Supporting Information for

Solvatochromic and Application in Dye-Sensitized Solar Cells of Sandwich-like Structure Cd(II) Complexes: Supramolecular Architectures Based on Schiff Base Ligand N^1, N^3-bis((6-methoxypyridin-2-yl) methylene) benzene-1,3-diamine

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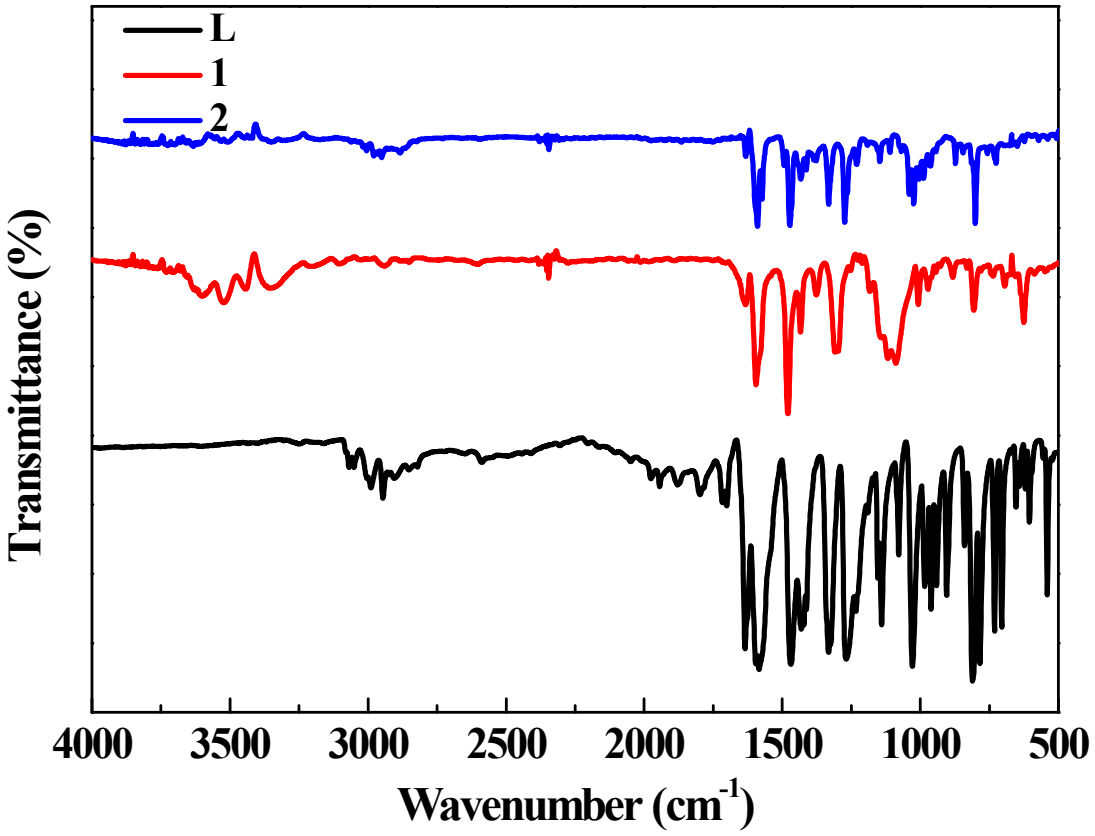

Figure S1. IR spectra of Schiff base ligand **L**, complex **1** and **2**

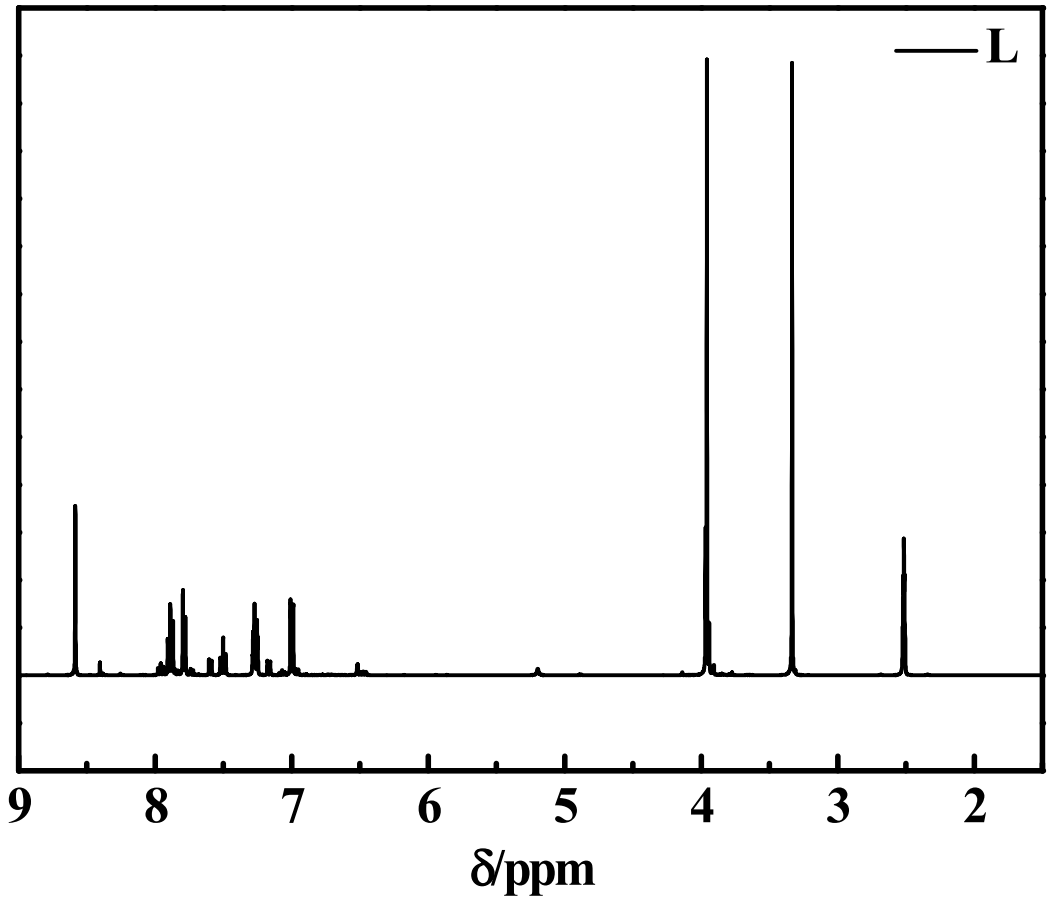

Figure S2. ^{1}H NMR spectrum of **L**

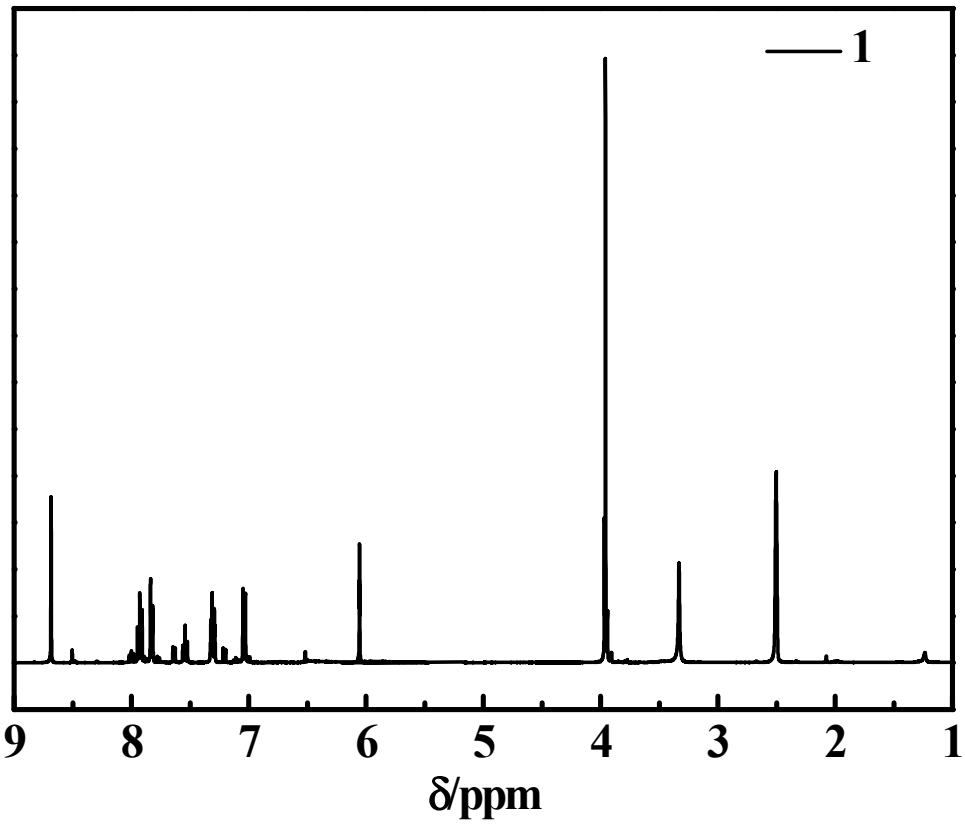

Figure S3. ^{1}H NMR spectrum of **1**

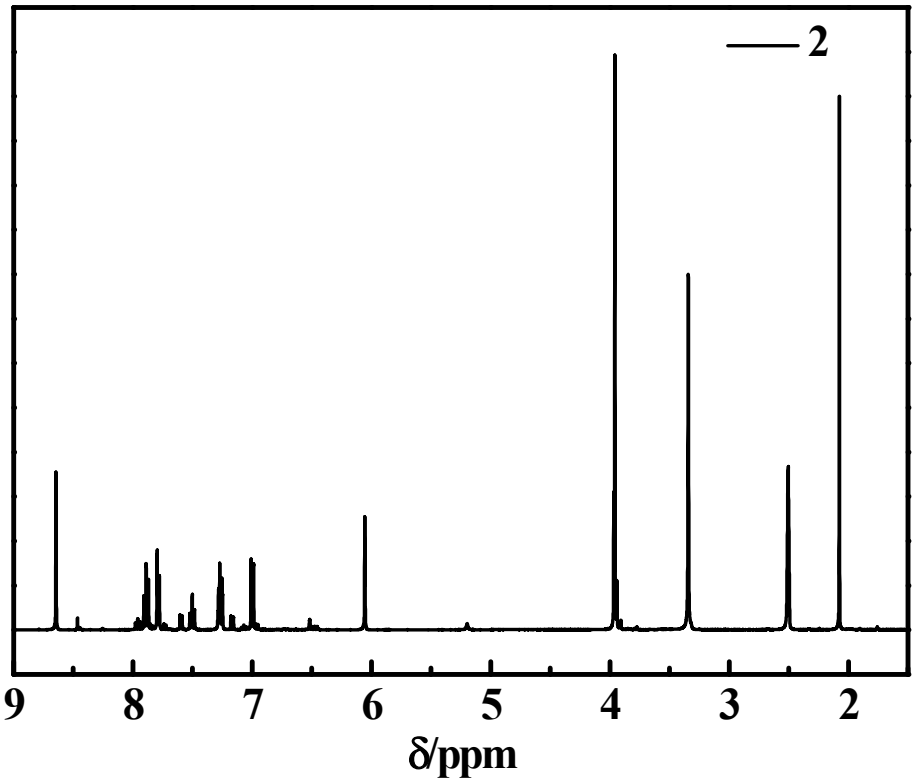

Figure S4. ^{1}H NMR spectrum of **2**

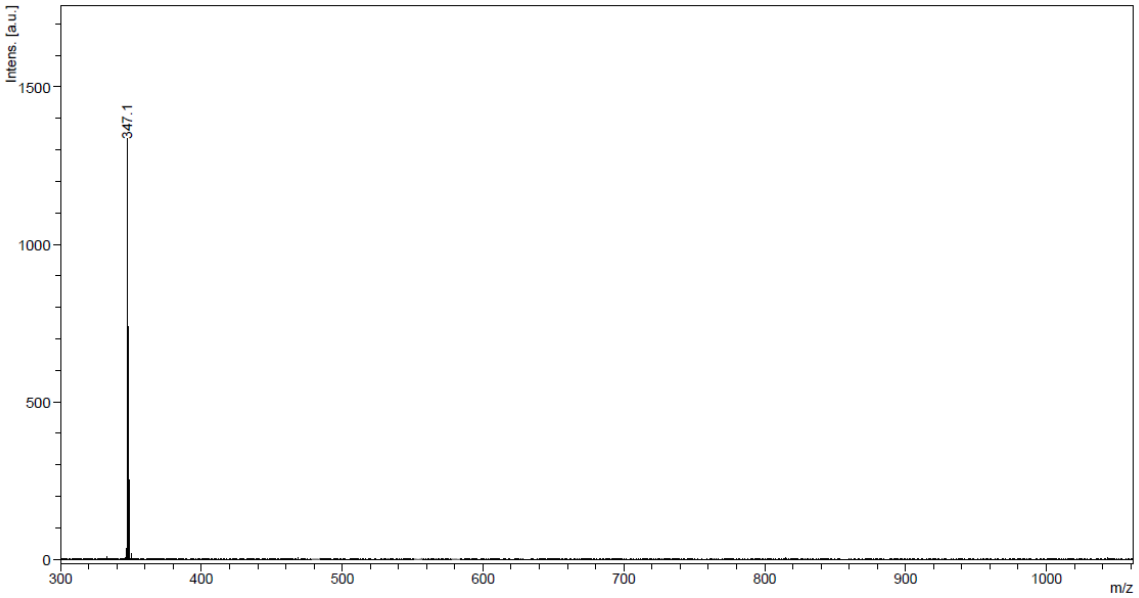

Figure S5. The ESI-MS spectrum of **L**

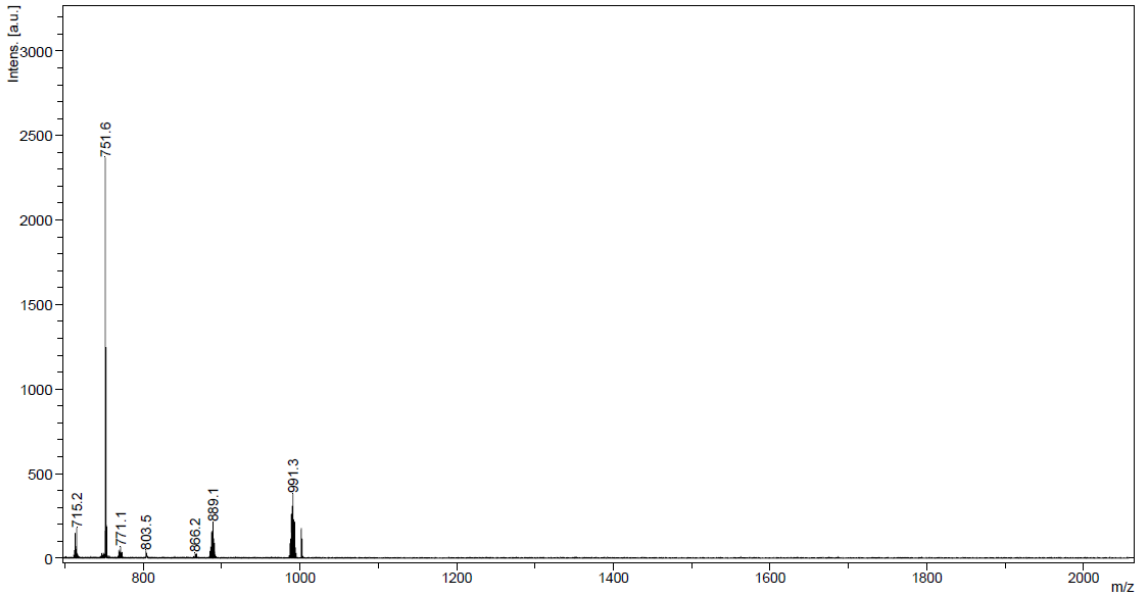

Figure S6. The ESI-MS spectrum of **1**

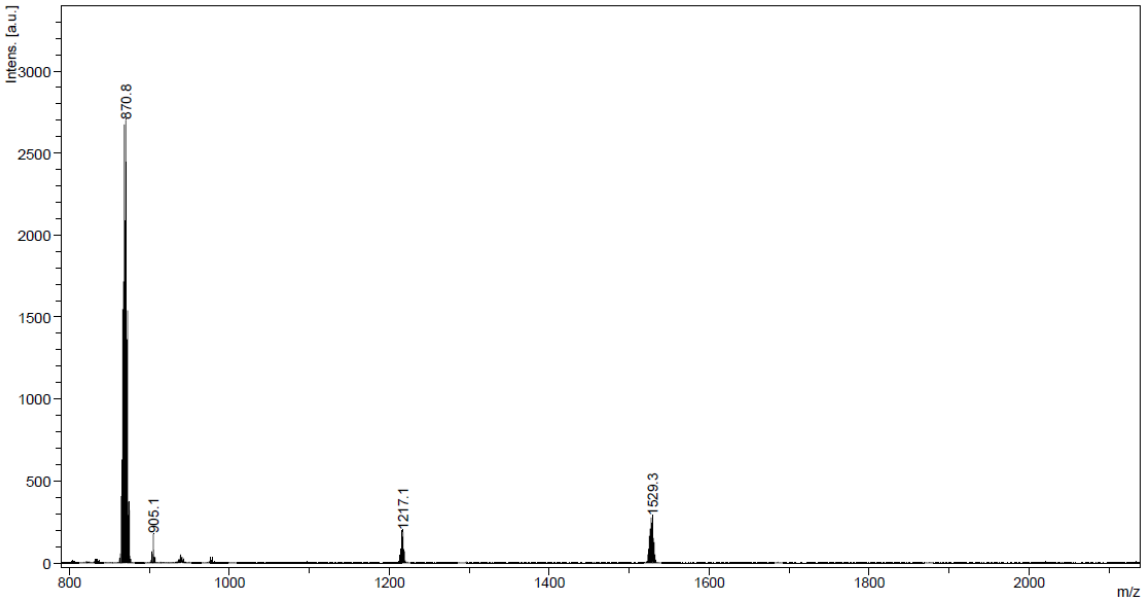

Figure S7. The ESI-MS spectrum of **2**

Table S1 Crystal data and structure parameters for ligand **L** and complexe **1**–**2**

Identification code		**L**	**1**	**2**
Empirical formula		$C_{20}H_{18}N_4O_2$	$C_{40}H_{40}Cd_2N_{12}O_{18}$	$C_{52}H_{58}Cd_2N_{14}O_{22}$
Formula weight		346.38	1201.66	1597.72
Crystal system		Monoclinic	Triclinic	Monoclinic
Space group		$P2_1/c$	P	$P2_1/c$
Unit cell dimensions	a(Å)	17.335(4)	8.8510(18)	12.217(2)
	b(Å)	13.207(3)	11.372(2)	20.167(4)
	c(Å)	7.7439(15)	12.324(3)	14.706(3)
	α(°)	90	90.55(3)	90
	β(°)	94.11(3)	100.25(3)	111.96(3)
	γ(°)	90	108.59(3)	90
Volume(Å^3)		1768.3(6)	1154.0(4)	3360.4(11)
Z		4	1	2
Calculated density(mg/m^3)		1.301	1.729	1.579
Absorption coefficient(mm^{-1})		0.087	1.011	0.875
Theta range for data collection		3.06 to 27.48	3.25 to 27.48	3.03 to 27.48
Limiting indices		-22<=h<=22 -17<=k<=17 -9<=l<=10	-11<=h<=11 -14<=k<=14 -16<=l<=15	-15<=h<=15 26<=k<=26 -16<=l<=19
Data / restraints / parameters		4029 / 0 / 235	5242 / 0 / 325	7653 / 0 / 427
Goodness-of-fit on F^2		0.902	1.086	1.067
Final R indices [I>2sigma(I)][a]	R_1	0.0534	0.0884	0.0394
	wR_2	0.1359	0.2108	0.1269
R indices (all data)	R_1	0.1109	0.1002	0.0453
	wR_2	0.1702	0.2210	0.1311
Largest diff. peak and hole(e·Å^{-3})		0.180 and -0.179	6.412 and -6.047	1.753 and -0.906

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum[w\ (F_o^2 - F_c^2)^2]/\sum[\ w\ (F_o^2)^2]]^{1/2}$.

Table S2 Selected bond lengths [Å] and angles [°] for **L**.

C(1)-O(1)	1.432(3)	C(8)-N(2)	1.424(3)	C(19)-N(4)	1.322(3)
C(2)-N(1)	1.320(3)	C(12)-N(3)	1.421(3)	C(19)-O(2)	1.355(3)
C(2)-O(1) C(6)-	1.360(3)	C(14)-N(3)	1.273(3)	C(20)-O(2)	1.435(3)
N(1)	1.358(3)	C(15)-N(4)	1.358(3)	C(7)-N(2)	1.272(3)
O(1)-C(1)-H(1A)	109.5	C(13)-C(8)-N(2)	116.7(2)	O(2)-C(20)-H(20B)	109.5
O(1)-C(1)-H(1B)	109.5	C(11)-C(12)-N(3)	117.65(19)	O(2)-C(20)-H(20C)	109.5
O(1)-C(1)-H(1C)	109.5	C(13)-C(12)-N(3)	122.5(2)	C(2)-O(1)-C(1)	117.2(2)
N(1)-C(2)-O(1)	119.3(2)	N(3)-C(14)-C(15)	122.5(2)	C(19)-O(2)-C(20)	117.34(18)
N(1)-C(2)-C(3)	124.5(2)	N(3)-C(14)-H(14A)	118.8	C(2)-N(1)-C(6)	116.9(2)
O(1)-C(2)-C(3)	116.1(2)	N(4)-C(15)-C(16)	123.07(19)	C(7)-N(2)-C(8)	118.5(2)
N(1)-C(6)-C(5)	123.0(2)	N(4)-C(15)-C(14)	114.34(19)	C(14)-N(3)-C(12)	118.89(18)

N(1)-C(6)-C(7)	113.7(2)	N(4)-C(19)-O(2)	135.63(9)	C(19)-N(4)-C(15)	116.9(2)
N(2)-C(7)-C(6)N	123.3(2)	N(4)-C(19)-C(18)	124.0(2)	O(2)-C(20)-H(20A)	109.5
N(2)-C(7)-H(7A)	118.3	O(2)-C(19)-C(18)	116.5(2)	C(9)-C(8)-N(2)	123.7(2)

Table S3 Selected bond lengths [Å] and angles [°] for **1**.

Cd(1)-O(4)	2.276(6)	N(3)-Cd(1)#1	2.370(6)	Cd(1)-O(3)	2.379(6)
Cd(1)-N(3)#1	2.370(6)	N(4)-Cd(1)#1	2.401(7)	Cd(1)-N(1)	2.453(6)
Cd(1)-N(2)	2.372(7)	Cd(1)-N(4)#1	2.401(7)	Cd(1)-O(6)	2.685(8)
O(4)-Cd(1)-N(3)#1	86.5(2)	N(2)-Cd(1)-N(4)#1	102.8(3)	N(3)#1-Cd(1)-O(6)	106.4(2)
O(4)-Cd(1)-N(2)	114.3(3)	O(3)-Cd(1)-N(4)#1	163.6(2)	N(2)-Cd(1)-O(6)	89.7(3)
N(3)#1-Cd(1)-N(2)	159.1(3)	O(4)-Cd(1)-N(1)	171.0(2)	O(3)-Cd(1)-O(6)	122.8(2)
O(4)-Cd(1)-O(3)	82.1(3)	N(3)#1-Cd(1)-N(1)	90.9(2)	N(4)#1-Cd(1)-O(6)	73.0(2)
N(3)#1-Cd(1)-O(3)	98.6(2)	N(2)-Cd(1)-N(1)	68.2(3)	N(1)-Cd(1)-O(6)	138.6(2)
N(2)-Cd(1)-O(3)	82.9(3)	O(3)-Cd(1)-N(1)	89.8(2)	Cd(1)-O(3)-H(3C)	109.5
O(4)-Cd(1)-N(4)#1	108.9(3)	N(4)#1-Cd(1)-N(1)	78.3(2)	Cd(1)-O(3)-H(3D)	109.5
N(3)#1-Cd(1)-N(4)#1	70.6(2)	O(4)-Cd(1)-O(6)	50.2(2)	N(5)-O(4)-Cd(1)	106.4(5)
N(5)-O(6)-Cd(1)	86.0(5)	C(14)-N(3)-Cd(1)#1	115.1(6)	C(12)-N(2)-Cd(1)	118.2(7)
C(7)-N(1)-Cd(1)	113.3(5)	C(6)-N(3)-Cd(1)#1	128.0(5)	C(8)-N(2)-Cd(1)	115.2(6)
C(2)-N(1)-Cd(1)	124.5(5)	C(19)-N(4)-Cd(1)#1	128.0(6)	C(15)-N(4)-Cd(1)#1	113.3(5)

Table S4 Selected bond lengths [Å] and angles [°] for **2**.

Cd(1)-N(5)	2.279(2)	Cd(1)-N(2)	2.392(2)	Cl(1)-O(6)	1.416(4)
Cd(1)-N(4)	2.306(2)	Cd(1)-N(3)	2.401(2)	Cl(1)-O(7)	1.428(3)
Cd(1)-N(1)	Cd(1)-2.321(2)	Cl(1)-O(4)	1.302(4)	Cl(2)-O(10)	1.410(3)
O(3)	2.354(2)	Cl(1)-O(5)	1.391(4)	Cl(2)-O(9)	1.421(3)
Cl(2)-O(8)	1.425(3)	Cl(2)-O(11)	1.427(2)		
N(5)-Cd(1)-N(4)	106.25(9)	N(4)-Cd(1)-N(1)	99.76(8)	N(4)-Cd(1)-O(3)	94.38(8)
N(5)-Cd(1)-N(1)	105.22(9)	N(5)-Cd(1)-O(3)	84.64(9)	N(1)-Cd(1)-O(3)	159.56(8)
N(5)-Cd(1)-N(2)	91.53(9)	N(4)-Cd(1)-N(2)	161.81(8)	N(1)-Cd(1)-N(2)	71.19(8)
O(3)-Cd(1)-N(2)	91.00(8)	N(5)-Cd(1)-N(3)	166.66(9)	N(4)-Cd(1)-N(3)	71.14(7)
N(1)-Cd(1)-N(3)	88.12(8)	O(3)-Cd(1)-N(3)	82.55(7)	N(2)-Cd(1)-N(3)	92.41(7)
O(4)-Cl(1)-O(5)	116.7(5)	O(4)-Cl(1)-O(6)	109.7(6)	O(5)-Cl(1)-O(6)	100.6(4)
O(4)-Cl(1)-O(7)	110.5(2)	O(5)-Cl(1)-O(7)	110.6(2)	O(6)-Cl(1)-O(7)	108.1(2)
O(10)-Cl(2)-O(9)	109.1(2)	O(10)-Cl(2)-O(8)	108.1(2)	O(9)-Cl(2)-O(8)	106.6(3)
O(10)-Cl(2)-O(11)	112.06(17)	O(9)-Cl(2)-O(11)	109.31(16)	O(8)-Cl(2)-O(11)	111.5(2)
Cd(1)-O(3)-H(3A)	109.4	Cd(1)-O(3)-H(3B)	109.4	C(2)-N(1)-Cd(1)	125.53(18)
C(6)-N(1)-Cd(1)	115.68(17)	C(8)-N(2)-Cd(1)	127.00(17)	C(10)#1-N(3)-Cd(1)	126.78(16)
C(7)-N(2)-Cd(1)	113.67(18)	C(14)-N(3)-Cd(1)	114.05(17)	C(19)-N(4)-Cd(1)	123.90(19)
C(15)-N(4)-Cd(1)	116.55(16)	C(22)-N(5)-Cd(1)	163.8(3)		

Table S5 Intermolecular interactions in the crystal structure of compounds

Compound	Interaction	H…A (Å)	D…A (Å)	Angle (Å)
L	C13–H13A···O1	2.583	3.486	163.73
	C18–H18A···N3	2.703	3.597	161.57
	π_{Cg1}–π_{Cg1}		3.442	
1	O3–H3D···O8^{i}	2.072	3.021	169.44
	O3–H3C···O7^{ii}	1.899	2.745	145.64
	O13–H13B···O9	2.582	3.275	129.20
	O1–H1A···O7	2.678	3.539	154.41
	C18–H18A···O4	2.501	3.288	142.61
	C7–H7A···O8	2.653	3.580	174.82
	C11–H11A···O6	2.510	3.341	148.92
	C10–H10A···O5	2.696	3.345	127.53
	π_{Cg1}–π_{Cg1}		3.428	
2	O3–H3A···N7^{ii}	2.003	2.886	152.05
	O3–H3B···O9^{iii}	2.548	3.202	125.47
	C7–H7B···O10	2.541	3.381	149.57
	C7–H7B···O8	2.681	3.540	152.85
	C18–H18A···O9	2.551	3.470	168.56
	C17–H17A···N7	2.727	3.627	163.01
	C16–H16A···O5	2.678	3.509	149.21
	C14–H14A···O5	2.718	3.541	147.92
	C21–H21B···O5	2.734	3.686	171.02
	C3–H3C···O4	2.527	3.379	152.61
	C23–H23C···N7	2.650	3.564	157.44
	π_{Cg1}–π_{Cg1}		3.422	

i: x+1,y,z; ii: -x+1,-y+1,-z+1;iii: -x+1,y+1/2,-z+1/2; Cg_1 is the centroid of the pyridine ring.

Table S6 Photoluminescent data for **L**, **1** and **2** in the solid state at 298 K and 77K

Compoud	Temperature(K)	Excitation (λ, nm)	Emission(λ_{max}, nm)	CIE (x, y)	τ_1 (μs)	τ_2 (μs)	$<\tau>$ (μs)
L	298	346	493	(0.30,0.46)	2.09 (42.59%)	14.89 (57.41%)	13.68
	77	346	485	(0.23,0.34)	0.61 (18.33%)	20.99 (81.67%)	20.86
1	298	346	555	(0.43,0.51)	1.02 (66.15%)	8.16 (33.85%)	6.75
	77	346	528	(0.41,0.53)	0.97 (22.55%)	21.01 (77.45%)	20.75
2	298	346	558	(0.41,0.50	1.00 (56.38%)	8.66 (43.62%)	7.67
	77	346	520	(0.38,0.56)	0.89 (22.80%)	20.9 (77.20%)	20.65

Table S7 Photoluminescent data for **L**, **1** and **2** in solution at 298 K

Compoud	Absorption (nm) ε/$dm^3cm^{-1}mol^{-1}$	Emission (λ_{max}, nm)	CIE (x, y)	Lifetime (μs)		$<\tau>$ (μs)	Quantum yields(Φ)[a]	Conditions[b]
				τ_1	τ_2			
L	349 (39103)	453	0.30, 0.62	2.23(29.98%)	18.74(70.02%)	17.93	0.114	CH_3CN
1	357 (42067)	421	0.16, 0.12	1.55(33.11%)	18.82(66.89%)	18.15	0.120	DMSO
	360 (39457)	433	0.16, 0.13	1.56(37.52%)	17.46 (62.48%)	16.66	0.163	CH_3CN
	366 (32648)	547	0.38, 0.60	1.89 (34.51%)	18.08 (65.49%)	17.24	0.085	CH_3OH
	360 (44213)	429	0.16, 0.13	1.76 (44.30%)	17.56 (55.70%)	16.39	0.178	CH_3COCH_3,
	353 (45087)	423	0.16, 0.14	1.73 (50.34%)	17.80 (49.66%)	16.36	0.207	CH_3Cl,
	351 (36977)	421	0.16, 0.14	1.38 (36.07%)	17.89 (63.93%)	17.20	0.223	THF
2	378 (38865)	501	0.21, 0.33	1.63 (34.63%)	19.95 (65.37%)	19.18	0.126	DMSO
	365 (38371)	490	0.21, 0.37	2.13 (35.24%)	19.95 (64.76%)	18.97	0.145	CH_3CN
	330 (17246), 363 (27289)	461	0.30, 0.35	1.63 (43.08%)	18.30 (56.92%)	17.25	0.093	CH_3OH
	329 (26380), 363 (40559)	484	0.22, 0.43	2.23 (37.07%)	20.15 (62.93%)	19.05	0.200	CH_3COCH3
	330 (26020), 371 (36156)	474	0.15, 0.31	2.05 (38.69%)	20.10 (61.31%)	17.87	0.213	CH_3Cl

	329 (26261), 361 (43985)	454	0.19, 0.20	1.96 (46.73%)	19.76 (53.27%)	18.34	0.225	THF

[a]Determined using quinine sulfate in 0.1 M sulphuric acid ($c = 1 \times 10^{-5}$ M, $\Phi = 0.546$).

[b]Concentration in solution: $c = 1 \times 10^{-5}$ M.

Table S8 Photoluminescent data for **1** and **2** in CH_3CN/CH_3OH mixed solvent with fixed concentration.

Compoud	Excitation (λ_{ex} nm)	Emission (λ_{max}, nm)	CIE (x, y)	Lifetime (μs)		<τ> (μs)	Quantum yields(Φ)[a]	CH_3OH content (Vol %)[b]
				τ_1	τ_2			
1	350	426	0.16, 0.13	2.13(35.24%)	19.95(64.76%)	18.97	0.163	0
	350	435	0.15, 0.20	1.94(44.17%)	22.17(55.83%)	20.87	0.143	20
	350	460	0.15, 0.29	2.31 (39.59%)	26.82 (60.41%)	25.51	0.139	40
	350	490	0.16, 0.42	2.08 (43.40%)	23.7 (56.6%)	22.33	0.138	60
	350	512	0.22, 0.64	1.95 (37.91%)	20.73 (62.09%)	19.71	0.117	80
	350	526	0.38, 0.60	1.63 (43.08%)	18.30 (56.92%)	17.25	0.093	100
2	360	490	0.21, 0.37	1.04 (21.29%)	27.49 (78.71%)	27.23	0.145	0
	360	494	0.34, 0.44	0.55 (19.84%)	24.13 (80.16%)	24.00	0.142	20
	360	502	0.36, 0.45	1.04 (23.64%)	18.72 (76.36%)	18.43	0.132	40
	360	511	0.36, 0.44	1.39 (27.94%)	17.30 (72.76%)	16.83	0.110	60
	360	521	0.36, 0.45	1.48(27.94%)	17.93 (72.76%)	17.42	0.103	80
	360	461	0.30, 0.35	1.25(52.93%)	11.45(47.07%)	10.33	0.085	100

[a]Determined using quinine sulfate in 0.1 M sulphuric acid ($c = 1 \times 10^{-5}$ M, $\Phi = 0.546$).

[b]Concentration in solution: $c = 1 \times 10^{-5}$ M.

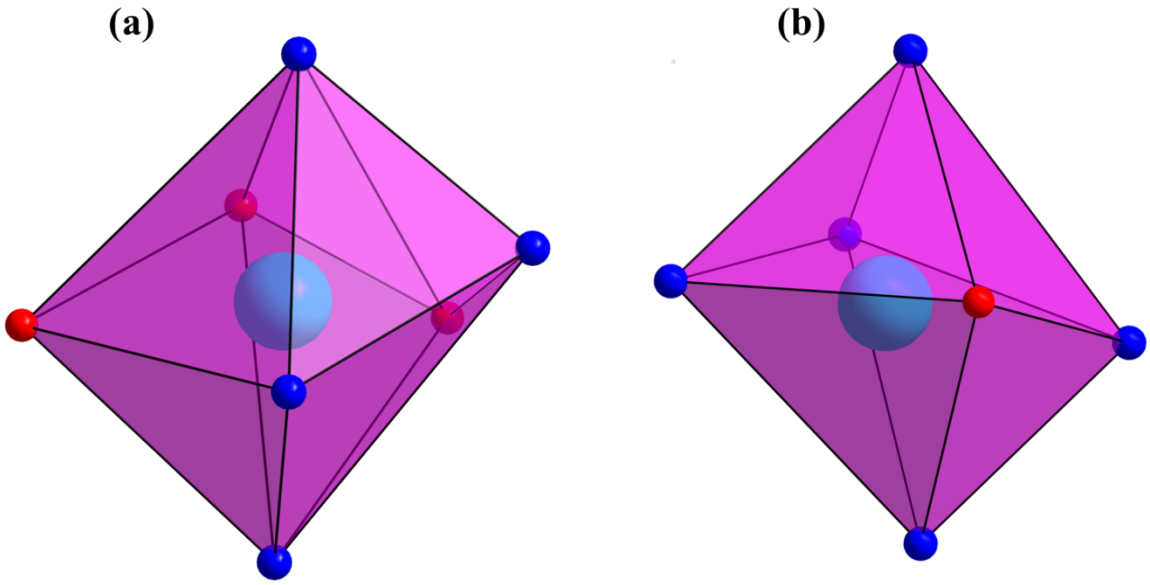

Figure S8. The coordinating polyhedron of **1** (a) and **2** (b)

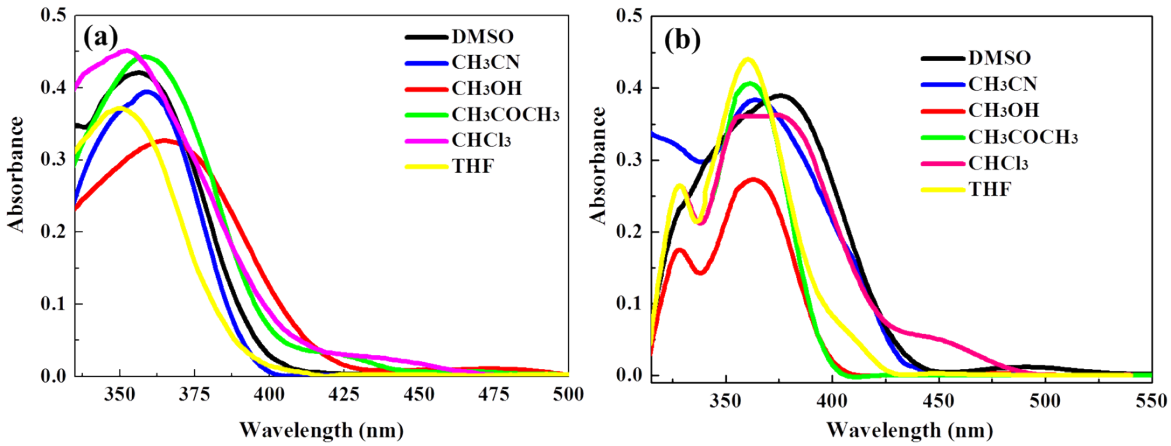

Figure S9. UV/vis absorption spectra of **1** and **2** in DMSO, CH_3CN, CH_3OH, CH_3COCH_3, $CHCl_3$ and THF (c =10^{-5} M) at 298 K.

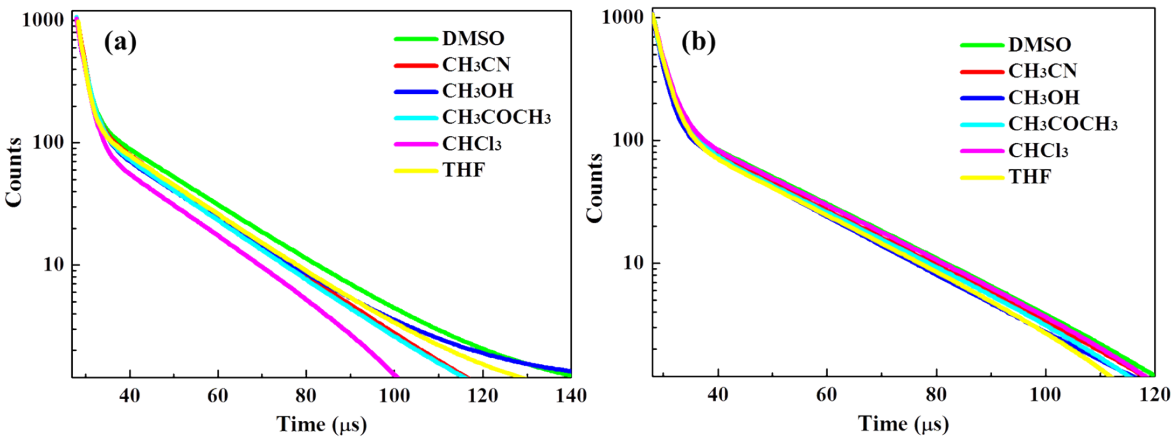

Figure S10. The luminescence decay curves of **1** and **2** in different solution at 298 K.

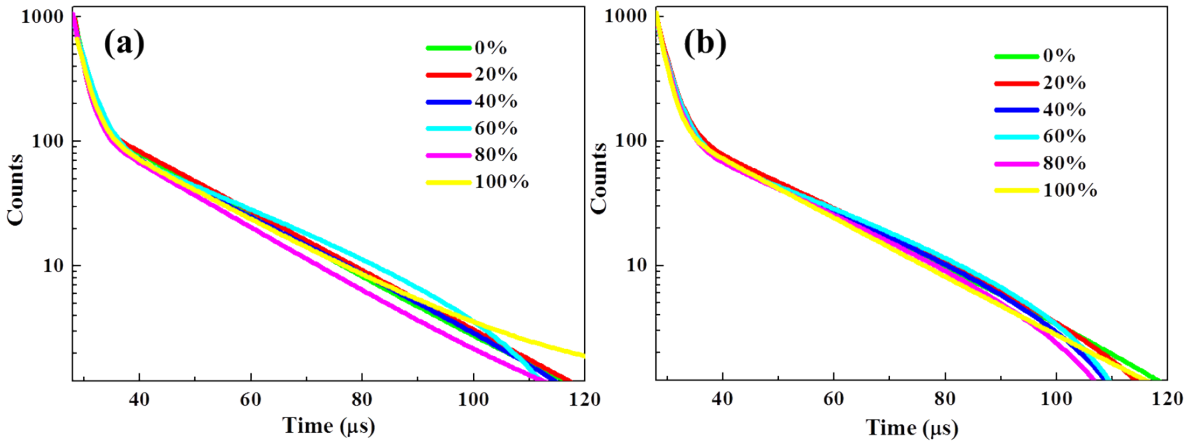

Figure S11. The luminescence decay curves of **1** and **2** in mixed solution as a function of CH_3OH content at 298 K.