Supporting Information

A multi-binding site hydrazone-based chemosensor for Zn(II) and Cd(II) : A new strategy for detection of metal ions based on aggregation- induced emission

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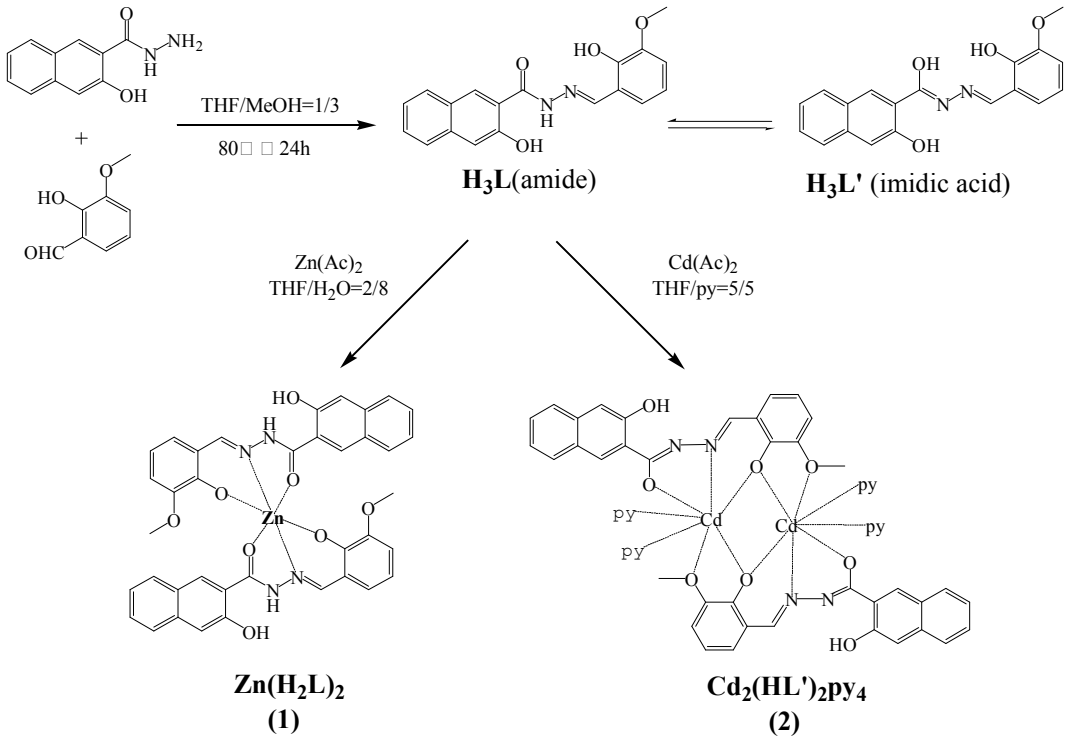
Experimental details

General materials and apparatus

All reagents and solvents (analytical and spectroscopic grade) were provided by commercial suppliers and used as received. Solutions of metal ions were prepared from LiCl, NaCl, KNO_3, $CaCl_2$, $MgCl_2·6H_2O$, $Al(ClO_4)_3·9H_2O$, $CrCl_3·6H_2O$, $Mn(ClO_4)_2·6H_2O$, $FeCl_3$, $Co(ClO_4)_2·6H_2O$, $Ni(ClO_4)_2·6H_2O$, $Cu(ClO_4)_2·6H_2O$, $Zn(Ac)_2·2H_2O$, $Cd(Ac)_2·2H_2O$, $Hg(ClO_4)_2·3H_2O$ and $Pb(ClO_4)_2·3H_2O$. Elemental analyses (CHN) were conducted using a Vario EL elemental analyzer. Fourier transform infrared (FT-IR) spectra were recorded on an Avatar 360 FT-IR spectrometer using KBr pellets in 4000-400 cm^{-1}. The ^{1}HNMR spectra were obtained on JEOL JNM-ECX600P (400 MHz) spectrometers with TMS as internal standard. Single crystal X-ray diffraction data were collected on an Oxford Diffraction SuperNova area-detector diffractometer using mirror optics monochromated Cu-Kα radiation (λ = 1.54184 Å) at low temperature (100 K). CrysAlisPro was used for the data collection, data reduction and empirical absorption correction. The structures were solved with the ShelXT[1] (direct methods) structure solution program and refined with the ShelXL[2] (Least Squares minimization) in the Olex2 package[3]. Fluorescence spectra were measured on a FS5 fluorescence spectrophotometer, with a xenon lamp as the excitation light source and a quartz cuvette (path length =1.0 cm). The dynamic light scattering (DLS) data were carried out by Brookhaven ZetaPlus Zeta Potential Analyzer. The morphologies of the samples were investigated by the field emission scanning electron microscope (FE-SEM, HITACHI, SU8010).

Synthesis of H_3L, complexes of Zn(II) and Cd(II)



Scheme S1 Synthesis route of **H_3L**, Zn(II) complex **1** and Cd(II) complex **2**.

Synthesis of **H_3L** (N-(3-methoxy-2-hydroxybenzylidene)-3-hydroxy-2-naphthahydrazone, $C_{19}H_{16}N_2O_4$): A mixture of 3-hydroxy-2-naphthoic acid hydrazide (0.0202 g, 0.1 mmol), 2-hydroxy-3-methoxybenzaldehyde (0.0152 g, 0.1 mmol), 2 ml tetrahydrofuran and 5 ml methanol was sealed in a 25 mL Teflon-lined autoclave and

heated at 80 °C for 24 h, cooled to room temperature. Colorless needle crystals (**H_3L**) suitable for X-ray crystallography were obtained, washed three times with methanol and filtered, and air-dried to obtain 0.0309 g of **H_3L** in a yield of 92.00%. Anal.Calcd for $C_{19}H_{16}N_2O_4$ (**H_3L**) (%): C, 67.85; H, 4.79; N, 8.33. Found: C, 67.96; H, 4.70; N, 8.32. IR for **H_3L** (KBr pellet, cm^{-1}): 3424w, 3173s, 2950w, 2322w, 1645s, 1630vs, 1611s, 1555s, 1506w, 1470w, 1452m, 1387w, 1356m, 1341w, 1227s, 1206s, 1171m, 1142w, 1123w, 1107w, 1070m, 1030m, 964m, 922w, 866w, 826w, 795w, 766w, 743w, 719w, 667w, 615w, 600w, 475m. ^{1}HNMR for **H_3L** (DMSO-d_6, 400 MHz) δ: 12.13 (s, 1H), 11.25 (s, 1H), 10.87 (s, 1H), 8.69 (s, 1H), 8.46 (s, 1H), 7.91 (d, 1H), 7.77 (d, 1H), 7.52 (t, 1H), 7.37 (t, 1H), 7.33(s,1H), 7.19(d, 1H), 7.06 (d, 1H), 6.89 (t, 1H), 3.83 (s, 3H).

Synthesis of Zn(II) complex **1** (**$Zn(H_2L)_2.H_2O$**, $ZnC_{38}H_{32}N_4O_9$): A mixture of **H_3L** (0.10 mmol, 0.0336 g), $Zn(Ac)_2{\cdot}2H_2O$ (0.05 mmol, 0.0110 g), 4 ml ultrapure water and 1ml tetrahydrofuran was sealed in a 25 mL Teflon-lined autoclave and heated at 80 °C for 48 h, cooled to room temperature. Yellow cube crystals suitable for X-ray crystallography were obtained. Washed three times with ethanol and filtered, and air-dried to obtain 0.0050 g crystals in a yield of 13.26%.

Synthesis of Zn-**H_3L** complex aggregations ($ZnC_{38}H_{32}N_4O_9$): 10 ml of $Zn(Ac)_2{\cdot}2H_2O$ (0.10 mmol, 0.0220 g) aqueous solution was added to 100 ml of **H_3L** (0.10 mmol, 0.0336 g) tetrahydrofuran solution and stirred for 5 hours. Then 390 ml water was slowly added to obtain THF/H_2O=2/8(v/v) mixed solution, and the solution gradually became turbid and finally formed precipitate. After standing for one day, filtered and washed three times with water, and then air-dried to obtain 0.0303 g yellow powder in a yield of 80.37%. Anal. Calcd for $ZnC_{38}H_{32}N_4O_9$ (%): C, 60.52; H, 4.28; N, 7.43. Found: C, 60.13; H, 4.49; N, 7.61.

Synthesis of Cd(II) complex **2** (**$Cd_2(HL')_2py_4$**, $Cd_2C_{58}H_{48}N_8O_8$): **H_3L** (0.05 mmol, 0.0168 g) was dissolved in 5 ml pyridine with stirring, $Cd(Ac)_2{\cdot}2H_2O$ (0.05mmol, 0.0133 g) was added to the above solution and stirred for 3 hours, filtered and dried to obtain light yellow powder. Recrystallized with 5ml tetrahydrofuran, light yellow block crystals suitable for X-ray crystallography were obtained, air-dried to obtain 0.0193 g crystals in a yield of 63.91%. Anal. Calcd for $Cd_2C_{58}H_{48}N_8O_8$ (%): C, 57.58; H, 4.00; N, 9.26. Found: C, 57.26; H, 4.33; N, 9.57.

Synthesis of Cd(II) complex polycrystals ($Cd_2C_{38}H_{28}N_4O_8$): A mixture of 1ml DMF solution of **H_3L** (0.05 mmol, 0.0168 g), 1ml methanol solution of $Cd(ClO_4)_2{\cdot}6H_2O$ (0.05 mmol,0.0210 g) and 6 ml methanol solution of acetic acid (0.10 mmol, 5.7 μL) was sealed in a 25 mL Teflon-lined autoclave and heated at 80 °C for 48 h, cooled to room temperature, yellow small polycrystals were obtained. Washed three times with methanol and filtered, and air-dried to obtain 0.0113 g crystalsin a yield of 50.67%. Anal. Calcd for $Cd_2C_{38}H_{28}N_4O_8$ (%): C, 51.08; H, 3.16; N, 6.27.Found: C, 51.00; H, 3.41;N, 6.10.

Synthesis of Cd(II)-**H_3L** complex aggregations ($Cd_2C_{38}H_{28}N_4O_8$): 15 ml of $Cd(ClO_4)_2{\cdot}6H_2O$ (0.15 mmol, 0.0618 g) aqueous solution (HEPES buffer solution, 20 mM, pH = 7.4) was added to 150 ml of **H_3L** (0.15 mmol, 0.0504 g) tetrahydrofuran solution and stirred for 5 hours. Then 335 ml HEPES buffer was slowly added to obtain THF/HEPES=3/7(v/v) mixed solution, and the solution gradually became turbid and finally formed precipitate. After standing for one day, filtered and washed three times with water, and then air-dried to obtain 0.0520 g yellow powder in a yield of 77.61 %. Anal. Calcd for $Cd_2C_{38}H_{28}N_4O_8$ (%): C, 51.08; H, 3.16; N, 6.27. Found: C, 5 1.00; H, 3.41; N, 6.10.

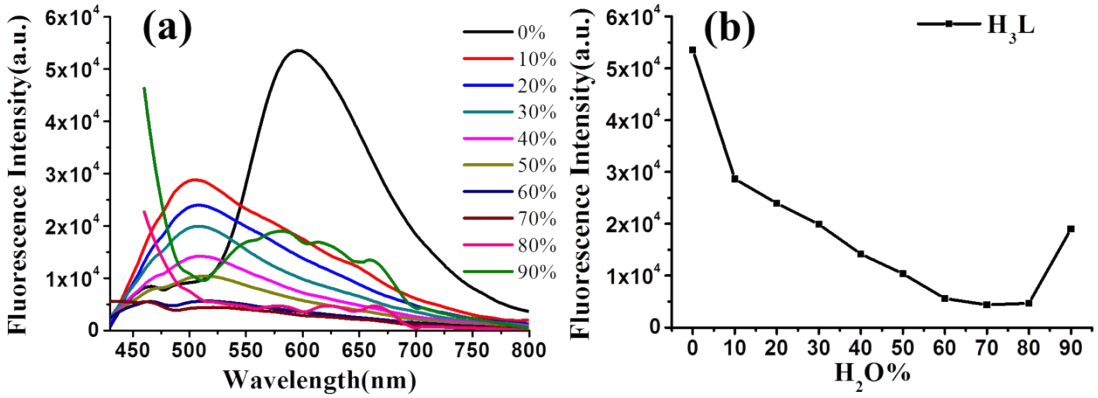


Fig.S1 (a) Fluorescence spectra and (b) the maximum emission intensity change of **H_3L** (100μM) in THF/H_2O solvents containing 100–10% THF and 0–90% water, λ_{ex}=400 nm.

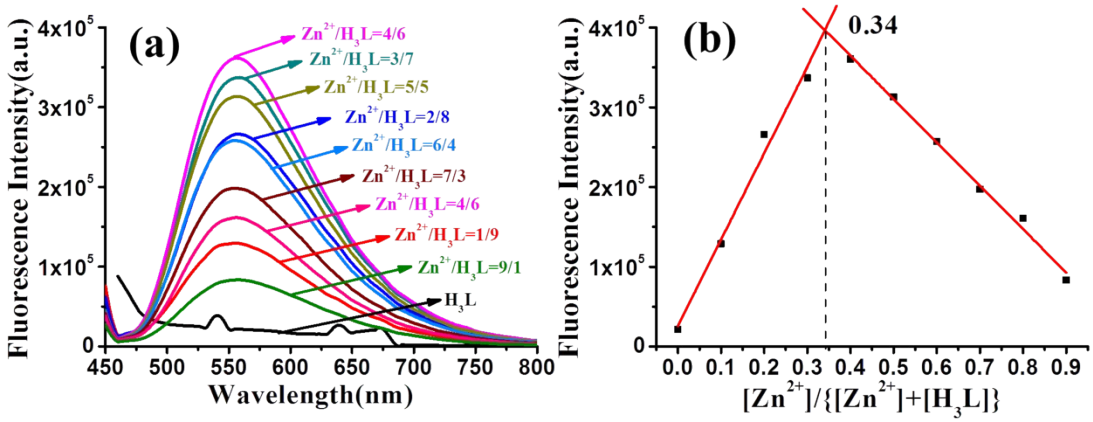


Fig.S2 (a) Fluorescence spectra of **H_3L** and Zn^{2+} in THF/H_2O (v/v, 2/8), the total concentration of Zn^{2+} and H_3L was 100 μM, λ_{ex}=440 nm; (b) Job's plot of Zn^{2+} vs H_3L in THF/H_2O (v/v, 2/8), λ_{em}=560 nm.

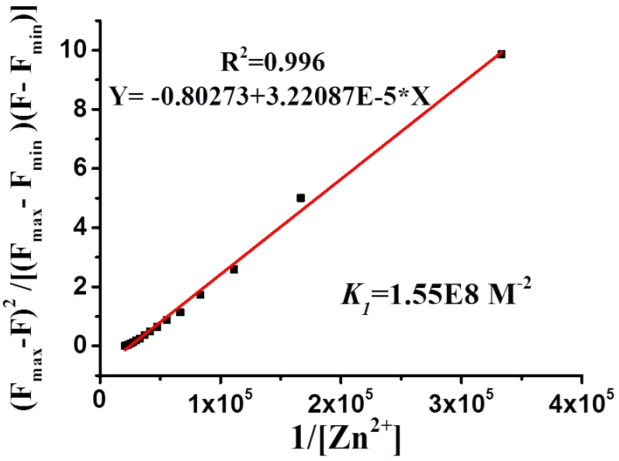


Fig.S3 Association constant calculations by plotting $(F_{max}-F_{min})^2$ /[(F_{max}- F_{min})(F- F_{min})] vs 1/[Zn^{2+}] with linear fitting as well to find out the binding constant of H_3L (100 μM) with Zn^{2+}， H_3L and Zn^{2+} assuming 2:1 stoichiometry for association in THF/ H_2O (v/v=2/8) solvent, λ_{ex}=440 nm, λ_{em}=560 nm.

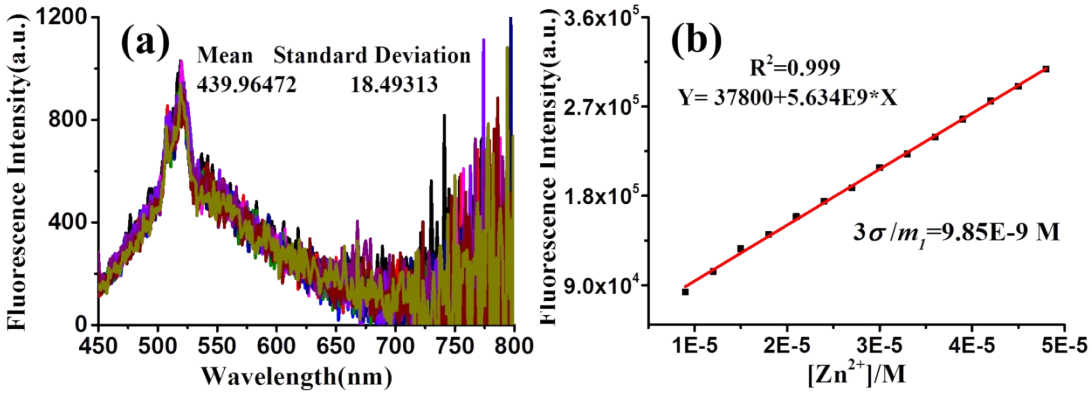


Fig.S4 (a) The standard deviation of the blank measurement was determined by measuring the emission intensity of the H_3L in THF/H_2O (v/v=2/8) without metal ions ten times. (b)The detection limit of H_3L (100 μM) for Zn^{2+} was calculated by 3σ/m formula based on the fluorescence titration data.

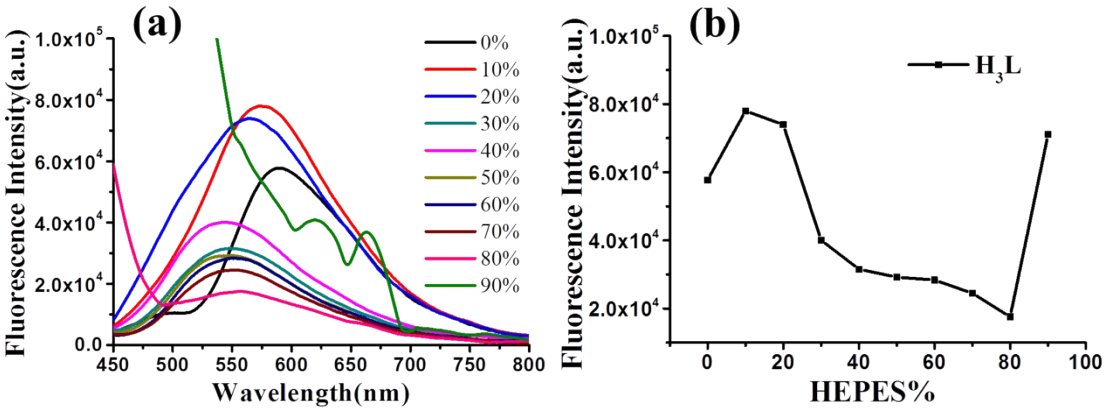


Fig.S5 (a) Fluorescence spectra and (b) the maximum emission intensity change of **H_3L** (100 μM) in THF/ HEPES solvents containing 100–10% THF and 0–90% HEPES buffer (water solution, 20 mM, pH = 7.42), λ_{ex}=430 nm.

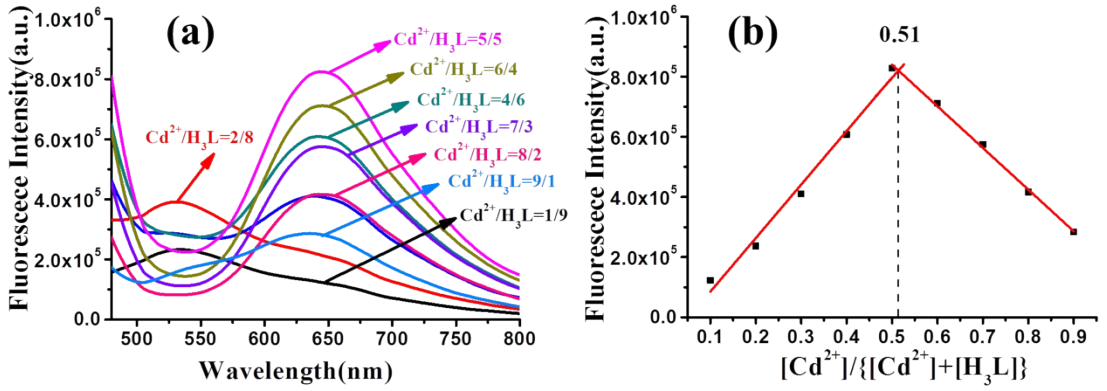


Fig.S6 (a) Fluorescence spectra of **H_3L** and Cd^{2+} in THF/ HEPES aqueous buffer(v/v, 3/7) solvent, the total concentration of Cd^{2+} and H_3L was 100 μM, λ_{ex}=430 nm; (b) Job's plot of Cd^{2+} vs H_3L in THF/HEPES (v/v, 3/7), λ_{em}=645 nm.

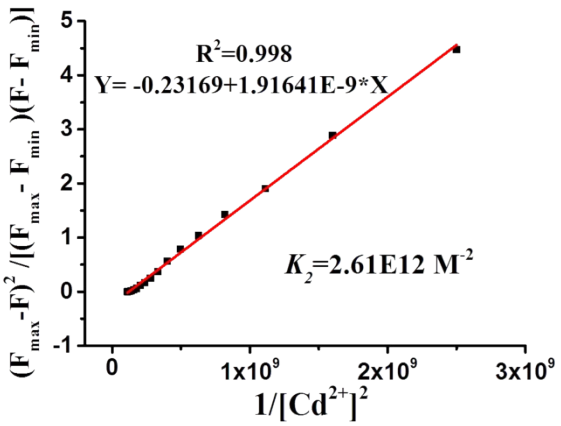


Fig.S7 Association constant calculations by plotting $(F_{max}-F_{min})^2$ /[$(F_{max}- F_{min})(F- F_{min})$] vs $1/[Cd^{2+}]^2$ with linear fitting as well to find out the binding constant of H_3L (100 μM) with Cd^{2+}， H_3L and Cd^{2+} assuming 2:2 stoichiometry for association in THF/ HEPES aqueous buffer (v/v, 3/7) solvent, λ_{ex}=430 nm, λ_{em}=645 nm.

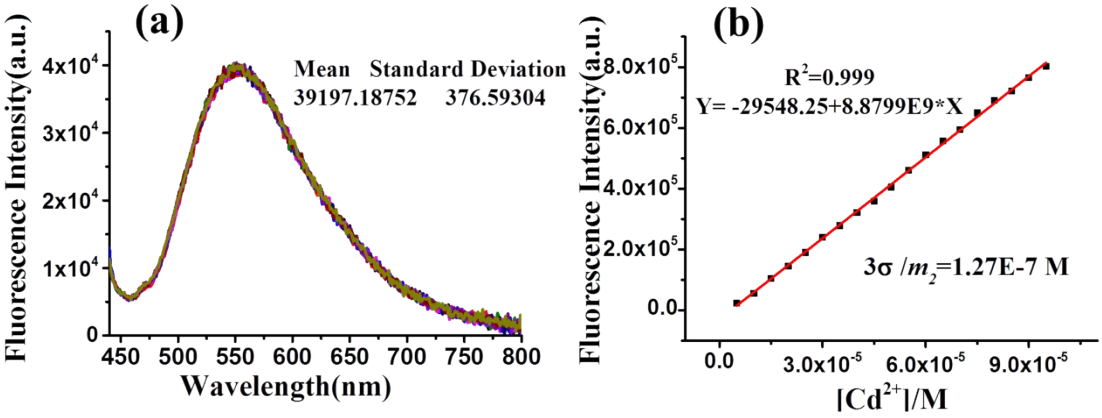


Fig.S8 (a) The standard deviation of the blank measurement was determined by measuring the emission intensity of the H_3L in THF/HEPES (v/v, 3/7) without metal ions ten times. (b)The detection limit of H_3L (100 μM) for Cd^{2+} was calculated by 3σ/m formula based on the fluorescence titration data.

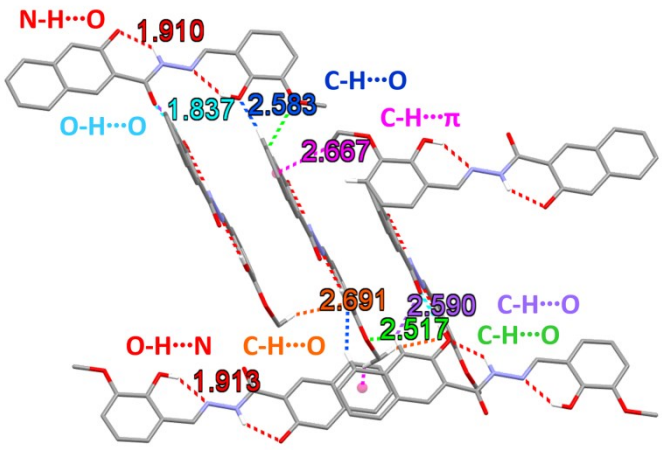


Fig.S9 Intramolecular and intermolecular interactions observed in **H_3L**.

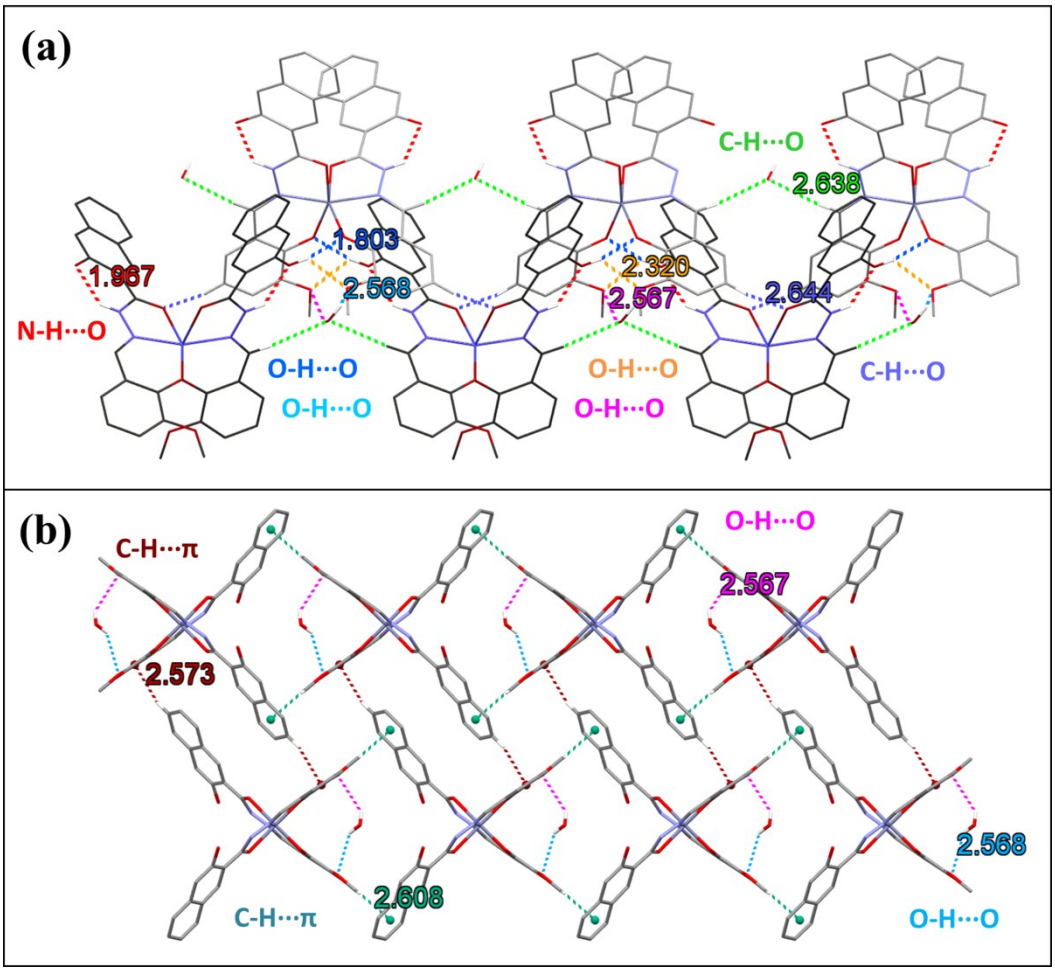


Fig.S10 The "head to tail" molecular packing directed by the O-H···O, C-H···O and C-H···π intermolecular interactions in the Zn (II) complex **1**; (a) N-H···O intramolecular hydrogen bond, O-H···O and C-H···O intermolecular interactions (b) O-H···O and C-H···π intermolecular interactions observed in the Zn (II) complex **1**.

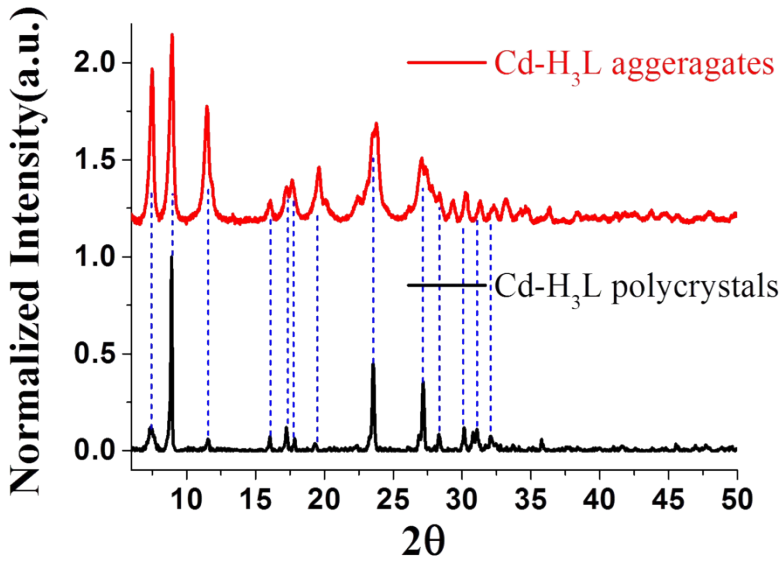


Fig.S11 PXRD of Cd (II) complex polycrystals and Cd-H_3L aggregates.

Table.S1 Crystal data and structure refinement parameters of **H_3L**, complex (**1**) and (**2**)

Compound and Complex	**H_3L**	**1**	**2**
Empirical formula	$C_{19}H_{16}N_2O_4$	$C_{38}H_{32}N_4O_9Zn$	$C_{58}H_{48}N_8O_8Cd_2$
Formula weight	336.34	754.04	1209.84
Temperature/K	100.02(10)	100.00(10)	100.01(10)
Crystal system	Monoclinic	Orthorhombic	monoclinic
Space group	$P2_1/n$	*Pbcn*	$P2_1/n$
a/Å	6.25880(10)	12.4075(6)	10.5367(3)
b/Å	19.4126(4)	11.7844(7)	18.9744(5)
c/Å	12.9577(3)	23.1020(11)	12.6319(4)
α/°	90	90	90
β/°	98.056(2)	90	92.946(3)
γ/°	90	90	90
Volume/$Å^3$	1558.82(5)	3377.9(3)	2522.13(13)
Z	4	4	4
ρcalcg/cm^3	1.433	1.483	3.168
μ/mm^{-1}	0.842	1.558	14.601
F(000)	704	1560	2448
Crystal size/mm^3	0.30 × 0.20× 0.15	0.15 × 0.15 × 0.15	0.2 × 0.1 × 0.1
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.260 to 146.324	7.654 to 152.116	8.416 to 144.06
Reflections collected	5764	11570	10544
R_{int}/R_{sigma}	0.0218/0.0267	0.0393/ 0.0370	0.0276/0.0369
Data/restraints/parameters	3028/0/229	3372/0/238	4846/0/345
Goodness-of-fit on F^2	1.066	1.062	1.063
R_1/wR_2 [I>=2σ (I)]	0.0391/0.1021	0.0470/ 0.1332	0.0297/0.0720
R_1/wR_2 [all data]	0.0434/0.1058	0.0544/ 0.1414	0.0344/0.0758
Largest diff. peak/hole / e $Å^{-3}$	0.27/-0.23	0.89/-0.59	0.70/-0.60

Table.S2 Selected bond distances (Å) and angles (˚) for **H_3L**

		H_3L	
O1—C1	1.3679 (16)	C5—C6	1.420 (2)
O2—C14	1.3509 (16)	C6—C7	1.369 (2)
O3—C11	1.2306 (16)	C7—C8	1.4157 (18)
O4—C15	1.3616 (16)	C8—C9	1.4133 (19)
O4—C19	1.4281 (16)	C9—C10	1.3731 (18)
N1—N2	1.3687 (15)	C10—C11	1.4985 (18)
N1—C11	1.3506 (17)	C12—C13	1.4522 (19)
N2—C12	1.2853 (18)	C16—C17	1.398 (2)
C1—C2	1.3725 (19)	C17—C18	1.376 (2)
C1—C10	1.4332 (17)	C13—C14	1.4031 (19)
C2—C3	1.4105 (18)	C13—C18	1.4052 (19)
C3—C4	1.4248 (18)	C14—C15	1.4096 (19)
C3—C8	1.4242 (18)	C15—C16	1.3841 (19)
C4—C5	1.3652 (19)	C11—N1—N2	120.31 (11)
O1—C1—C10	118.89 (11)	C12—N2—N1	115.82 (11)
O1—C1—C2	120.94 (11)	C15—O4—C19	116.85 (11)
C2—C1—C10	120.17 (12)	O3—C11—N1	122.78 (12)
C1—C2—C3	121.28 (12)	O3—C11—C10	121.33 (12)
C8—C3—C4	118.72 (12)	N1—C11—C10	115.90 (11)
C2—C3—C8	119.34 (12)	N2—C12—C13	121.37 (12)
C2—C3—C4	121.93 (12)	C14—C13—C12	121.53 (12)
C5—C4—C3	120.35 (12)	C14—C13—C18	119.49 (13)
C4—C5—C6	120.87 (13)	C18—C13—C12	118.98 (12)
C5—C6—C7	119.97 (13)	O2—C14—C15	117.57 (11)
C6—C7—C8	120.66 (12)	O2—C14—C13	123.08 (12)
C9—C8—C3	117.93 (12)	C13—C14—C15	119.35 (12)
C9—C8—C7	122.65 (12)	O4—C15—C14	114.40 (12)
C7—C8—C3	119.40 (12)	O4—C15—C16	125.31 (12)
C8—C9—C10	122.77 (12)	C16—C15—C14	120.28 (12)
C1—C10—C9	118.46 (12)	C15—C16—C17	120.04 (13)
C1—C10—C11	125.62 (12)	C18—C17—C16	120.31 (13)
C9—C10—C11	115.92 (11)	C17—C18—C13	120.52 (13)

Table.S3 Selected bond distances (Å) and angels (°) for Zn(II) complex (**1**)

		1	
Zn1—O2	2.0506 (17)	C3—C4	1.416 (4)
Zn1—O2^{i}	2.0506 (17)	C3—C8	1.424 (3)
Zn1—O3	2.2085 (18)	C4—C5	1.370 (4)
Zn1—O3^{i}	2.2085 (18)	C5—C6	1.416 (4)
Zn1—N2	2.102 (2)	C6—C7	1.367 (4)
Zn1—N2^{i}	2.102 (2)	C7—C8	1.421 (3)
O1—C1	1.353 (3)	C8—C9	1.413 (3)
O2—C14	1.323 (3)	C9—C10	1.377 (3)
O3—C11	1.245 (3)	C10—C11	1.489 (3)
O4—C15	1.371 (3)	C12—C13	1.438 (3)
O4—C19	1.420 (4)	C13—C14	1.413 (3)
N1—N2	1.380 (3)	C13—C18	1.412 (3)
N1—C11	1.340 (3)	C14—C15	1.423 (3)
N2—C12	1.295 (3)	C15—C16	1.372 (4)
C1—C2	1.375 (3)	C16—C17	1.404 (4)
C1—C10	1.432 (3)	C17—C18	1.366 (4)
C2—C3	1.414 (3)	O2—Zn1—N2	85.27 (7)
O2^{i}—Zn1—O2	90.20 (10)	O2^{i}—Zn1—N2^{i}	85.27 (7)
O2—Zn1—O3^{i}	91.85 (7)	O3—Zn1—O3^{i}	93.56 (10)
O2^{i}—Zn1—O3	91.85 (7)	N2—Zn1—O3^{i}	93.84 (7)
O2—Zn1—O3	159.14 (7)	N2^{i}—Zn1—O3	93.85 (7)
O2^{i}—Zn1—O3^{i}	159.14 (7)	N2—Zn1—O3	74.28 (7)
O2^{i}—Zn1—N2	107.01 (7)	N2^{i}—Zn1—O3^{i}	74.28 (7)
O2—Zn1—N2^{i}	107.01 (7)	N2^{i}—Zn1—N2	162.88 (12)

^{i}[1-X,+Y,3/2-Z]

Table.S4 Selected bond distances (Å) and angles (˚) for Cd(II) complex (**2**)

Cd1—O2	2.3273 (18)	C14—C15	1.416 (4)
Cd1—O2^{i}	2.3396 (18)	C15—C16	1.386 (4)
Cd1—O3	2.3233 (19)	C16—C17	1.391 (4)
Cd1—O4^{i}	2.4859 (19)	C17—C18	1.369 (4)
Cd1—N4	2.378 (2)	C20—C21	1.384 (4)
Cd1—N3	2.389 (2)	C21—C22	1.378 (4)
Cd1—N2	2.368 (2)	C22—C23	1.388 (5)
O2—Cd1^{i}	2.3396 (18)	C23—C24	1.386 (4)
O4—Cd1^{i}	2.4860 (19)	C25—C26	1.385 (4)
C1—C2	1.374 (4)	C26—C27	1.371 (5)
C1—C10	1.434 (4)	C27—C28	1.375 (5)
C2—C3	1.413 (4)	C28—C29	1.382 (4)
C3—C4	1.415 (4)	N2—N1	1.404 (3)
C3—C8	1.432 (4)	N1—C11	1.330 (4)
C4—C5	1.368 (5)	N2—C12	1.293 (4)
C5—C6	1.409 (5)	N3—C20	1.342 (4)
C6—C7	1.365 (4)	N3—C24	1.342 (4)
C7—C8	1.417 (4)	N4—C29	1.347 (4)
C8—C9	1.417 (4)	N4—C25	1.335 (4)
C9—C10	1.371 (4)	O1—C1	1.351 (4)
C10—C11	1.499 (4)	O2—C14	1.323 (3)
C12—C13	1.444 (4)	O3—C11	1.265 (3)
C13—C14	1.420 (4)	O4—C15	1.373 (3)
C13—C18	1.413 (4)	O4—C19	1.430 (3)
O2—Cd1—O2^{i}	76.20 (7)	O3—Cd1—O4^{i}	72.91 (7)
O2—Cd1—O4^{i}	142.39 (6)	O3—Cd1—N4	88.06 (8)
O2^{i}—Cd1—O4^{i}	66.22 (6)	O3—Cd1—N3	87.66 (8)
O2^{i}—Cd1—N4	85.69 (7)	O3—Cd1—N2	68.31 (7)
O2—Cd1—N4	94.80 (7)	N4—Cd1—O4^{i}	84.17 (7)
O2^{i}—Cd1—N3	87.09 (7)	N4—Cd1—N3	163.44 (8)
O2—Cd1—N3	97.93 (7)	N3—Cd1—O4^{i}	79.28 (7)
O2—Cd1—N2	76.67 (7)	N2—Cd1—O4^{i}	140.48 (7)
O2^{i}—Cd1—N2	152.39 (7)	N2—Cd1—N4	101.62 (8)
O3—Cd1—O2^{i}	139.06 (7)	N2—Cd1—N3	91.63 (8)
O3—Cd1—O2	144.69 (7)		

^{i}[-x+1, -y+1, -z+1]

Table.S5 Intramolecular and intermolecular interactions for **H_3L**

Type	D-H···A	D-H(Å)	H···A(Å)	D..A(Å)	D-H-A(˚)
Intra	O2-H2···N2	0.82	1.913	2.631	146
Intra	N1-H1A···O1	0.86	1.910	2.618	139
Inter	O1-H1···O3^{i}	0.82	1.837	2.654	174
Inter	C2-H2A···O3^{i}	0.93	2.590	3.263	130
Inter	C2-H2A···O4^{ii}	0.93	2.517	3.104	121
Inter	C4-H4···O2^{ii}	0.93	2.583	3.440	153
Inter	C19-H19B···O2^{ii}	0.96	2.691	3.565	152
Inter	C19-H19C···Cg2^{iii}	0.96	2.667	3.429	137

^{i}[-1/2+x,1/2-y,-1/2+z], ^{ii}[-3/2+x,1/2-y,-1/2+z], ^{iii}[1/2-X,-1/2+Y,1/2-Z]

Table.S6 Intramolecular and intermolecular interactions for Zn(II) complex (**1**)

Type	D-H···A	D-H (Å)	H···A (Å)	D..A (Å)	D-H-A(˚)
Intra	N1-H1A···O1	0.86	1.967	2.627	133
Inter	O1-H1···O2^{i}	0.82	1.803	2.604	165
Inter	O1-H1···O4^{i}	0.82	2.320	2.796	118
Inter	O5-H5A···O4^{ii}	0.84	2.568	3.173	130
Inter	O5-H5B···O4^{iii}	0.73	2.567	3.173	141
Inter	C12-H12···O5^{i}	0.93	2.638	3.556	169
Inter	C15-H15···O3^{i}	0.93	2.644	3.282	127
Inter	C5-H5···Cg7^{iv}	0.93	2.573	3.447	157
Inter	C19-H19C···Cg7^{v}	0.93	2.608	3.282	128

^{i}[1/2+x,-1/2+y,3/2-z], ^{ii}[1-x,-1+y,3/2-z], ^{iii}[x,-1+y,z], ^{iv}[X,1-Y,-1/2+Z], ^{v}[1-X,1+Y,3/2-Z]

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