** (10μM) for Zn^{2+} with a linearity range of 1×10^{-6} to 9×10^{-6} M.

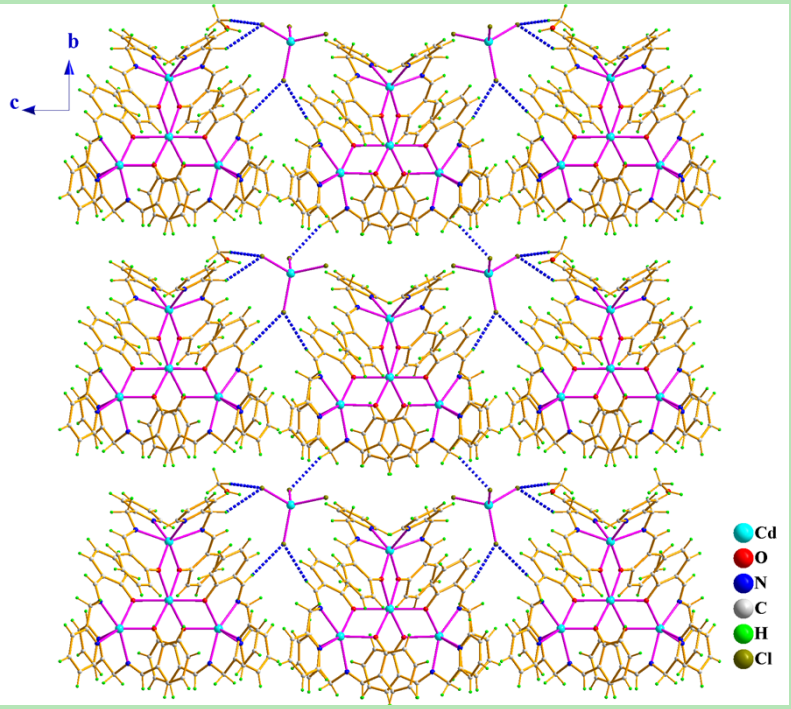


Figure S11. 2-D supramolecular layer of compound **4** correlated by cationic $[Cd_4\mathbf{L}^2_6]^{2+}$ unit, anionic $[CdCl_4]^{2-}$, lattice methanol and water molecules through C-H…Cl hydrogen bonds along bc plane

Table S1. Crystal data and structure refinement of four compounds **1-4.**

	1	**2**	**3**	**4**
Chemical formula	$C_{45}H_{44}Cl_5N_6O_6Zn_4$	$C_{34}H_{42}Cd_4Cl_6N_4O_6S_2$	$C_{26}H_{22}Cl_2N_4O_2Zn_2$	$C_{158}H_{142}Cd_{10}Cl_8N_{24}O_{15}$
M	1203.59	1329.14	624.12	4024.56
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	P-1	P-1	P2(1)/n	P2/c
a /Å	12.2973(12)	8.495(4)	9.330(3)	20.1807(10)
b /Å	13.6411(13)	8.812(5)	9.003(3)	14.3707(7)
c /Å	15.1641(15)	16.014(8)	15.332(4)	29.3758(12)
α /°	90.4330(10)	96.662(7)	90	90
β /°	91.7110(10)	93.244(6)	103.388(4)	111.272(3)
γ/°	92.5060(10)	106.658(6)	90	90
V/Å^3	2540.1(4)	1135.6(10)	1252.8(6)	7938.9(6)
Z	2	1	2	4
T /*K*	296(2)	296(2)	296(2)	293(2)
F(000)	1218	648	632	3968
D_{calcd}/ g cm^{-3}	1.574	1.944	1.655	1.676
μ /mm^{-1}	2.180	2.337	2.160	1.513
λ /Å	0.71073	0.71073	0.71073	0.71073
R_{int}	0.0183	0.0329	0.0247	0.0380
data/restraint/parm	9003 / 0 / 598	3799 / 0 / 256	2203 / 0 / 163	13295 / 0 / 973
GOF	1.033	1.094	1.063	1.047
R_1 [$I = 2\sigma(I)$][a]	0.0566	0.1107	0.0371	0.0688
wR_2 [$I = 2\sigma(I)$][b]	0.0928	0.2751	0.0721	0.0920

[a] $R_1 = \Sigma||F_o| - |F_c||/|F_o|$, [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)_2 + bP]$. $P = (F_o^2 + 2F_c^2)/3$.

Table S2. The selected bond lengths and angles for compounds **1-4.**

		1	
Zn(1)-O(3)	1.9628(19)	O(5)-Zn(1)-N(4)	162.73(8)
Zn(1)-O(5)	2.015(2)	N(3)-Zn(1)-N(4)	78.26(10)
Zn(1)-O(1)	2.0974(19)	O(1)-Zn(1)-N(4)	84.76(8)
Zn(2)-O(3)	2.000(2)	O(3)-Zn(2)-Cl(1)	127.06(7)
Zn(3)-O(1)	1.985(2)	O(3)-Zn(2)-Cl(2)	104.04(6)
Zn(3)-O(5)	2.062(2)	Cl(1)-Zn(2)-Cl(2)	117.60(4)
Zn(1)-N(3)	2.030(3)	O(3)-Zn(2)-Cl(3)	97.10(6)
Zn(1)-N(4)	2.300(2)	Cl(1)-Zn(2)-Cl(3)	104.71(4)
Zn(3)-N(6)	2.026(3)	Cl(2)-Zn(2)-Cl(3)	101.29(4)
Zn(3)-N(5)	2.088(3)	O(1)-Zn(3)-N(6)	159.12(11)
Zn(4)-N(1)	2.064(3)	O(1)-Zn(3)-O(5)	79.47(8)
Zn(4)-N(2)	2.080(2)	N(6)-Zn(3)-O(5)	87.41(11)
Zn(2)-Cl(1)	2.1861(10)	O(1)-Zn(3)-N(5)	109.31(11)
Zn(2)-Cl(2)	2.2377(9)	N(6)-Zn(3)-N(5)	81.08(13)
Zn(2)-Cl(3)	2.3810(9)	O(5)-Zn(3)-N(5)	166.36(10)
Zn(3)-Cl(3)	2.4237(10)	O(1)-Zn(3)-Cl(3)	89.33(7)
Zn(4)-Cl(4)	2.1958(12)	N(6)-Zn(3)-Cl(3)	108.94(9)
Zn(4)-Cl(5)	2.1997(11)	O(5)-Zn(3)-Cl(3)	99.41(6)
O(3)-Zn(1)-O(5)	98.26(9)	N(5)-Zn(3)-Cl(3)	91.28(8)
O(3)-Zn(1)-N(3)	143.04(10)	N(1)-Zn(4)-N(2)	83.15(10)
O(5)-Zn(1)-N(3)	104.97(10)	N(1)-Zn(4)-Cl(4)	115.33(9)
O(3)-Zn(1)-O(1)	113.76(8)	N(2)-Zn(4)-Cl(4)	106.32(8)
O(5)-Zn(1)-O(1)	77.98(8)	N(1)-Zn(4)-Cl(5)	110.69(8)
N(3)-Zn(1)-O(1)	99.10(10)	N(2)-Zn(4)-Cl(5)	115.16(8)
O(3)-Zn(1)-N(4)	87.99(8)	Cl(4)-Zn(4)-Cl(5)	120.27(4)
		2	
Cd(2)-O(3)	2.239(17)	O(3)-Cd(2)-Cl(2)	88.8(5)
Cd(2)-O(1)	2.233(13)	O(1)-Cd(2)-Cl(2)	81.2(4)
Cd(2)-O(2)	2.494(16)	O(2)-Cd(2)-Cl(2)	145.9(4)
Cd(2)-Cl(3)	2.581(6)	Cl(3)-Cd(2)-Cl(2)	96.6(2)
Cd(2)-Cl(3)#1	2.583(6)	Cl(3)#1-Cd(2)-Cl(2)	115.8(2)
Cd(2)-Cl(2)	2.630(6)	O(1)-Cd(1)-N(1)	132.0(6)
Cd(1)-O(1)	2.243(14)	O(1)-Cd(1)-N(2)	77.5(5)
Cd(1)-N(1)	2.312(15)	N(1)-Cd(1)-N(2)	72.3(5)
Cd(1)-N(2)	2.317(17)	O(1)-Cd(1)-Cl(1)	120.0(4)
Cd(1)-Cl(1)	2.453(6)	N(1)-Cd(1)-Cl(1)	105.6(4)
Cd(1)-Cl(2)	2.560(6)	N(2)-Cd(1)-Cl(1)	111.4(4)
O(3)-Cd(2)-O(1)	94.8(6)	O(1)-Cd(1)-Cl(2)	82.6(3)
O(3)-Cd(2)-O(2)	80.9(6)	N(1)-Cd(1)-Cl(2)	98.1(4)
O(1)-Cd(2)-O(2)	67.6(5)	N(2)-Cd(1)-Cl(2)	140.9(4)
O(3)-Cd(2)-Cl(3)	169.5(5)	O(3)-Cd(2)-Cl(3)#1	86.2(5)

O(1)-Cd(2)-Cl(3)	95.0(4)	O(1)-Cd(2)-Cl(3)#1	163.1(4)
O(2)-Cd(2)-Cl(3)	99.2(4)	O(2)-Cd(2)-Cl(3)#1	96.0(4)
Cl(3)-Cd(2)#1	2.583(6)	Cl(3)-Cd(2)-Cl(3)#1	83.34(18)
		S(1)-O(3)-Cd(2)	119.8(9)
		3	
Zn(1)-O(1)#2	2.0017(17)	N(2)-Zn(1)-O(1)	84.02(7)
Zn(1)-N(2)	2.058(2)	O(1)#2-Zn(1)-N(1)	102.75(7)
Zn(1)-O(1)	2.1398(17)	N(2)-Zn(1)-N(1)	77.87(8)
Zn(1)-N(1)	2.159(2)	O(1)-Zn(1)-N(1)	160.96(7)
Zn(1)-Cl(1)	2.2580(9)	O(1)#2-Zn(1)-Cl(1)	117.12(6)
O(1)-Zn(1)#2	2.0017(17)	N(2)-Zn(1)-Cl(1)	125.77(6)
O(1)#2-Zn(1)-N(2)	116.69(7)	O(1)-Zn(1)-Cl(1)	98.82(5)
O(1)#2-Zn(1)-O(1)	80.10(7)	N(1)-Zn(1)-Cl(1)	96.54(6)
		4	
Cd(1)-O(2)	2.297(4)	O(3)-Cd(3)-O(2)	77.75(15)
Cd(1)-O(2)#3	2.297(4)	O(3)-Cd(3)-N(4)	113.13(18)
Cd(1)-O(1)#3	2.321(4)	O(2)-Cd(3)-N(4)	80.97(18)
Cd(1)-O(1)	2.321(4)	O(3)-Cd(3)-N(6)	80.8(2)
Cd(1)-O(3)#3	2.337(4)	O(2)-Cd(3)-N(6)	121.16(18)
Cd(1)-O(3)	2.337(4)	N(4)-Cd(3)-N(6)	156.8(2)
O(4)-Cd(7)	2.254(4)	O(3)-Cd(3)-N(5)	137.40(19)
O(4)-Cd(5)	2.306(4)	O(2)-Cd(3)-N(5)	89.40(19)
Cd(5)-O(5)	2.288(4)	N(4)-Cd(3)-N(5)	104.4(2)
Cd(5)-O(5)#4	2.288(4)	N(6)-Cd(3)-N(5)	71.6(2)
Cd(5)-O(4)#4	2.306(4)	O(3)-Cd(3)-N(3)	109.39(19)
Cd(5)-O(6)	2.329(4)	O(2)-Cd(3)-N(3)	151.40(18)
Cd(5)-O(6)#4	2.329(4)	N(4)-Cd(3)-N(3)	70.7(2)
Cd(3)-O(3)	2.245(4)	N(6)-Cd(3)-N(3)	87.4(2)
Cd(3)-O(2)	2.263(4)	N(5)-Cd(3)-N(3)	101.2(2)
Cd(3)-N(4)	2.274(5)	O(1)#3-Cd(2)-O(1)	75.8(2)
Cd(3)-N(6)	2.285(6)	O(1)#3-Cd(2)-N(2)#3	81.2(2)
Cd(3)-N(5)	2.393(6)	O(1)-Cd(2)-N(2)#3	131.30(18)
Cd(3)-N(3)	2.440(5)	O(1)#3-Cd(2)-N(2)	131.30(18)
Cd(2)-O(1)#3	2.248(4)	O(1)-Cd(2)-N(2)	81.2(2)
Cd(2)-O(1)	2.248(4)	N(2)#3-Cd(2)-N(2)	142.6(3)
Cd(2)-N(2)#3	2.277(6)	O(1)#3-Cd(2)-N(1)	96.7(2)
Cd(2)-N(2)	2.277(6)	O(1)-Cd(2)-N(1)	135.43(19)
Cd(2)-N(1)	2.444(6)	N(2)#3-Cd(2)-N(1)	89.1(2)
Cd(2)-N(1)#3	2.444(6)	N(2)-Cd(2)-N(1)	71.3(2)
Cd(6)-O(6)	2.242(4)	O(1)#3-Cd(2)-N(1)#3	135.43(19)
Cd(6)-N(12)	2.282(6)	O(1)-Cd(2)-N(1)#3	96.7(2)
Cd(6)-O(5)	2.275(4)	N(2)#3-Cd(2)-N(1)#3	71.3(2)

Cd(6)-N(10)	2.284(5)	N(2)-Cd(2)-N(1)#3	89.1(2)
Cd(6)-N(11)	2.395(6)	N(1)-Cd(2)-N(1)#3	116.6(3)
Cd(6)-N(9)	2.447(5)	O(6)-Cd(6)-N(12)	80.23(18)
Cd(7)-O(4)#4	2.254(4)	O(6)-Cd(6)-O(5)	77.22(14)
Cd(7)-N(8)#4	2.290(6)	N(12)-Cd(6)-O(5)	123.64(18)
Cd(7)-N(8)	2.291(6)	O(6)-Cd(6)-N(10)	118.86(17)
Cd(7)-N(7)	2.446(6)	N(12)-Cd(6)-N(10)	153.7(2)
Cd(7)-N(7)#4	2.446(6)	O(5)-Cd(6)-N(10)	80.39(17)
O(2)-Cd(1)-O(2)#4	179.0(2)	O(6)-Cd(6)-N(11)	133.31(18)
O(2)-Cd(1)-O(1)#4	98.31(15)	N(12)-Cd(6)-N(11)	71.5(2)
O(2)#2-Cd(1)-O(1)#4	82.51(15)	O(5)-Cd(6)-N(11)	88.27(18)
O(2)-Cd(1)-O(1)	82.51(15)	N(10)-Cd(6)-N(11)	101.5(2)
O(2)#3-Cd(1)-O(1)	98.31(15)	O(6)-Cd(6)-N(9)	110.04(17)
O(1)#4-Cd(1)-O(1)	73.0(2)	N(12)-Cd(6)-N(9)	86.2(2)
O(2)-Cd(1)-O(3)#3	103.94(15)	O(5)-Cd(6)-N(9)	150.11(17)
O(2)#3-Cd(1)-O(3)#3	75.27(15)	N(10)-Cd(6)-N(9)	70.69(19)
O(1)#2-Cd(1)-O(3)#3	102.86(14)	N(11)-Cd(6)-N(9)	104.4(2)
O(1)-Cd(1)-O(3)#3	172.94(15)	O(4)-Cd(7)-O(4)#4	75.9(2)
O(2)-Cd(1)-O(3)	75.27(15)	O(4)-Cd(7)-N(8)#4	131.32(18)
O(2)#3-Cd(1)-O(3)	103.94(15)	O(4)#4-Cd(7)-N(8)#4	80.42(18)
O(1)#3-Cd(1)-O(3)	172.94(15)	O(4)-Cd(7)-N(8)	80.42(18)
O(1)-Cd(1)-O(3)	102.86(14)	O(4)#4-Cd(7)-N(8)	131.32(18)
O(3)#3-Cd(1)-O(3)	81.8(2)	N(8)#4-Cd(7)-N(8)	143.5(3)
O(5)-Cd(5)-O(5)#3	179.7(2)	O(4)-Cd(7)-N(7)	136.1(2)
O(5)-Cd(5)-O(4)#4	84.01(15)	O(4)#3-Cd(7)-N(7)	98.7(2)
O(5)#3-Cd(5)-O(4)#4	96.23(15)	N(8)#3-Cd(7)-N(7)	88.9(2)
O(5)-Cd(5)-O(4)	96.23(15)	N(8)-Cd(7)-N(7)	70.9(2)
O(5)#4-Cd(5)-O(4)	84.02(15)	O(4)-Cd(7)-N(7)#4	98.7(2)
O(4)#4-Cd(5)-O(4)	73.9(2)	O(4)#4-Cd(7)-N(7)#4	136.1(2)
O(5)-Cd(5)-O(6)	75.25(14)	N(8)#4-Cd(7)-N(7)#4	70.9(2)
O(5)#4-Cd(5)-O(6)	104.51(14)	N(8)-Cd(7)-N(7)#4	88.9(2)
O(4)#4-Cd(5)-O(6)	102.64(14)	N(7)-Cd(7)-N(7)#4	112.8(3)
O(4)-Cd(5)-O(6)	171.21(14)	Cl(3)-Cd(4)-Cl(4)	110.54(9)
O(5)-Cd(5)-O(6)#4	104.51(14)	Cl(3)-Cd(4)-Cl(2)	109.28(9)
O(5)#4-Cd(5)-O(6)#4	75.25(14)	Cl(4)-Cd(4)-Cl(2)	111.35(9)
O(4)#4-Cd(5)-O(6)#4	171.21(14)	Cl(3)-Cd(4)-Cl(1)	108.52(10)
O(4)-Cd(5)-O(6)#4	102.64(14)	Cl(4)-Cd(4)-Cl(1)	109.33(10)
O(6)-Cd(5)-O(6)#4	81.9(2)	Cl(2)-Cd(4)-Cl(1)	107.73(9)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+2,-z+1; #2 -x+1,-y,-z; #3 -x+1,y,-z+3/2; #4 -x,y,-z+3/2.