ESI

A novel 2,6-diformyl-4-methyl phenol based chemosensor for Zn(II) ion by ratiometric displacement of Cd(II) ion and its application for cell imaging on human melanoma cancer cells

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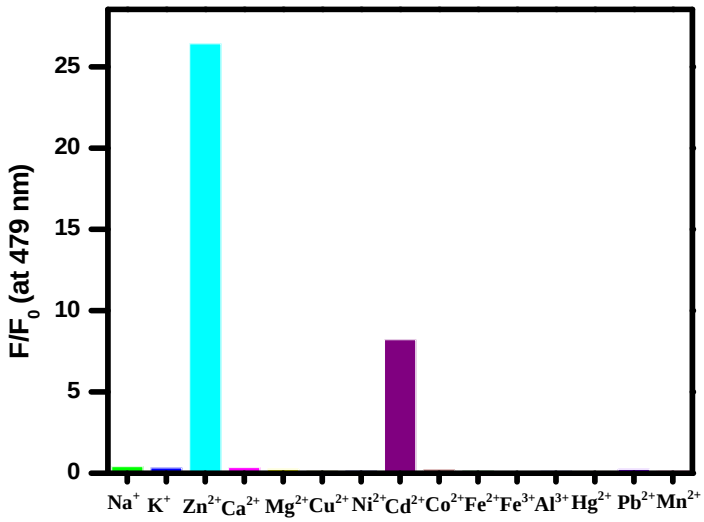

Fig. S1. Relative emission intensity change profile of the chemosensor **1** (1.0 μM) in the presence of various metal ions at 25°C (λ_{exc} = 350 nm) in a HEPES buffer (50 μM, DMSO:water = 1:9 (v/v), pH=7.2).

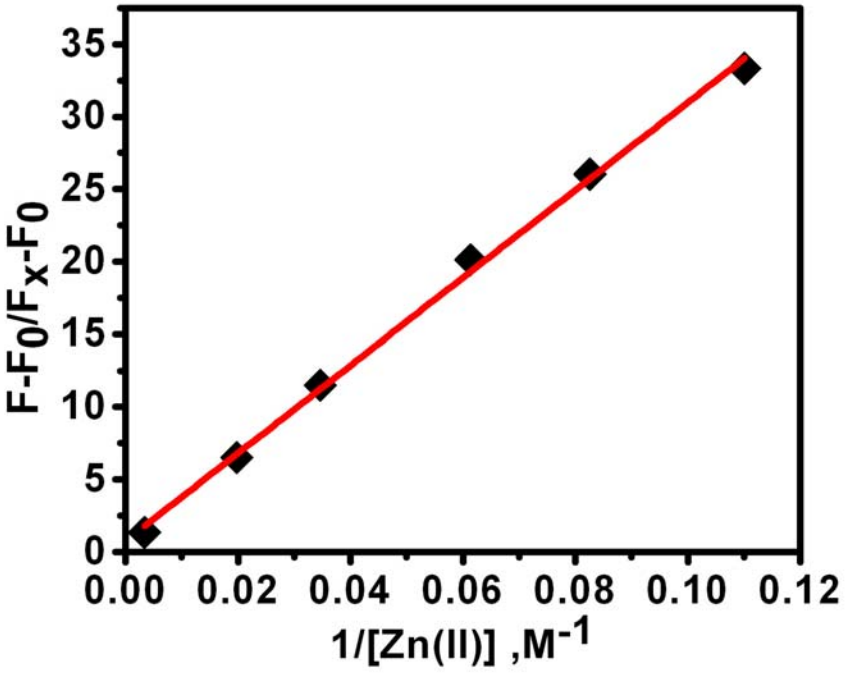

Fig. S2. Plot of $\{(F - F_o)/(F_x - F_o)\}$ vs. 1/[Zn(II)]; $R^2 = 0.99737$

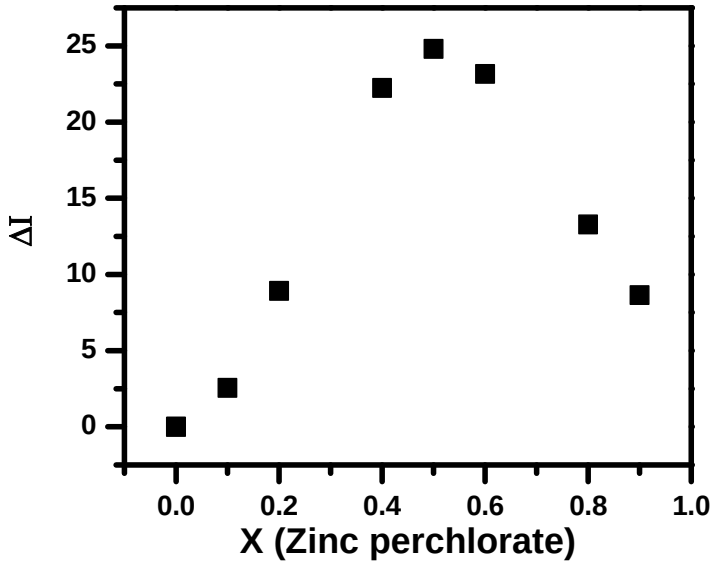

Fig. S3a. Job's plot analysis in HEPES buffer (50 mM, DMSO/water = 1:9, v/v, pH = 7.2) shows that the maximum intensity was obtained at X = 0.50 indicates the probable 1:1 binding of **1** : Zn^{2+} (excitation wavelength: 350 nm).

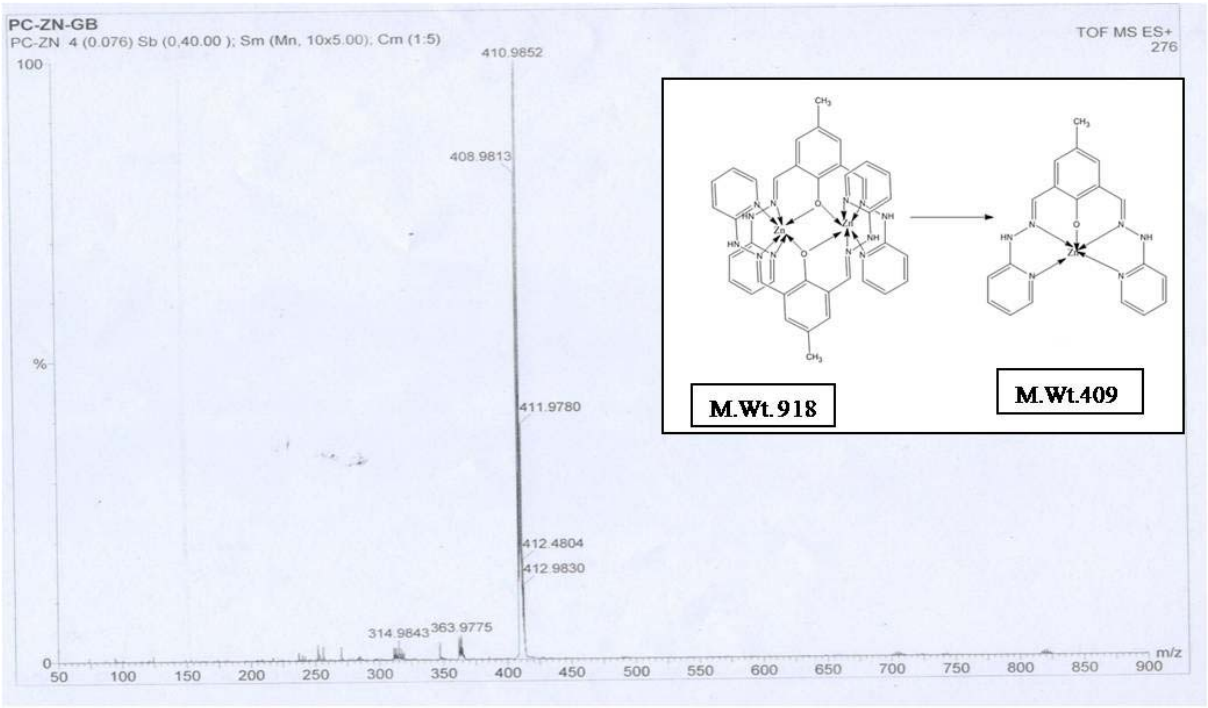

Fig. S3b. HRMS analysis of the solution **1**+ Zn^{2+} and complex **2** (solid state)**.** In both solution state and solid state a peak appeared at 409. This indicates that the probable molecular formula is $[Zn_2(L)_2](ClO_4)_2$.

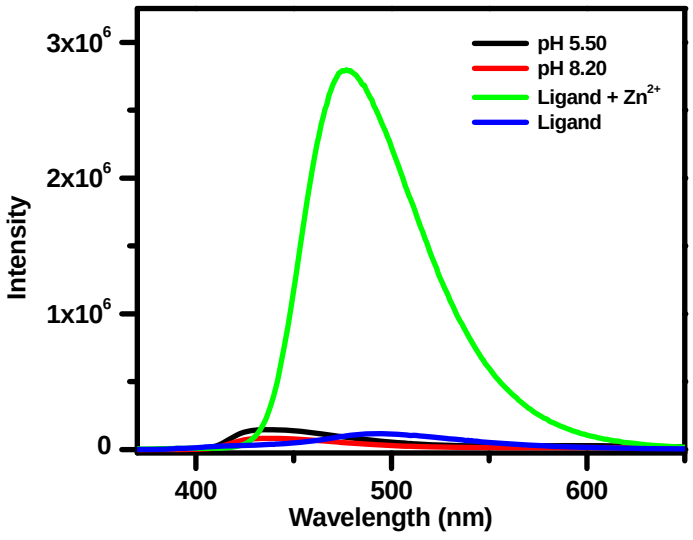

Fig. S4: Effect of the pH on the fluorescence intensity of **1** (40 μM)

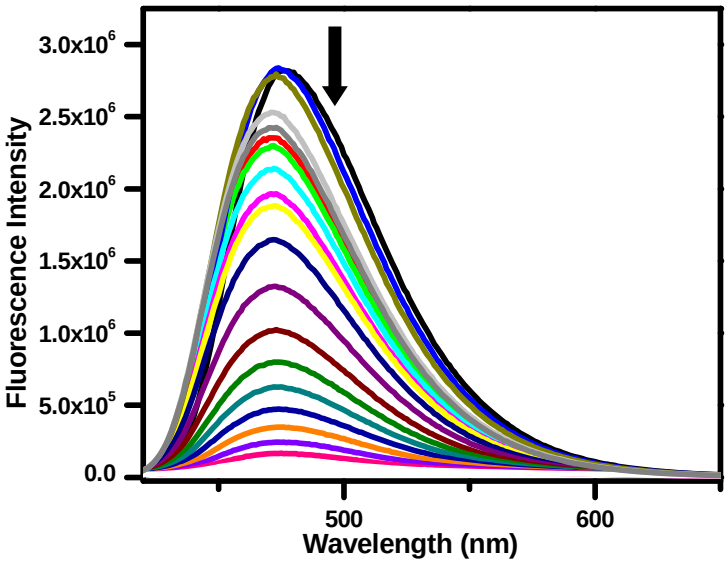

Fig. S5. Fluorescence Titration of **1**+Zn^{2+} complex with EDTA in a HEPES buffer [50 mM, DMSO:water =1:9 (v/v), pH= 7.2] at 25°C (λ_{exc} = 350 nm). Intensity gradually decreases upon gradual addition of EDTA (total 100 μM) solution.

Table-S1

Crystallographic data of **2**

Compound	**2**
Empirical formula	$C_{38}H_{34}Cd_2Cl_2N_{12}O_{10}$
Formula weight	1114.47
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	
a (Å)	23.0762(15)
b (Å)	12.6124(6)
c (Å)	17.5274(13)
α (˚)	90.00
β (˚)	116.6010(10)
γ (˚)	90.00
Volume ($Å^3$)	4561.3(5)
z	4
$Density_{cal}$ (Mg m^{-3})	1.623
Absorption coefficient (mm^{-1})	1.117
F(000)	2224
θ Range (˚) for data collection	1.89 to 27.98
Index ranges	$-30 \le h \le 29$
	$-16 \le k \le 16$
	$-23 \le l \le 22$
Goodness-of-fit on F^2	1.036
Completeness to theta	
Independent reflections [R_{int}]	5299 [0.036]
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	5299/0/ 299
Reflections collected	29240
Final R indices [$I > 2\sigma(I)$]	R_1= 0.0627, wR_2= 0.0581
R indices (all data)	R_1= 0.0341, wR_2= 0.0237
Largest difference peak and hole ($eÅ^{-3}$)	-0.42 and 0.56

Table-S2

Selected bond distances (Å) and angles (°) data for **1** and **2**

Selected Bonds	Value(Å)	Selected Angles	(°)
3			
Cd1-O1	2.2440(13)	O1-Cd1-N1	141.53(7)
Cd1-N1	2.2946(19)	O1-Cd1-N3	74.75(6)
Cd1-N3	2.339(2)	O1-Cd1-O1_a	73.94(5)
Cd1-O1_a	2.2440(13)	O1-Cd1-N1_a	107.57(6)
Cd1-N1_a	2.2946(19)	O1-Cd1-N3_a	117.86(6)
Cd1-N3_a	2.339(2)	N1-Cd1-N3	70.93(6)
Cd2-O1	2.2449(13)	O1_a-Cd1-N1	107.57(6)
Cd2-N4	2.301(2)	N1-Cd1-N1_a	94.49(7)
Cd2-N6	2.3627(18)	N1-Cd1-N3_a	98.82(6)
Cd2-O1_a	2.2449(13)	O1_a-Cd1-N3	117.86(6)
Cd2-N4_a	2.301(2)	N1_a-Cd1-N3	98.82(6)
Cd2-N6_a	2.3627(18)	N3-Cd1-N3_a	165.31(6)
		O1_a-Cd1-N1_a	141.53(7)
		O1_a-Cd1-N3_a	74.75(6)
		N1_a-Cd1-N3_a	70.93(6)
		O1-Cd2-N4	103.06(6)
		O1-Cd2-N6	125.23(6)
		O1-Cd2-O1_a	73.90(5)
		O1-Cd2-N4_a	132.74(7)
		O1-Cd2-N6_a	74.04(6)
		N4-Cd2-N6	70.21(6)
		O1_a-Cd2-N4	132.74(7)
		N4-Cd2-N4_a	111.06(7)
		N4-Cd2-N6_a	97.17(7)

		O1_a-Cd2-N6	74.04(6)
		N4_a-Cd2-N6	97.17(7)
		N6-Cd2-N6_a	158.22(6)
		O1_a-Cd2-N4_a	103.06(6)
		O1_a -Cd2-N6_a	125.23(6)
		N4_a-Cd2-N6_a	70.21(6)
		Cd2 -N6-N5	113.82(12)

Table-S3

Fluorescence lifetimes of free chemosensor **1** and its complexes in MeOH solvent

MeOH	τ_1(ns)	τ_2 (ns)	τ_3 (ns)	a_1	a_2	a_3	χ^2	τ_{av}	φ	k_r (s^{-1})×10^8	fold w.r.t. **1**	k_{nr} (s^{-1}) ×10^8
1	3.58	26.21	0.72	0.84	0.13	0.67	1.16	14.39	0.020	0.013	-	0.681
2(1+Cd^{2+})	1.91	12.92	0.12	4.68	4.88	0.99	1.144	11.38	0.13	0.114	8	0.764
3(1+Zn^{2+})	1.38	12.37	0.17	0.05	1.44	4.14	1.23	0.54	0.280	5.09	366	13.103

Table-S4.

Correlation between experimental and theoretical bond lengths and bond angles of **2**

Bonds (Å)	X-ray	DFT
Cd1-O1	2.2440(13)	2.301
Cd1-N1	2.2946(19)	2.367
Cd1-N3	2.339(2)	2.402
Cd2-O1	2.2449(13)	2.302
Cd2-N4	2.301(2)	2.368
Cd2-N6	2.3627(18)	2.403
Angles (^{0})		
O1-Cd1-N1	141.53(7)	138.6
O1-Cd1-N3	74.75(6)	74.07
O1-Cd1-O1_a	73.94(5)	75.49
O1-Cd1-N1_a	107.57(6)	105.6
O1-Cd1-N3_a	117.86(6)	119.2
N1-Cd1-N3	70.93(6)	69.60
N1-Cd1-N1_a	94.49(7)	95.61
N1-Cd1-N3_a	98.82(6)	97.61
N3-Cd1-N3_a	165.31(6)	163.0
O1-Cd2-N4	103.06(6)	103.6
O1-Cd2-N6	125.23(6)	123.9
O1-Cd2-O1_a	73.90(5)	74.45
O1-Cd2-N4_a	132.74(7)	133.8
O1-Cd2-N6_a	74.04(6)	74.07
N4-Cd2-N6	70.21(6)	69.06
N4-Cd2-N4_a	111.06(7)	109.0
N4-Cd2-N6_a	97.17(7)	97.80
N6-Cd2-N6_a	158.22(6)	159.4
Cd2 -N6-N5	113.82(12)	113.2

Table-S5.
Theoretical bond lengths and bond angles of **3**

Bonds (Å)	Calc.
Zn1-O1	2.117
Zn1-N1	2.243
Zn1-N3	2.299
Zn2-O1	2.118
Zn2-N4	2.243
Zn2-N6	2.297
Angles (^{0})	
O1-Zn1-N1	139.6
O1-Zn1-N3	76.42
O1-Zn1-O1_a	74.51
O1-Zn1-N1_a	101.9
O1-Zn1-N3_a	122.6
N1-Cd1-N3	72.27
N1-Zn1-N1_a	101.2
N1-Zn1-N3_a	95.08
N3-Zn1-N3_a	159.9
O1-Zn2-N4	101.9
O1-Zn2-N6	122.7
O1-Zn2-O1_a	74.51
O1-Zn2-N4_a	139.6
O1-Zn2-N6_a	76.42
N4-Zn2-N6	72.27
N4-Zn2-N4_a	105.1
N4-Zn2-N6_a	94.09
N6-Zn2-N6_a	157.9
Zn2 -N6-N5	113.3

Table-S6.

Vertical electronic transition calculated by TDDFT/CPCM method for Cd-complex

$E_{excitation}$ (eV)	$\lambda_{excitation}$ (nm)	Osc. Strength (f)	Key transitions	Character
2.9695	417.5	0.2009	(55%)HOMO-1→LUMO (42%)HOMO→LUMO+1	L(π)→L(π^*), ILCT
2.9999	413.3	0.4052	(87%)HOMO→LUMO	L(π)→L(π^*), ILCT
3.1579	392.6	0.1055	(87%)HOMO-1→LUMO+1	L(π)→L(π^*), ILCT
3.6655	338.2	0.1958	(68%)HOMO-2→LUMO+2	L(π)→L(π^*), ILCT
3.7193	333.4	0.4935	(63%)HOMO-2→LUMO+1 (32%)HOMO-3→LUMO	L(π)→L(π^*), ILCT
3.9335	315.2	0.1465	(44%)HOMO→LUMO+5 (35%)HOMO-1→LUMO+4	L(π)→L(π^*), ILCT
3.9509	313.8	0.1826	(72%)HOMO-1→LUMO+5	L(π)→L(π^*), ILCT

Table-S7

Vertical electronic transition calculated by TDDFT/CPCM method for Zn-complex

$E_{excitation}$ (eV)	$\lambda_{excitation}$ (nm)	Osc. Strength (f)	Key transitions	Character
3.0105	411.9	0.1560	(54%)HOMO-1→LUMO (44%)HOMO→LUMO+1	L(π)→L(π^*), ILCT
3.0202	410.5	0.2017	(94%)HOMO→LUMO	L(π)→L(π^*), ILCT
3.2101	386.2	0.1320	(93%)HOMO-1→LUMO+1	L(π)→L(π^*), ILCT
3.5915	345.2	0.2382	(92%)HOMO-2→LUMO+2	L(π)→L(π^*), ILCT
3.7037	334.8	0.5327	(61%)HOMO-2→LUMO+1 (30%)HOMO-3→LUMO	L(π)→L(π^*), ILCT
3.9088	317.2	0.2042	(78%)HOMO→LUMO+4	L(π)→L(π^*), ILCT
4.0147	308.8	0.1255	(52%)HOMO→LUMO+5 (39%)HOMO-1→LUMO+4	L(π)→L(π^*), ILCT
4.3844	282.8	0.1685	(84%)HOMO-2→LUMO+5	L(π)→L(π^*), ILCT