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Supporting information

Construction of four 3d-4d/4d complexes based on salen-type Schiff base ligands

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Materials and physical measurements: All reagents were commercially available and used without further purification. Infrared spectra were obtained from KBr pellets on a Bruker TENSOR 27 Fourier transformation infrared spectrometer in the 400-4000 cm^{-1} region. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240 elemental analyzer. The mass spectra (FAB-MS) were recorded on a ZAB-HS spectrometer. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku D/M-2200T automated diffractometer. Thermogravimetric analyses were performed on Perkin-Elmer TGA7 analyzer with a heating rate of 10 °C/min in flowing air atmosphere. The luminescent spectra for the solid state were recorded at room temperature on an Aminco Bowman Series 2 spectrofluorometer with a xenon arc lamp as the light source. In the measurements of emission and excitation spectra the pass width is 5.0 nm. The antioxidative activity was performed in methanol with a 72 spectrophotometer.

Crystallographic Studies: X-ray diffraction data were collected on a Bruker Apex II diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at 298 K. Absorption corrections were applied by using multi-scan program SADABS. All the structures were solved by direct methods and refined with full-matrix least-squares technique using SHELXTL. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms on organic ligands were generated by the riding mode (C-H 0.96 Å).

Syntheses of 1 and 2. A mixture of Schiff-base ligand H_2L^a (0.4 mmol, 0.141 g) and $Zn(OAc)_2{\cdot}2H_2O$ (0.4 mmol,0.0878 g) in methanol (20 mL) was stirred for 30 min at room temperature. Then, a solution of $Cd(NO_3)_2/CdCl_2$ (0.2mmol, 0.0597/0.0457 g) in methanol/DMF was added dropwise, and the mixture was kept stirring for another 2 hours at 70 °C. After being filtered, the reaction solution was put into the fridge to allow for solvent evaporation at 5 °C for one week, providing yellow single crystals at a yield of 0.078 g, 52% for 1 (based on Cd). Found: C 39.75, H 3.43, N 9.51%. Anal. calcd for $C_{25}H_{25}N_5O_{11}ZnCd_2$: C 40.04, H 3.34, N 9.34%. IR (KBr, cm^{-1}): ν 3565 (br, s), 2995 (m), 2963 (s), 2892 (s), 2797 (s), 1632 (vs), 1595 (s), 1541 (s), 1470 (vs),

1445 (vs), 1290 (vs), 1189 (vs), 1150 (s), 1021 (vs), 900 (vs), 792 (m), 765 (s), 676 (m), 637 (m), 601 (m), 572 (m), 531 (m), 468 (w). FAB-MS: m/z 676 ($[M]^+$-DMF, 79%). For 2, 0.0512g, yield: 47% (based on Cd). Found: C 48.77, H 3.57, N 5.28%. Anal. calcd for $C_{44}H_{38}Cl_2N_4O_9Zn_2Cd$: C 48.89, H 3.54, N 5.18%. IR (KBr, cm^{-1}): ν 3242–3208 (br, m), 2943 (m), 1639 (vs), 1462 (s), 1384 (w), 1241 (s), 1152 (m), 1043 (m), 896 (w), 750 (s), 644 (m), 570 (w), 473 (w). FAB-MS: m/z 1063 ($[M]^+$-H_2O, 83%).

Syntheses of 3 and 4. The compounds 3 and 4 were obtained using the same reaction procedure as described for compounds 1 and 2, respectively, but using HLb instead of H2La. The yellow powder of 3 was isolated in about 52% yield (based on Cd). Found: C 40.51; H 4.01; N 10.95%. Anal. calcd for $C_{34}H_{40}Cl_2N_8O_{14}Cd_2$: C 40.42, H 3.96, N 11.10%. IR (KBr, cm^{-1}): ν 3493–3694 (br, w), 2957 (m), 2981 (m), 2842 (m), 1648 (vs), 1597 (s), 1468 (s), 1449 (s), 1396 (w), 1375 (w), 1338 (w), 1295 (s), 1239 (s), 1217 (vs), 1080 (s), 967 (m), 931 (m), 885 (m), 848 (m), 782 (m), 745 (s), 731 (s), 630 (w), 562 (w), 475 (w). FAB-MS: m/z 775 ($[M]^+$-2DMF-2H_2O, 85%). For **4**, 65% yield (based on Cd). Found: C 42.55, H 4.25, N 8.73%. Anal. calcd for $C_{34}H_{40}Cl_2N_6O_8Cd_2$: C 42.66, H 4.18, N 8.78%. IR (KBr, cm^{-1}): ν 3531-3678 (br, w), 2926 (m), 2874 (w), 1636 (m), 1568 (s), 1471 (w), 1439 (m), 1410 (w), 1384 (w), 1342 (w), 1115 (w), 1021 (w), 928 (w), 654 (m), 527 (w), 479 (w). FAB-MS: m/z 828 ($[M]^+$-2DMF-2H_2O, 85%).

Table **S1** Crystal data and structure refinement for the compounds **1, 2** and **4**.

Complex	**1**	**2**	**4**
Empirical formula	$C_{25}H_{25}N_5O_{11}ZnCd_2$	$C_{44}H_{38}Cl_2N_4O_9Zn_2Cd$	$C_{34}H_{40}Cl_2N_6O_8Cd_2$
Formula weight	749.27	1080.82	956.42
Temperature	298(2) K	298(2) K	298(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
Unit cell dimensions			
a (Å)	9.9306(7)	13.148(3)	16.6799(12)
b (Å)	18.8619(13)	25.385(6)	10.6208(8)
c (Å)	15.0246(10)	16.826(4)	21.4547(16)
α (°)	90	90	90
β (°)	97.4010(10)	110.160(9)	92.3120(10)
γ (°)	90	90	90
V (Å^3)	2790.8(3)	5272(2)	3797.7(5)
Z	4	4	4
ρ (cald.) (mg m^{-3})	1.783	1.362	1.673
μ (m^{-1})	1.691	1.454	1.318
F(000)	1504	2175	1920
Crystal size (mm)	0.23 × 0.18 × 0.12	0.20 × 015 × 0.09	0.22 × 017 × 0.11
θ range for data collection (°)	1.90 to 25.25	1.89 to 25.00	1.95 to 24.85
$h/k/l$ (max, min)	-11,11/-22,22/-9,18	-15,15/-16,30/-20,19	-19,19/-12,11/-25,22
Reflections collected	14328	26034	18537
Unique	5032 [R(int) = 0.0304]	9246 [R(int) = 0.0656]	6566 [R(int) = 0.0443]
Completeness to θ = 27.13	99.8 %	98.3 %	99.6 %
Absorption correction	empirical	empirical	empirical
Max. and min. transmission	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data / restraints / parameters			
Goodness-of-fit on F^2	5032 / 0 / 392	9246 / 9 / 556	6566 / 6 / 487
Final $R1$[a], $wR2$ [b] indices	1.028	1.076	1.031
[$I > 2\sigma(I)$]	0.0281, 0.0622	0.0754, 0.1523	0.0408, 0.0858
$R1$, $wR2$ indices (all data)	0.0419, 0.0683	0.0892, 0.2012	0.0641, 0.0979
Largest diff. Peak and hole (e Å^{-3})	0.308 / -0.347	1.034/ -0.953	1.007/ -0.727

[a] $R = \Sigma \| |F_o| - |F_c| / S |F_o|$. [b] $wR = [\Sigma w(|F_o|^2 - |F_c|^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$. $w = 1/[\sigma^2(F_o^2)+(0.0269P)^2+0.8714P]$ for **1**, $w = 1/[\sigma^2(F_o^2)+(0.1014P)^2+0.0000P]$ for **2** and $w = 1/[\sigma^2(F_o^2)+(0.0363P)^2+3.5809P]$ for **4**, $P = (F_o^2 + 2F_c^2)/3$.

Table S2 Selected Bond Distances (Å) and Angles (°) for complexes **1** and **4**.

1

O(1)-C(2)	1.380(3)	Cd(1)-O(1)-C(2)	112.66(12)
C(2)-C(7)	1.415(4)	O(1)-C(2)-C(7)	114.05(12)
O(2)-C(7)	1.319(3)	O(2)-C(7)-C(2)	118.76(13)
C(6)-C(7)	1.419(4)	O(2)-C(7)-C(6)	123.59(14)
C(6)-C(8)	1.440(4)	C(7)-C(6)-C(8)	124.84(15)
N(1)-C(8)	1.278(3)	C(6)-C(8)-N(1)	126.28(15)
N(1)-C(9)	1.417(3)	C(8)-N(1)-Zn(1)	125.84(13)
C(9)-C(14)	1.409(4)	C(1)-N(1)-Zn(1)	111.07(14)
N(2)-C(14)	1.423(3)	N(1)-C(9)-C(14)	116.26(14)
N(2)-C(15)	1.281(3)	C(9)-C(14)-N(2)	115.42 (14)
C(15)-C(16)	1.444(4)	C(14)-N(2)-Zn(1)	110.54(15)
C(16)-C(21)	1.409(4)	C(15)-N(2)-Zn(1)	125.53(15)
C(20)-C(21)	1.416(4)	N(2)-C(15)-C(16)	125.77(15)
O(3)-C(21)	1.321(3)	C(15)-C(16)-C(21)	124.76(16)
O(4)-C(20)	1.374(3)	O(3)-C(21)-C(16)	124.09(16)
O(3)-C(21)-C(20)	117.67(15)	C(21)-C(20)-O(4)	113.13(16)
C(20)-O(4)-Cd(1)	115.89(15)	O(2)-Cd(1)-O(3)	71.02(7)
O(2)-Cd(1)-O(9)	98.59(8)	O(3)-Cd(1)-O(9)	103.28(8)
O(2)-Cd(1)-O(8)	135.85(8)	O(3)-Cd(1)-O(8)	141.71(8)
O(9)-Cd(1)-O(8)	53.97(8)	O(2)-Cd(1)-O(6)	129.53(10)
O(3)-Cd(1)-O(6)	102.87(10)	O(9)-Cd(1)-O(6)	130.53(11)
O(3)-Zn(1)-O(2)	83.01(8)	O(8)-Cd(1)-O(6)	80.06(11)
O(3)-Zn(1)-O(11)	102.01(9)	O(2)-Cd(1)-O(5)	80.16(9)
O(2)-Zn(1)-O(11)	103.39(9)	O(3)-Cd(1)-O(5)	103.51(9)
O(3)-Zn(1)-N(1)	152.01(9)	O(9)-Cd(1)-O(5)	151.11(10)
O(2)-Zn(1)-N(1)	91.40(9)	O(8)-Cd(1)-O(5)	107.52(9)
O(11)-Zn(1)-N(1)	105.97(9)	O(6)-Cd(1)-O(5)	51.79(11)
O(3)-Zn(1)-N(2)	90.82(8)	O(2)-Cd(1)-Zn(1)	36.95(5)
O(2)-Zn(1)-N(2)	151.74(9)	O(3)-Cd(1)-Zn(1)	36.23(5)
O(11)-Zn(1)-N(2)	104.87(9)	O(9)-Cd(1)-Zn(1)	112.93(6)
N(1)-Zn(1)-N(2)	81.21(9)	O(8)-Cd(1)-Zn(1)	166.72(6)
O(3)-Zn(1)-Cd(1)	42.78(5)	O(6)-Cd(1)-Zn(1)	113.04(9)
O(2)-Zn(1)-Cd(1)	42.92(5)	O(5)-Cd(1)-Zn(1)	83.46(7)
O(11)-Zn(1)-Cd(1)	95.30(6)	N(2)-Zn(1)-Cd(1)	132.76(6)
N(1)-Zn(1)-Cd(1)	133.48(7)		

		2	
N(3)-Cd(1)-N(2)	121.57(14)	O(4)-Cd(2)-O(2)	76.62(11)
N(3)-Cd(1)-O(2)	155.29(13)	O(4)-Cd(2)-Cl(1)	130.71(10)
N(2)-Cd(1)-O(2)	82.52(13)	O(2)-Cd(2)-Cl(1)	102.86(10)
N(3)-Cd(1)-O(4)	81.18(13)	O(4)-Cd(2)-Cl(2)	102.59(9)
N(2)-Cd(1)-O(4)	154.91(13)	O(2)-Cd(2)-Cl(2)	124.25(10)
O(2)-Cd(1)-O(4)	76.49(11)	Cl(1)-Cd(2)-Cl(2)	116.04(6)
N(3)-Cd(1)-O(5)	87.23(14)	O(4)-Cd(2)-O(3)	65.25(11)
N(2)-Cd(1)-O(5)	92.52(15)	O(2)-Cd(2)-O(3)	132.21(12)
O(2)-Cd(1)-O(5)	86.17(13)	Cl(1)-Cd(2)-O(3)	82.94(10)
O(4)-Cd(1)-O(5)	99.57(14)	Cl(2)-Cd(2)-O(3)	92.46(10)
N(3)-Cd(1)-O(6)	86.72(14)	O(4)-Cd(2)-O(1)	134.84(12)
N(2)-Cd(1)-O(6)	84.97(14)	O(2)-Cd(2)-O(1)	64.48(11)
O(2)-Cd(1)-O(6)	102.05(13)	Cl(1)-Cd(2)-O(1)	81.80(10)
O(4)-Cd(1)-O(6)	86.10(13)	Cl(2)-Cd(2)-O(1)	82.61(9)
O(5)-Cd(1)-O(6)	170.98(15)	O(3)-Cd(2)-O(1)	159.89(11)

Table S3. Hydrogen bond parameters of complexes **1** and **4**.

D-H…A	d (H…A). Å	d (D…A). Å	∠(DHA). °
	1		
C(1)-H(41C)···O(7)#1	2.632(2)	3.311(2)	128(3)
C(13)-H(13)···O(5)#1	2.647(2)	3.280(2)	126(3)
C(8)-H(8)···O(9)#1	2.464(2)	3.331(2)	155(3)
	4		
O(8)-H(8B)···Cl(1)#2	2.621(2)	3.334(3)	143(5)
O(7)-H(7B)···Cl(1)#2	2.406(2)	3.212(3)	161(5)
N(4)-H(4)···Cl(2)#2	2.811(2)	3.652(4)	166(5)

Symmetry codes: #1-x,2-y,-z; #2 1-x,1-y,-z.

Table S4 Fluorescence lifetimes (τ), fluorescence quantum yields (Φ), optical density (A), maximum excitation wavelength (λ_{max}), fitted value (χ^2)

compound	Φ	A	$\lambda_{max\text{-}ex}$	$\lambda_{max\text{-}em}$	τ (ns)	χ^2
1	0.85	0.031	315	449	16.8	0.97
2	0.81	0.029	347	469	15.6	0.99
3	0.86	0.033	315	495	17.2	0.97
4	0.84	0.031	358	461	18.5	0.98
H_2L[a]	0.66	0.013	347	470	10.3	0.95
HL[b]	0.59	0.015	358	485	9.8	0.94

Notes: Samples were prepared to have an optical density of ≤0.05 at the λ_{max}. The χ^2 for each decay profile is also presented. All of these photophysical properties were measured in DMF/acetonitrile, except for the fluorescence quantum yields measured in ethanol.

Figure S1. Molecular structure of hetero-trinuclear Zn_2Cd-type compound **2**.

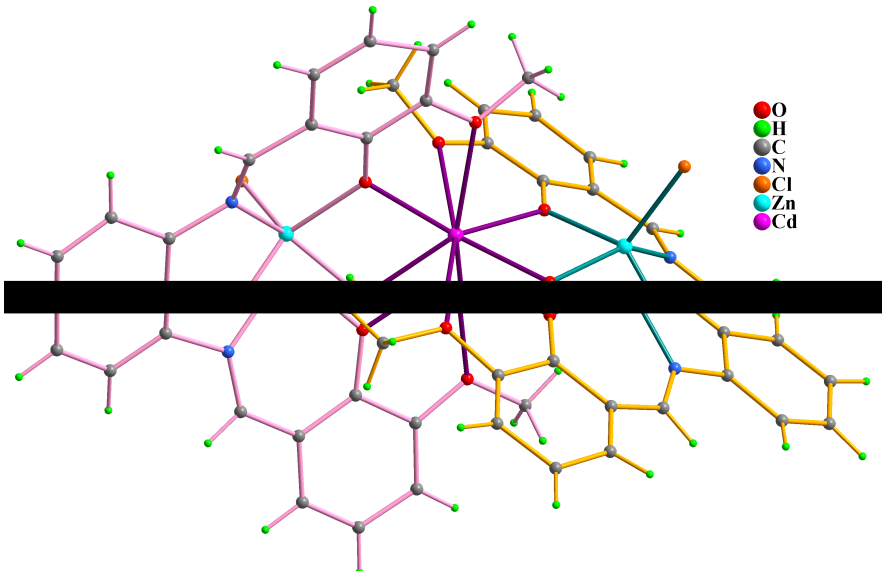
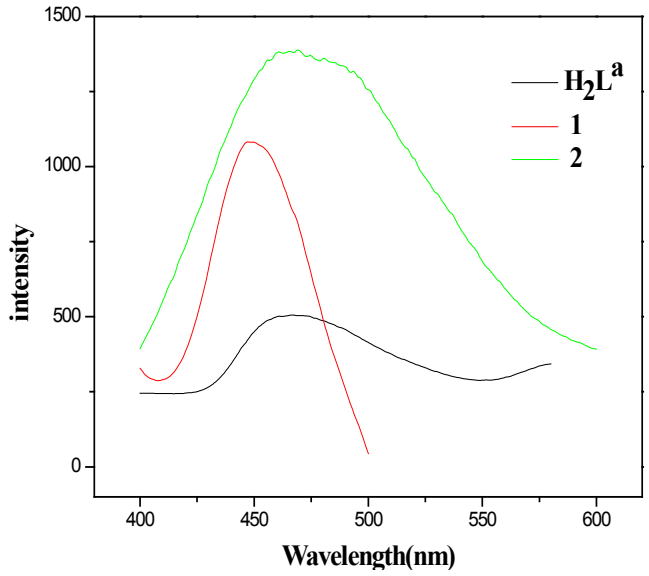


Figure S2 (1) Emission spectra of complexes **1**, **2** and ligand H_2L^a in solid state at room temperature, respectively. (2) Emission spectra of complexes **3**, **4** and ligand HL^b in solid state at room temperature, respectively.

(1)



(2)

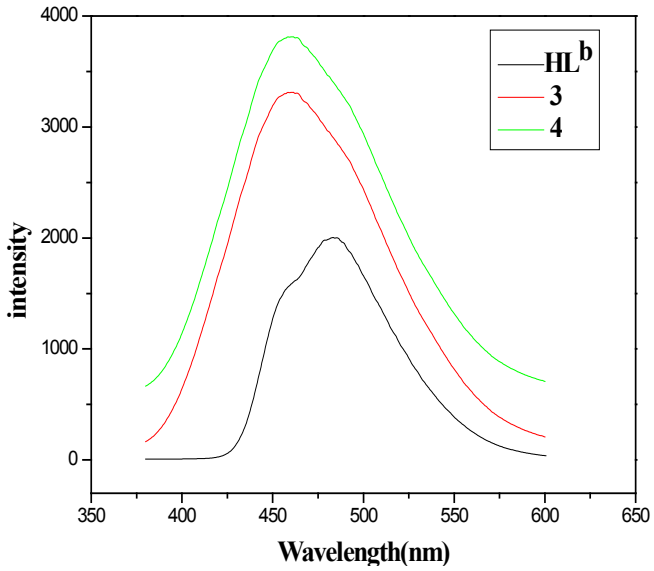


Figure S3 TGA curves of compounds **1**-**3**.

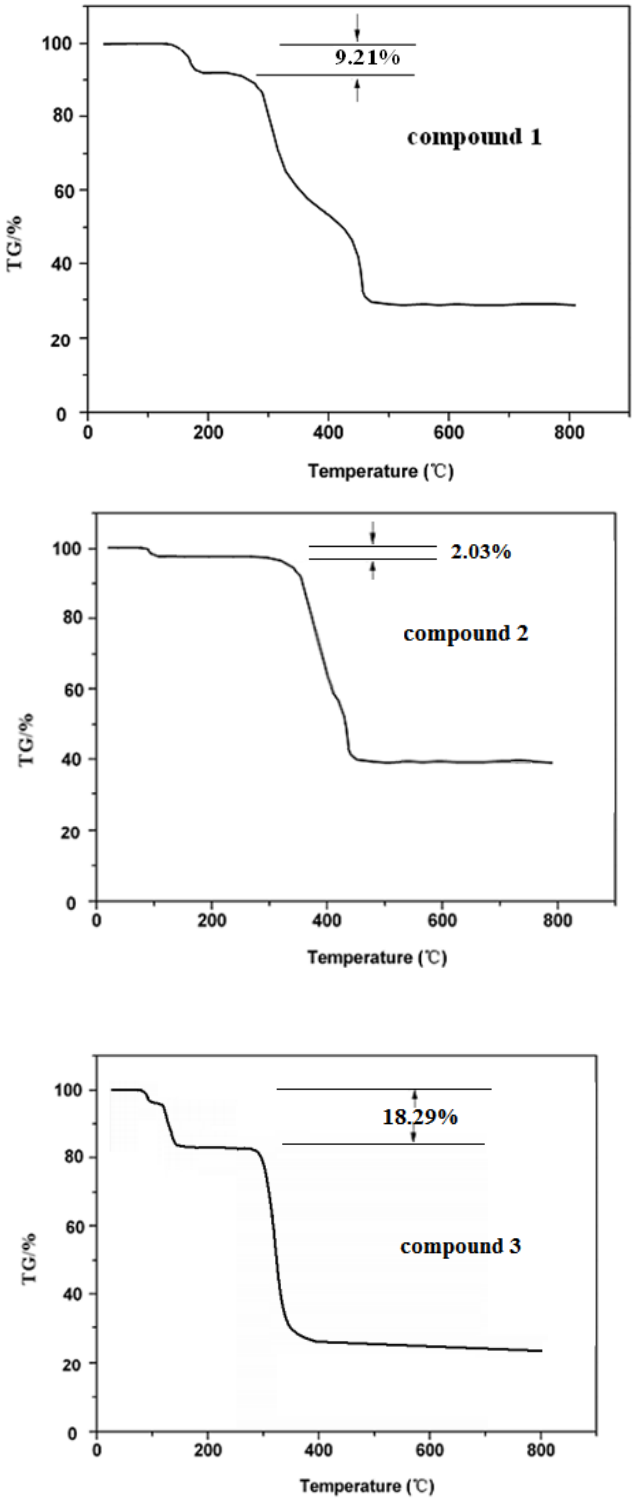


Figure S4 Scavenging activity of the methanol extracts of ligands $\mathbf{H_2L}^a$ and $\mathbf{HL}^b$ as well as compounds **1**-**4**.