Supporting Information

Coordination-driven Self-assembled Zn^{II}_6-Ln^{III}_3 Metallocycles Based on a Salicylamide Imine Ligand: Synthesis, Structure and Selective Luminescence Enhancement induced by OAc^-

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Instrument and physical determination

All solvents and chemicals were from commercial sources and not further purified. 1-(2-hydroxy-3-methoxy-benzamido)-2-(2-hydroxy-3-methoxy-benzylideneamino)-ethane (H_2L) was prepared previously. [1]

Elemental analysis (CHN) was performed on a Thermo Flash 2000 elemental analyzer. Luminescence excitation and emission spectra in visible range are obtained at F-7000 fluorescence spectrophotometer (Japan Hitachi company) at room temperature. Luminescence measurements of NIR emission were performed on an Edinburgh Instruments FLSP920. UV-Vis-NIR spectrometer setup using a 450 W xenon lamp as the steady state excitation source. UV-Vis spectra were measured on a UV-1800 Shimadzu spectrophotometer. High resolution ESI-MS spectra was carried out on an LTQ Orbitrap XL ETD mass spectrometer. ^{1}H NMR spectra were recorded in CD_3OD +CD_3CN (V : V = 1 : 4) solution at room temperature on a Bruker instrument operating at a frequency of 500 MHz and referenced to tetramethylsilane (0.00 ppm) as an internal standard. Infrared spectra (4000~400 cm^{-1}) were obtained with KBr discs on a Therrno Mattson FTIR spectrometer.

Details of Single Crystal X-ray Diffraction

1) X-ray Data Collection and Reduction.

Suitable pale yellow block crystals of **ZnLn-1**, **ZnNd-2** and **ZnNd-3** were coated with perfluoropolyether oil before mounting. Intensity data for the aligned crystals of all the complexes were recorded at 293(2) K for **ZnLn-1** and 173 (2) K for **ZnNd-2** and **ZnNd-3** employing a Bruker SMART APEX II CCD diffractometer equipped with a monochromatized Mo Kα radiation (λ= 0.71073 Å) source. No crystal decay was observed during the data collections. The frames were integrated with the Bruker SAINT software package using a narrowframe algorithm. Data were corrected for absorption effects using the empirical multiscan method (SADABS).[2]

2) Structure Solution and Refinement.

The structures were solved by direct methods and refined on F^2 by a full-matrix least-squares procedure. SHELXL-2014/2016 was used for both structure solutions and refinements.[3] All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated and isotropically fixed in the final refinement [d(C−H) = 0.95 Å, with the isotropic thermal parameter of Uiso(H) = 1.2 Uiso(C)]. Crystallographic diagrams were drawn using the

DIAMOND software package.[4] Also severely disordered solvents molecules in **ZnNd-1**, **ZnNd-2** and **ZnNd-3** were removed by SQUEEZE during the structural refinements.[5] For details about the squeezed material, see cif data in Supporting Information. Therefore, solvent molecules which were determined on the basis of elemental microanalysis and the data treated with the SQUEEZE routine within PLATON were added to the molecular formula of **ZnLn-1**, **ZnNd-2** and **ZnNd-3** respectively.

Table S1. Crystal data and structure refinement parameters for **ZnLn-1**(Ln= Pr, Nd, Eu, Tb, Yb)

	ZnPr-1	**ZnNd-1**	**ZnEu-1**	**ZnTb-1**	**ZnYb-1**
CCDC number	1845799	1821832	1845802	1845800	1845801
Empirical formula	$C_{114}H_{121}N_{22}O_{54}Pr_3Zn_6$	$C_{108}H_{112}N_{19}Nd_3O_{54}Zn_6$	$C_{108}H_{112}N_{19}Eu_3O_{54}Zn_6$	$C_{108}H_{112}N_{19}Tb_3O_{54}Zn_6$	$C_{112}H_{118}N_{21}Yb_3O_{54}Zn_6$
Formula weight	3478.41	3365.23	3388.26	3409.30	3533.61
Temperature	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal system, space group	Triclinic, P-1	Triclinic, P-1	Triclinic, P-1	Triclinic, P-1	Triclinic, P-1
Unit cell dimensions	a = 16.7497(6) Å	a = 16.7356(8) Å,	a = 16.7237(6) Å	a = 16.7070(16) Å	a = 16.7192(7) Å
	b = 20.5447(11) Å	b = 20.4144(16) Å,	b = 20.4561(8) Å	b = 20.183(2) Å	b = 20.4687(9) Å
	c = 26.2491(8) Å	c = 26.2143(13) Å,	c = 26.1203(8) Å	c = 26.065(2) Å	c = 26.1110(14) Å
	α = 67.834(4) ˚	α = 67.339(6)˚	α = 67.625(3)˚	α = 67.578(9)˚	α = 67.834(5)˚
	β = 75.467(3) ˚	β = 75.613(4) ˚	β = 75.650(3)˚	β = 76.121(8)˚	β = 75.745(4)˚
	γ =65.994(4) ˚	γ = 66.103(6)˚	γ = 65.967(3)˚	γ =66.630(9)˚	γ = 66.098(4)˚
Volume (Å^3), *Z*	7590.8(6), 2	7510.7(9), 2	7501.0(5)	7417.5(14)	7519.5(7)
Absorption coefficient	1.958 mm^{-1}	2.042 mm^{-1}	2.261 mm^{-1}	2.448 mm^{-1}	2.870 mm^{-1}
F(000)	3496	3370	3388	3400	3518
θ range for data collection	3.28 to 25.02˚	3.32 to 25.20˚	3.31 to 25.20˚	3.28 to 25.20˚	3.33 to 25.00˚
Limiting indices	-20 ≤ h ≤ 20	-20 ≤ h ≤ 19	-20 ≤ h ≤ 19	-20 ≤ h ≤ 19	-20 ≤ h ≤ 20
	-24 ≤ k ≤ 24	-24 ≤ k ≤ 24	-24 ≤ k ≤ 24	-24 ≤ k ≤ 24	-21 ≤ k ≤ 24
	-31 ≤ l ≤ 31	-31≤ l ≤ 30	-30 ≤ l ≤ 31	-31 ≤ l ≤ 31	-31 ≤ l ≤ 31
R_{int}	0.0576	0.0742	0.0560	0.0608	0.0539
Reflections collected / unique	72885/26731	62671/27064	61148/26957	57396/26650	63179/26405
Completeness	99.7 %	99.7 %	99.7 %	99.7 %	99.7 %
Absorption correction	Multi-Scan	Multi-Scan	Multi-Scan	Multi-Scan	Multi-Scan
Data/restraints /parameters	26731/96/1832	27064/44/1742	26957/54/1742	26650/36/1741	26405/52/1789
Goodness-of-fit on F^2	1.062	1.066	0.985	1.036	1.066
Final *R* indices [I>2sigma(I)]	R_1 = 0.0676	R_1 = 0.0767	R_1 = 0.0523	R_1 = 0.0721	R_1 = 0.0805
	wR_2 = 0.1444	wR_2 = 0.1905	wR_2 = 0.1141	wR_2 = 0.1761	wR_2 = 0.1932
R indices (all data)	R_1 = 0.0989	R_1 = 0.1285	R_1 = 0.0812	R_1 = 0.0995	R_1 = 0.1115
	wR_2 = 0.1604	wR_2 = 0.2142	wR_2 = 0.1282	wR_2 = 0.1912	wR_2 = 0.2119

Table S2. Crystal data and structure refinement parameters for **ZnNd-2** and **ZnNd-3**

	ZnNd-2	**ZnNd-3**
CCDC number	1821833	1845803
Empirical formula	$C_{120}H_{126}N_{15}Nd_3O_{51}Zn_6$	$C_{220}H_{228}Cl_4N_{42}Nd_8O_{114}Zn_{12}$
Formula weight	2365.32	7364.59
Temperature	173(2)	173(2)
Crystal system, space group	Monoclinic, $P2_1/c$	Tetragonal, P-4c2
Unit cell dimensions	a = 32.041(2) Å, α = 90 ˚ b = 31.5429(12) Å, β = 115.807(7) ˚ c = 34.6303(16) Å, γ = 90˚	a = 32.9711(4) Å, α = 90˚ b = 32.9711(4) Å, β = 90˚ c = 30.8292(5) Å, γ = 90 ˚
Volume ($Å^3$), Z	31509(3) , 8	33514.2(10), 4
Absorption coefficient	1.947 mm^{-1}	11.18
F(000)	13572	14656
θ range for data collection	0.957 to 26.00˚	6.874 to 139.514˚
Limiting indices	-38 ≤ h ≤ 39; -31 ≤ k ≤ -38; -42≤ l ≤ 41	-40 ≤ h ≤ 36; -40 ≤ k ≤ 35; -37 ≤ l ≤
R_{int}	0.0395	0.0568
Reflections collected / unique	121466/61784	62967/ 28977
Completeness	99.7 %	96.9 %
Absorption correction	Multi-Scan	Multi-Scan
Data/restraints /parameters	61784/ 0 / 3543	28977 / 67/ 1819
Goodness-of-fit on F^2	1.064	1.028
Final R indices [I>2sigma(I)]	R_1 = 0.0460, wR_2 = 0.1245	R_1 = 0.0466, wR_2 = 0.1135
R indices (all data)	R_1 = 0.0768, wR_2 = 0.1337	R_1 = 0.0619, wR_2 = 0.1245

Table S3. Selected bond lengths (Å) for **ZnNd-1**, **ZnNd-2** and **ZnNd-3**.

$[Zn_6Nd_3(HL)_6(OH)_2(NO_3)_4(H_2O)]\cdot 3NO_3\cdot 2CH_3CN$ (**ZnNd-1**)									
Zn1–N4	2.070(8)	Zn1–O32	1.960(6)	Zn1–O3	2.029(6)	Zn1–O9	2.067(6)	Zn1–O2	2.086(7)
Zn2–N2	2.071(7)	Zn2 –O32	1.938(7)	Zn2–O8	2.031(7)	Zn2–O7	2.072(7)	Zn2–O4	2.076(6)
Zn3–N10	2.024(8)	Zn3–O40	2.034(9)	Zn3–O17	2.034(7)	Zn3–O18	2.067(7)	Zn3–O24	2.064(6)
Zn4–N8	2.056(10)	Zn4 –O43	2.018(9)	Zn4–O19	2.032(7)	Zn4–O22	2.045(7)	Zn4–O23	2.082(8)
Zn5–N12	2.038(8)	Zn5–O31	1.956(6)	Zn5–O13	2.053(7)	Zn5–O29	2.056(7)	Zn5–O12	2.071(6)
Zn6–N6	2.045(8)	Zn6–O31	1.955(6)	Zn6–O28	2.038(1)	Zn6–O14	2.052(6)	Zn6–O27	2.092(7)
Nd1–O39	2.359(7)	Nd1–O2	2.371(6)	Nd1–O27	2.400(6)	Nd1–O9	2.427(7)	Nd1–O14	2.437(7)
Nd1–O1	2.524(6)	Nd1–O26	2.536(6)	Nd1–O15	2.689(6)	Nd1–O10	2.715(6)	Nd2–O17	2.373(7)
Nd2–O7	2.415(6)	Nd2–O4	2.437(6)	Nd2–O24	2.532(6)	Nd2–O36	2.562(7)	Nd2–O37	2.564(6)
Nd2–O6	2.586(7)	Nd2–O16	2.606(7)	Nd2–O25	2.662(6)	Nd2–O5	2.666(6)	Nd3–O22	2.364(7)
Nd3–O12	2.439(7)	Nd3–O29	2.442(6)	Nd3–O19	2.530(6)	Nd3–O34	2.580(7)	Nd3–O11	2.596(7)
Nd3–O33	2.596(6)	Nd3–O21	2.638(7)	Nd3–O20	2.648(6)	Nd3–O30	2.680(7)		
$[Zn_6Nd_3(HL)_2(OAc)_6]_2\cdot 6NO_3\cdot 6CH_3CN$ (**ZnNd-2**)									
Zn1–N7	2.100(4)	Zn1–O31	1.990(3)	Zn1–O17	2.017(3)	Zn1–O13	2.038(3)	Zn1–O14	2.055(3)
Zn2–N1	2.059(4)	Zn2–O28	2.003(3)	Zn2–O2	2.009(3)	Zn2–O34	2.017(3)	Zn2–O29	2.064(3)
Zn3–N11	2.080(4)	Zn3–O35	1.982(3)	Zn3–O27	2.019(3)	Zn3–O3	2.065(3)	Zn3–O4	2.047(3)
Zn4–N3	1.959(4)	Zn4–O24	1.999(3)	Zn4–O38	1.999(3)	Zn4–O23	2.000(3)	Zn4–O7	2.017(3)
Zn5–N9	2.101(4)	Zn5–O8	1.965(3)	Zn5–O22	1.984(3)	Zn5–O39	2.009(4)	Zn5–O9	2.049(3)

Zn6–N5	2.073(4)	Zn6–O12	2.041(3)	Zn6 –O18	2.002(3)	Zn6–O42	2.037(3)	Zn6–O19	2.057(3)
Zn7–N23	2.044(3)	Zn7–O55	1.989(3)	Zn7–O76	1.993(3)	Zn7–O59	2.018(3)	Zn7–O56	2.091(3)
Zn8–N13	2.067(3)	Zn8–O44	2.021(3)	Zn8–O71	2.040(3)	Zn8–O70	2.043(3)	Zn8–O73	2.062(3)
Zn9–N21	2.062(3)	Zn9–O84	1.985(3)	Zn9– O45	2.016(3)	Zn9– O69	2.040(3)	Zn9–O46	2.057(3)
Zn10–N15	2.089(4)	Zn10–O81	1.934(3)	Zn10–O65	1.990(3)	Zn10– O49	2.010(3)	Zn10–O66	2.062(3)
Zn11–N19	2.055(4)	Zn11–O80	1.966(3)	Zn11–O50	2.002(3)	Zn11–O51	2.020(3)	Zn11–O64	2.034(3)
Zn12–N17	2.074(3)	Zn12–O77	1.945(3)	Zn12–O60	1.956(3)	Zn12–O54	2.037(3)	Zn12–O61	2.044(3)
Nd1–O32	2.388(3)	Nd1–O17	2.457(3)	Nd1–O29	2.462(3)	Nd1–O2	2.464(3)	Nd1–O14	2.470(3)
Nd1–O33	2.490(3)	Nd1–O16	2.705(3)	Nd1–O15	2.740(3)	Nd1–O30	2.746(3)	Nd1–O1	2.756(3)
Nd2–O37	2.451(3)	Nd2–O36	2.454(3)	Nd2–O7	2.457(3)	Nd2–O24	2.468(3)	Nd2–O4	2.474(3)
Nd2–O27	2.484(3)	Nd2–O25	2.696(3)	Nd2–O5	2.717(3)	Nd2–O6	2.735(3)	Nd2–O26	2.743(3)
Nd3–O12	2.411(3)	Nd3–O40	2.466(3)	Nd3–O19	2.491(3)	Nd3–O22	2.494(3)	Nd3–O41	2.498(3)
Nd3–O9	2.500(3)	Nd3–O10	2.708(3)	Nd3–O21	2.743(3)	Nd3–O11	2.744(3)	Nd3– O20	2.766(3)
Nd4–O75	2.398(3)	Nd4–O59	2.441(3)	Nd4–O44	2.470(3)	Nd4–O74	2.474(3)	Nd4–O56	2.478(3)
Nd4–O71	2.538(3)	Nd4–O72	2.695(3)	Nd4–O58	2.729(3)	Nd4 –O57	2.751(3)	Nd4 –O43	2.762(3)
Nd5–O82	2.390(3)	Nd5–O83	2.411(3)	Nd5–O49	2.431(3)	Nd5–O66	2.435(3)	Nd5–O69	2.464(3)
Nd5–O46	2.486(3)	Nd5–O67	2.717(3)	Nd5–O48	2.719(3)	Nd5–O47	2.732(3)	Nd5–O68	2.806(3)
Nd6–O78	2.433(3)	Nd6–O54	2.436(3)	Nd6–O64	2.449(3)	Nd6–O79	2.454(3)	Nd6–O61	2.487(3)
Nd6–O51	2.492(3)	Nd6–O52	2.687(3)	Nd6–O62	2.718(3)	Nd6–O53	2.720(3)	Nd6–O63	2.759(3)
$[Zn_6Nd_3(HL)_6(OH)_2Cl_2(NO_3)_4(H_2O)]\cdot[Nd(NO_3)_6]\cdot H_2O\cdot 3CH_3CN$ **(ZnNd-3)**									
Nd1–O1	2.624(9)	Nd1–O2	2.424(8)	Nd1–O9	2.436(8)	Nd1–O10	2.565(9)	Nd1–O11	2.618(9)
Nd1–O12	2.496(9)	Nd1–O14	2.359(9)	Nd1–O15	2.618(9)	Nd1–O55	2.624(9)	Nd1–O57	2.557(7)
Nd2–O58	2.380(13)	Nd2–O4	2.369(7)	Nd2–O5	2.573(9)	Nd2–O6	2.694(9)	Nd2–O7	2.423(8)
Nd3–O16	2.595(9)	Nd3–O17	2.389(8)	Nd3–O24	2.419(7)	Nd3–O25	2.660(9)	Nd3–O26	2.656(9)
Nd3–O27	2.348(7)	Nd3–O29	2.498(7)	Nd3–O30	2.606(8)	Nd3–O52	2.637(9)	Nd3–O53	2.562(9)
Nd4–O19	2.428(8)	Nd4–O20	2.670(8)	Nd4–O21	2.565(8)	Nd4–O22	2.394(8)	Nd4–O49	2.370(11)
Zn1–Cl1	2.290(5)	Zn1–N5	2.057(12)	Zn1–O12	2.063(9)	Zn1–O14	2.067(9)	Zn1–O13	2.079(9)
Zn2–N1	2.048(10)	Zn2–O2	2.055(8)	Zn2–O8	2.070(8)	Zn2–O9	2.101(8)	Zn2–O51	1.949(9)
Zn3–N3	2.050(10)	Zn3–O3	2.028(8)	Zn3–O4	2.097(8)	Zn3–O7	2.055(8)	Zn3–O51	1.953(9)
Zn4–Cl2	2.285(3)	Zn4–N11	2.083(11)	Zn4–O27	2.076(8)	Zn4–O28	2.069(9)	Zn4–O29	2.053(8)
Zn5–N10	2.072(9)	Zn5–O17	2.107(8)	Zn5–O18	2.035(8)	Zn5–O24	2.055(8)	Zn5–O50	1.966(8)
Zn6–N8	2.048(9)	Zn6–O19	2.053(8)	Zn6–O22	2.094(8)	Zn6–O23	2.052(8)	Zn6–O50	1.950(8)

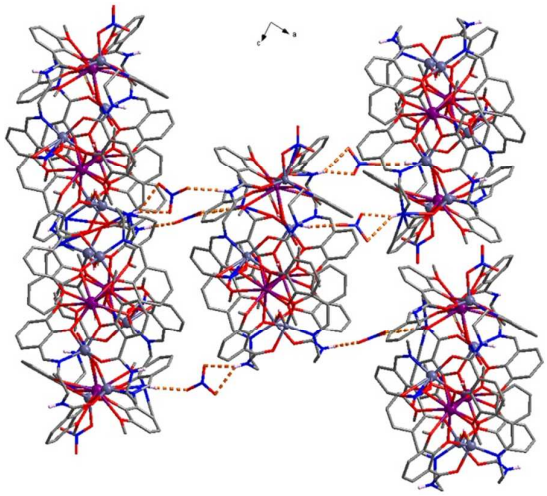

Figure S1. Two dimensional supramolecular architecture of ZnNd-1constructed by hydrogen bond between amide and crystalline nitrates. The intramolecular O–H···O hydrogen bonds are shown as dashed lines. (Color modes: Gray , C; Red, O; Blue, N; Violet, Nd; Blue gray, Zn; Pale pink, H.).

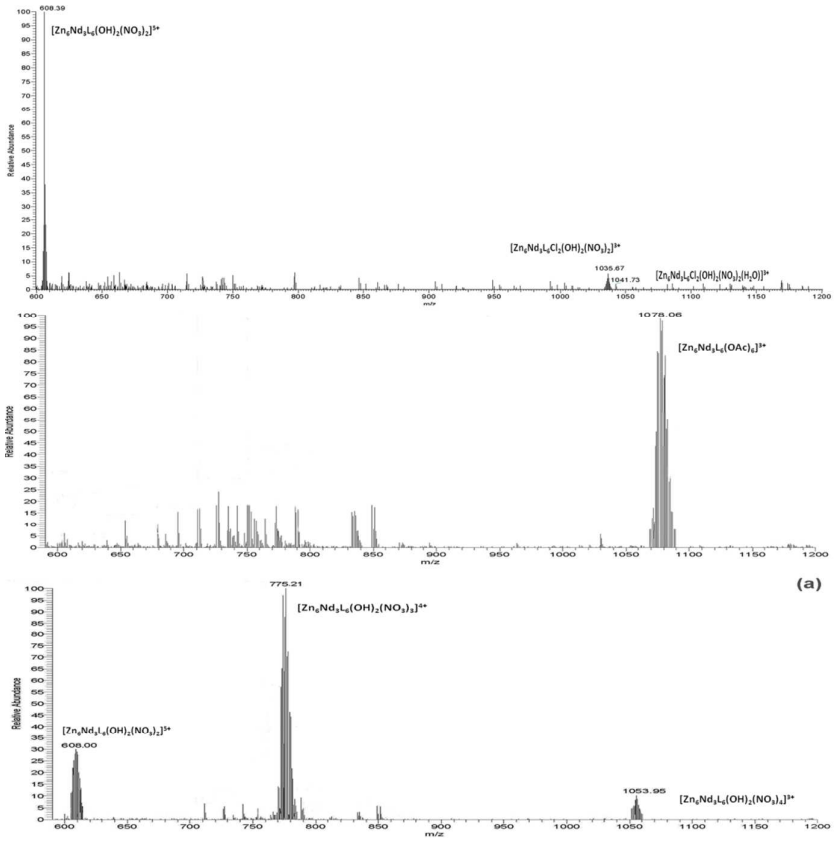

Figure S2. a) The high resolution ESI mass spectrum of H_2L+2NEt_3+2$Zn(NO_3)_2$+$Nd(NO_3)_3$ in mixed CH_3CN - CH_3OH (V : V = 1 : 4) solution; b) The high resolution ESI mass spectrum of H_2L+2NEt_3+2$Zn(NO_3)_2$+$Nd(NO_3)_3$+3$Zn(OAc)_2$ in mixed CH_3OH-CH_3CN (V : V =1:4) solution; c) H_2L+2NEt_3+2$Zn(NO_3)_2$+$Nd(NO_3)_3$+3$ZnCl_2$ in mixed CH_3OH-CH_3CN (V : V =1:4).

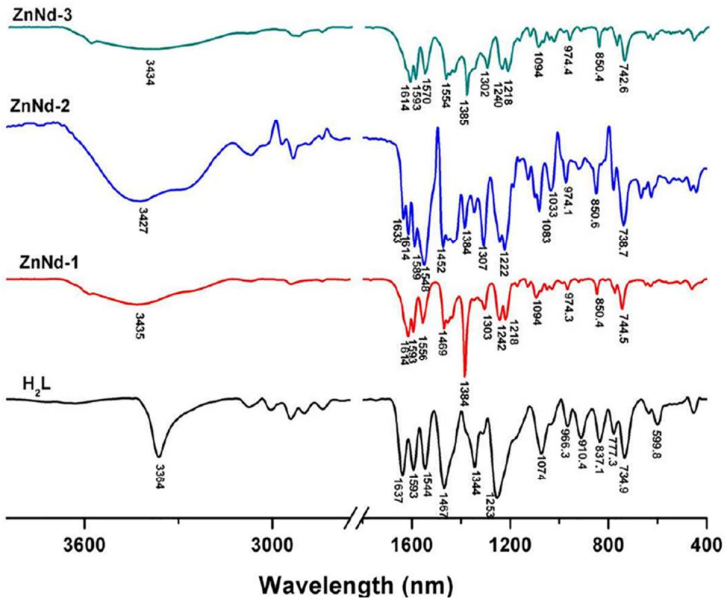

Figure S3. IR spectra of **H_2L**, **ZnNd-1**, **ZnNd-2** and **ZnNd-3** in solid state at room temperature.

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