Supporting Information

Multi-stimuli-responsive Zn(II)-Schiff base complexes adjusted by rotatable aromatic rings

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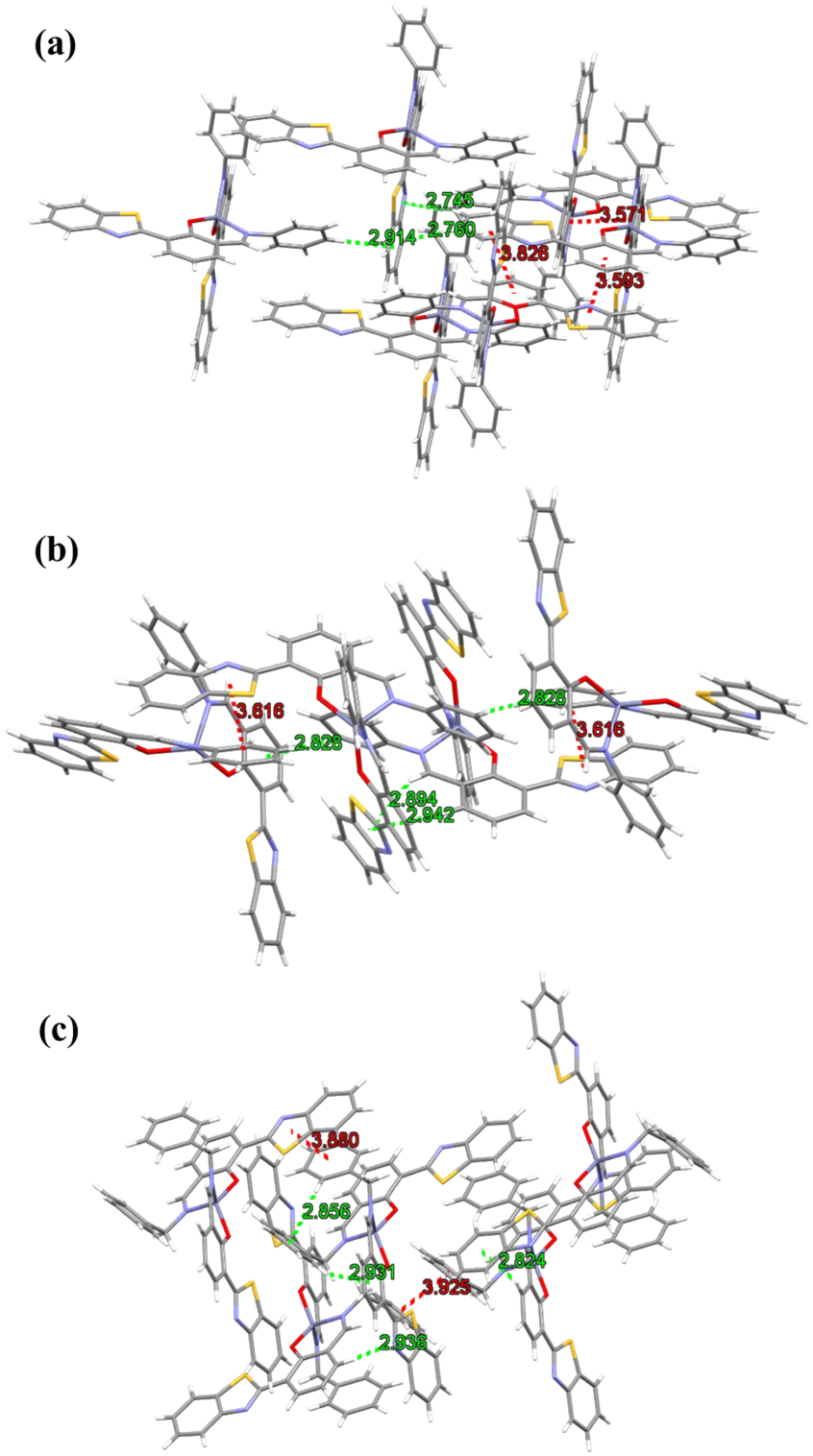


Figure S1. The packing mode and multiple intermolecular interactions in (a) ZnL^{1}_{2}, (b) ZnL^{1a}_{2} and (c) ZnL^{2}_{2} (C-H···π interactions: green, π···π stacking: red).

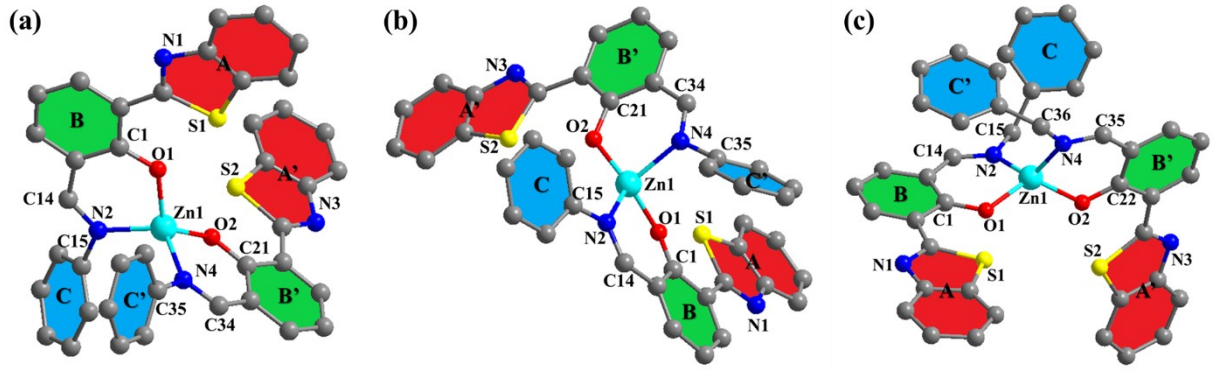


Figure S2. The molecular structures of (a) ZnL^{1}_{2}, (b) ZnL^{1a}_{2} and (c) ZnL^{2}_{2}.

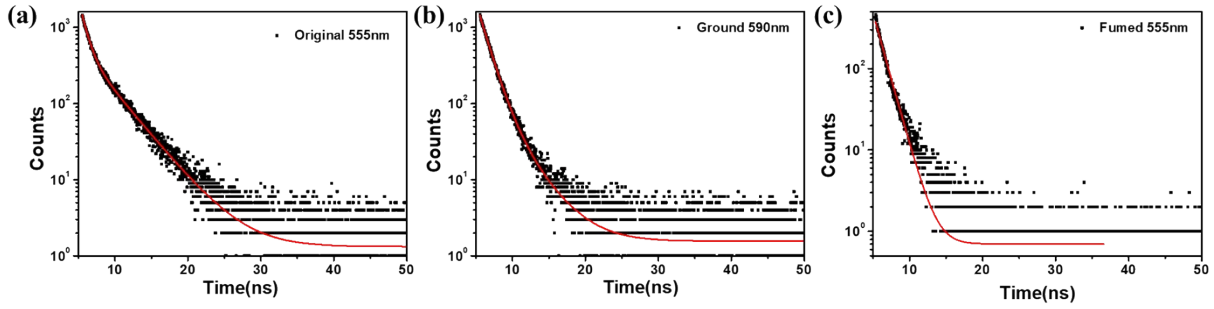


Figure S3. Fluorescence decay curves and fit results of ZnL^{1}_{2} in different states (excited at 371.8 nm): (a) Original sample monitored at 555 nm, (b) Ground sample monitored at 590 nm, (c) Fumed sample monitored at 555 nm.

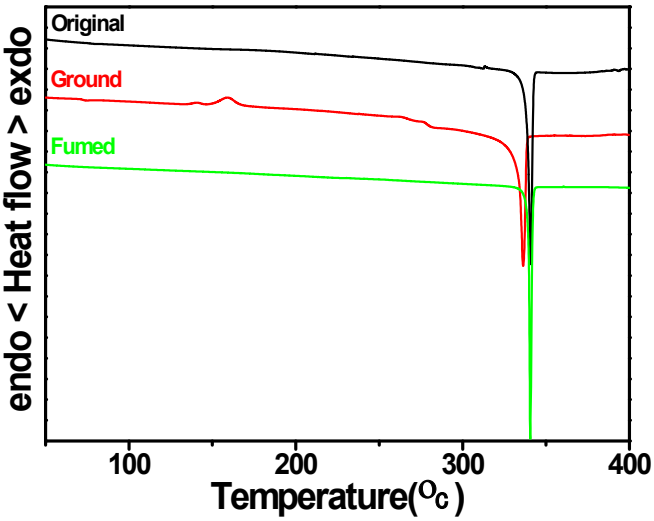


Figure S4. DSC curves of ZnL^{1}_{2} original, ground, fumed samples.

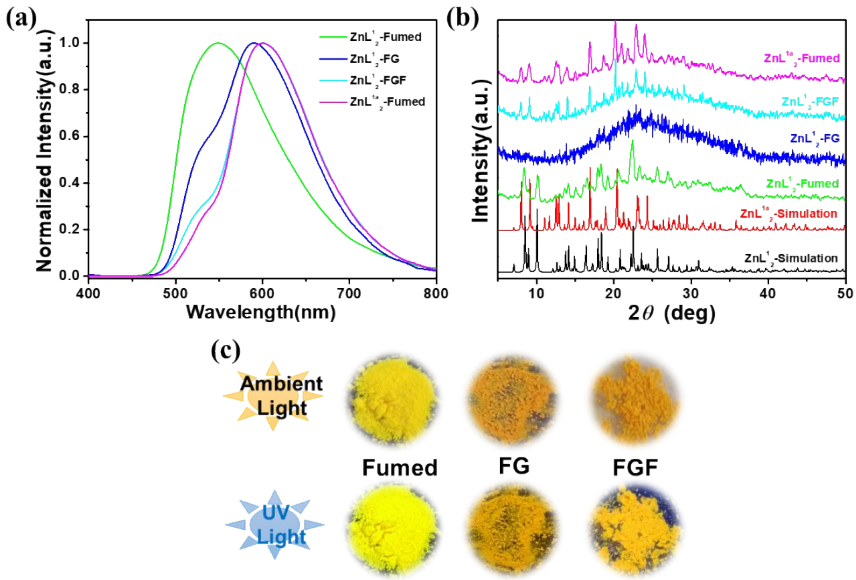


Figure S5. (a) Fluorescence emission spectra (excited at 365 nm) and (b) PXRD patterns of ZnL^{1}_{2} Fumed, FG, FGF samples, and ZnL^{1a}_{2} fumed, (c) photographs of ZnL^{1}_{2} Fumed, FG, and FGF samples under ambient light and UV (365 nm) light.

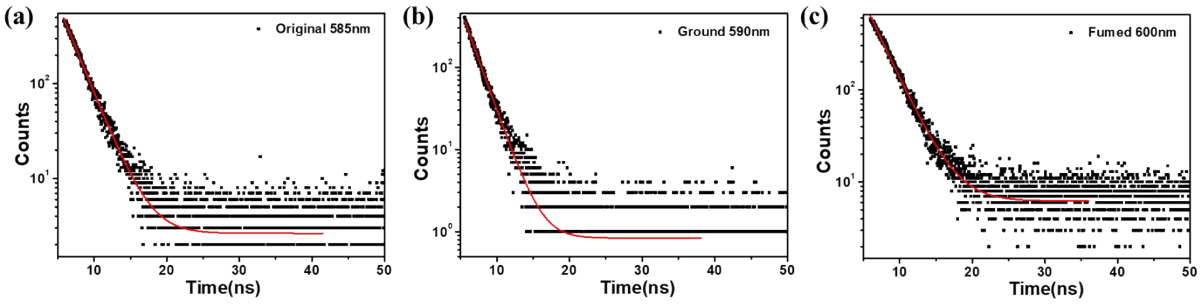


Figure S6. Fluorescence decay curves and fit results of ZnL^{1a}_2 in different states (excited at 371.8 nm): (a) Original sample monitored at 585 nm, (b) Ground sample monitored at 590 nm, (c) Fumed sample monitored at 600 nm.

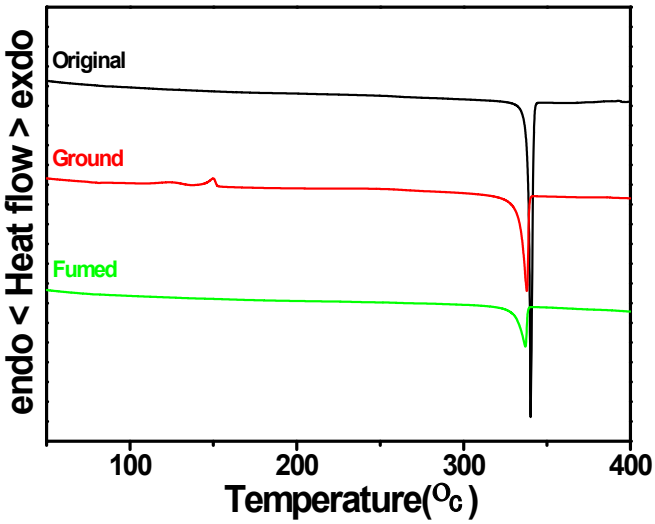


Figure S7. DSC curves of ZnL^{1a}_2 original, ground, fumed samples.

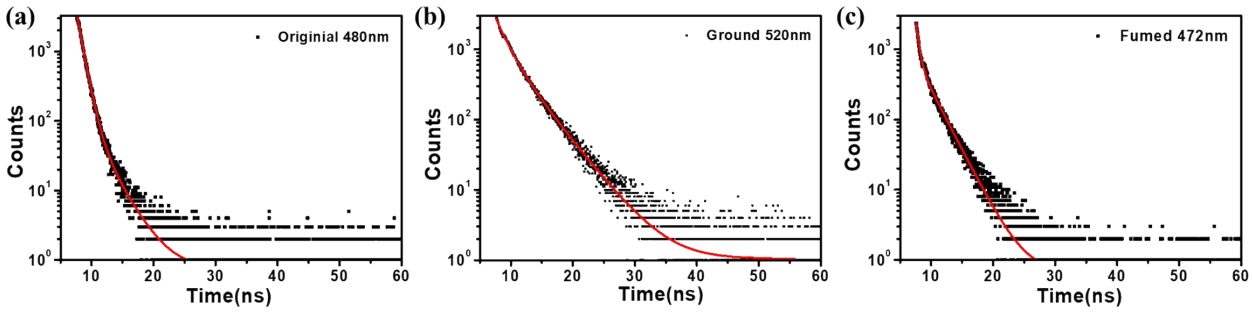


Figure S8. Fluorescence decay curves and fit results of ZnL^2_2 in different states (excited at 371.8 nm): (a) Original sample monitored at 480 nm, (b) Ground sample monitored at 520 nm, (c) Fumed sample monitored at 472 nm.

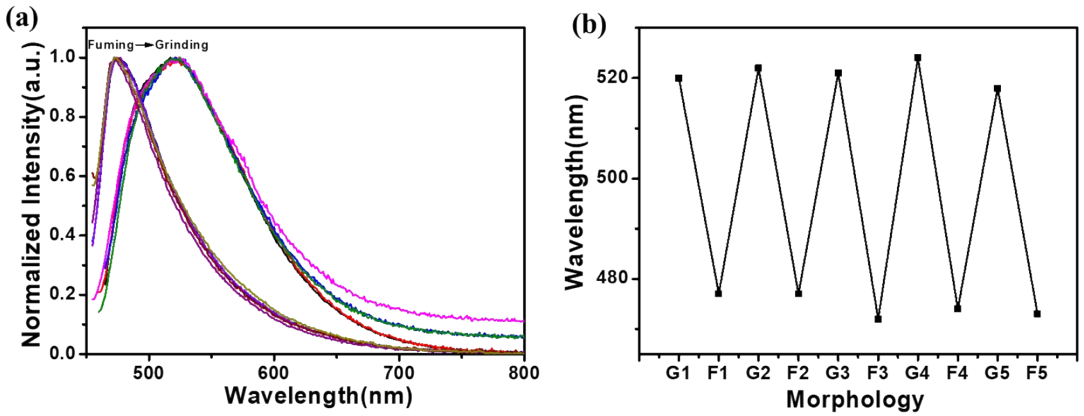


Figure S9. (a) Fluorescence emission spectra, and (b) emission switching characteristics of ZnL^2_2 upon repeating the grinding-fuming processes.

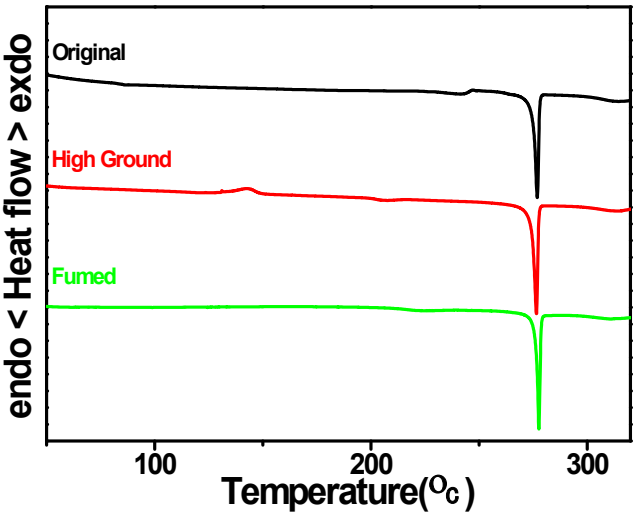


Figure S10. DSC curves of ZnL^2_2 original, high ground, fumed samples.

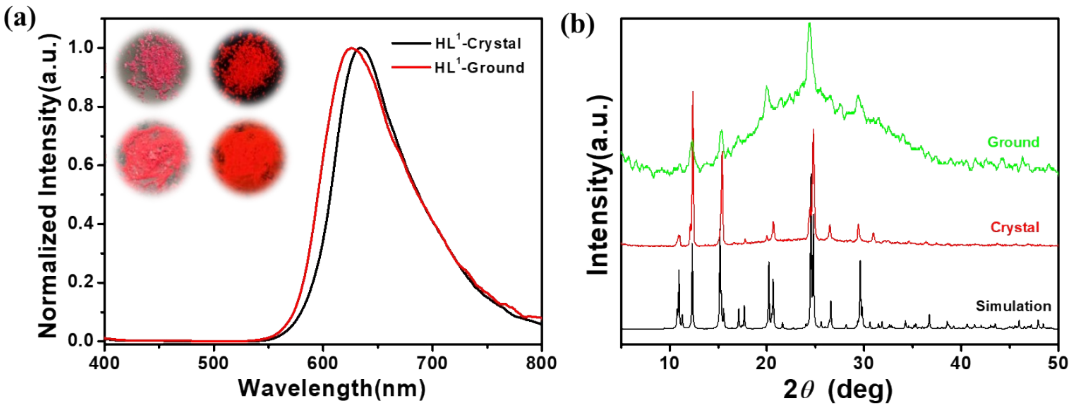


Figure S11. (a) Fluorescence emission spectra (excited at 365 nm), (b) PXRD patterns of the HL^1 before and after grinding. (Insert photographs: the HL^1 samples under ambient light and UV light).

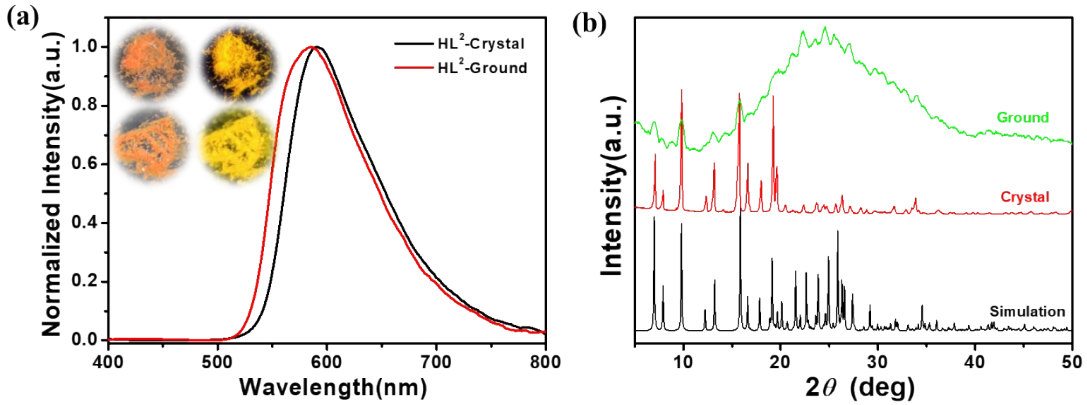


Figure S12. (a) Fluorescence emission spectra (excited at 365 nm), (b) PXRD patterns of the HL^2 before and after grinding. (Insert photographs: the HL^2 samples under ambient light and UV light).

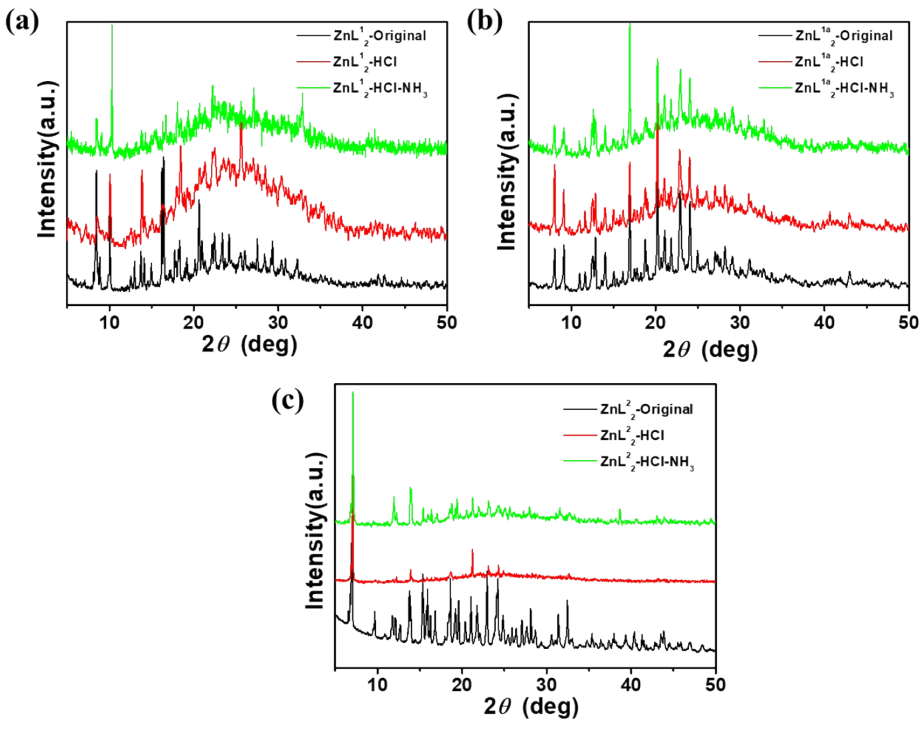


Figure S13. PXRD patterns of Zn(II) complexes after HCl/NH_3 simulation: (a) $ZnL^1{}_2$, (b) $ZnL^{1a}{}_2$ and (c) $ZnL^2{}_2$.

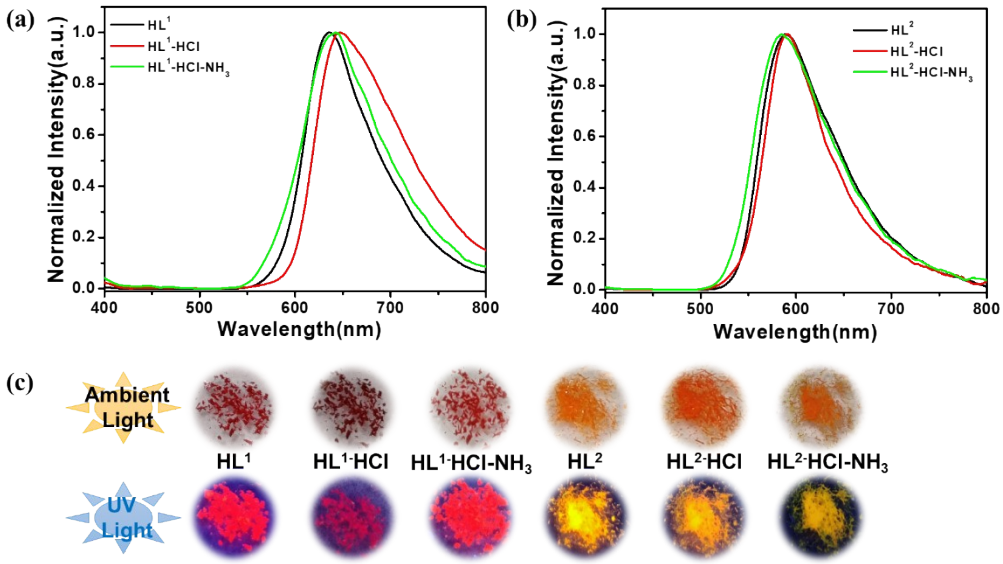


Figure S14. Fluorescence emission spectra of the original sample of (a) HL^1, (b)HL^2 and the samples exposed to HCl/NH_3 vapor (excited at 365 nm), (c) photographs of the samples in different states under ambient light and UV light.

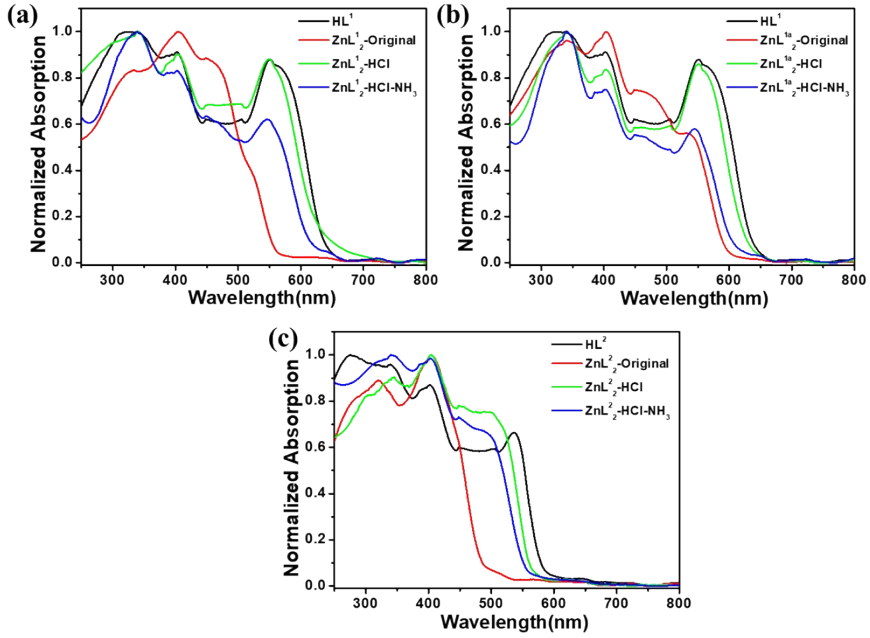


Figure S15. UV–Vis absorption spectra of the ligands (HL^1 and HL^2), original crystals of Zn (II) complexes and the samples exposed to HCl/NH_3 vapor on solid state, (a) $ZnL^1{}_2$, (b) $ZnL^{1a}{}_2$ and (c) $ZnL^2{}_2$.

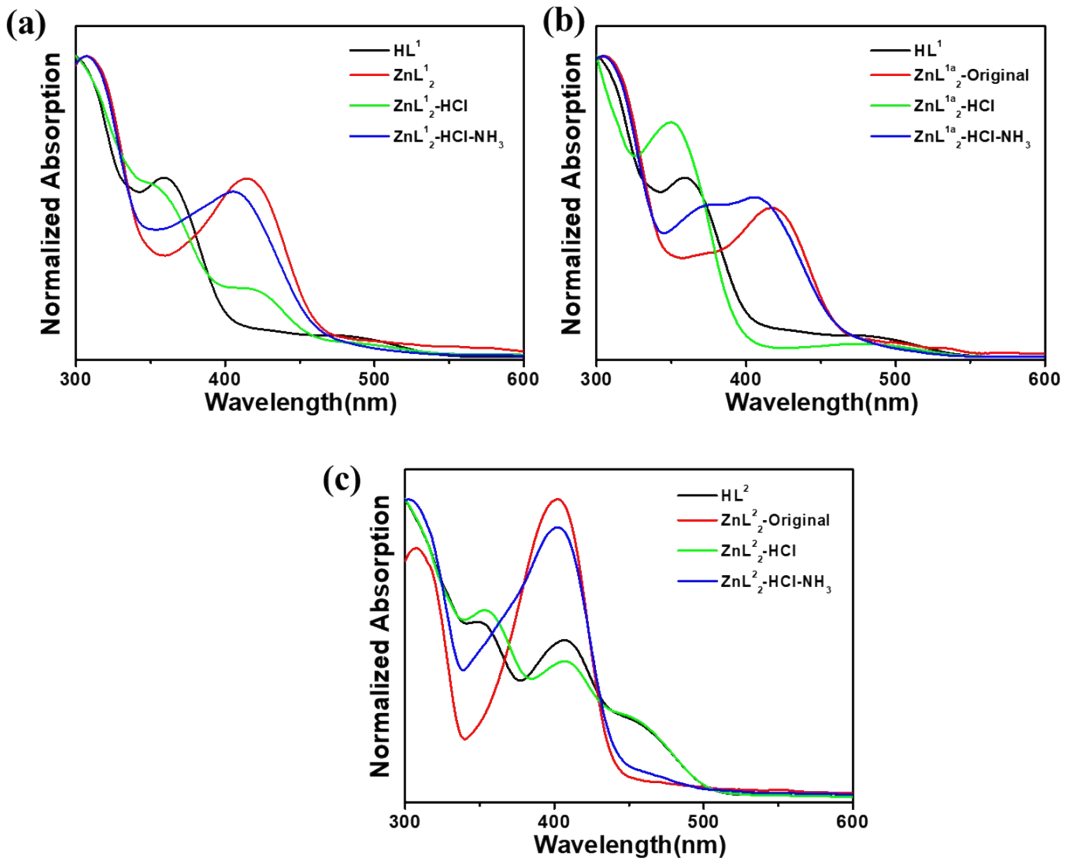


Figure S16. The normalized absorption spectra in ethanol of HL^2 and ZnL^2_2 and the leaching solution after the fumigation of HCl/NH_3 vapor.

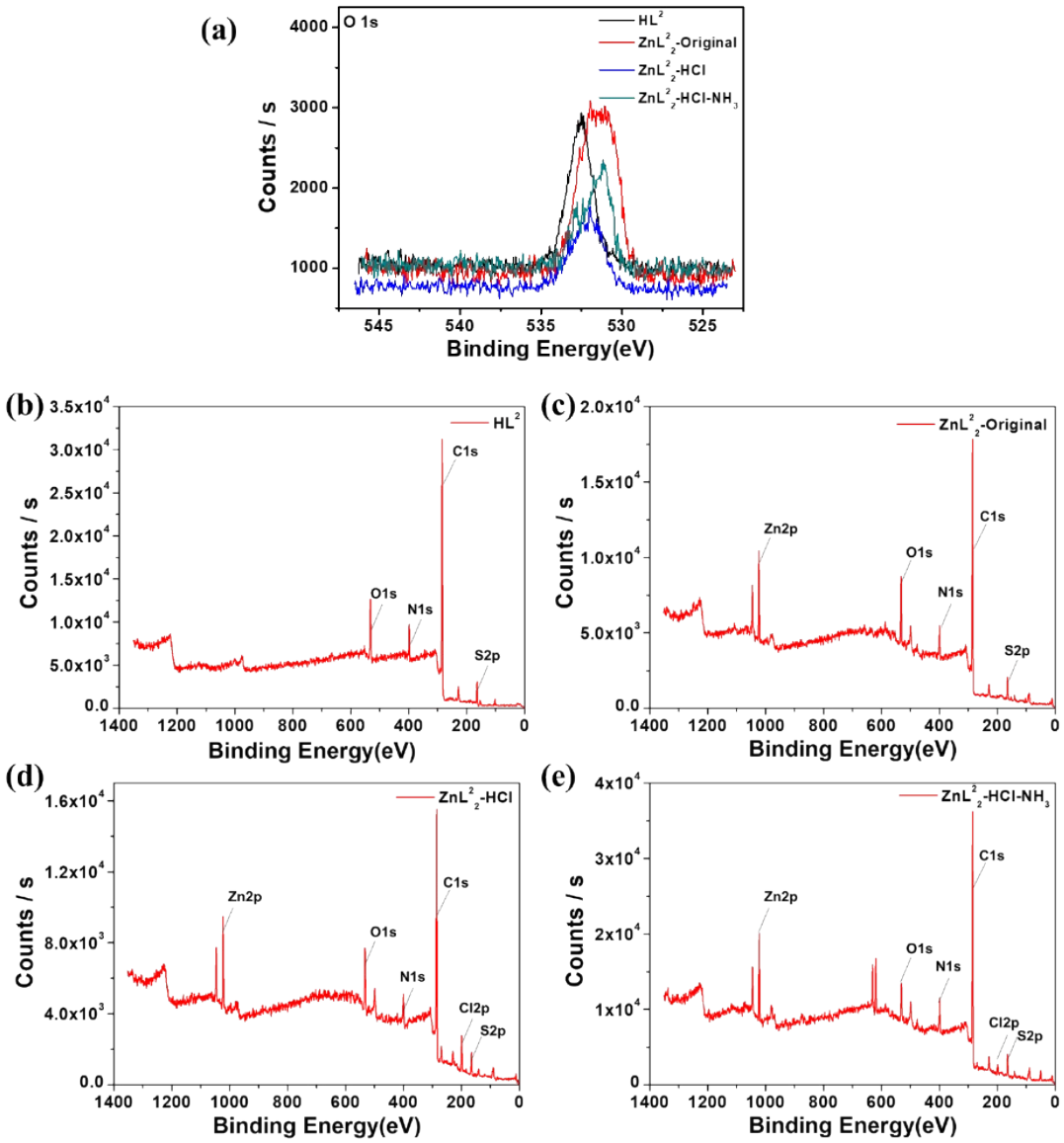


Figure S17. XPS spectra of (a) O 1s, (b) HL^2, (c) ZnL^2_2-Original, (d) ZnL^2_2-HCl and (e) ZnL^2_2-HCl-NH_3.

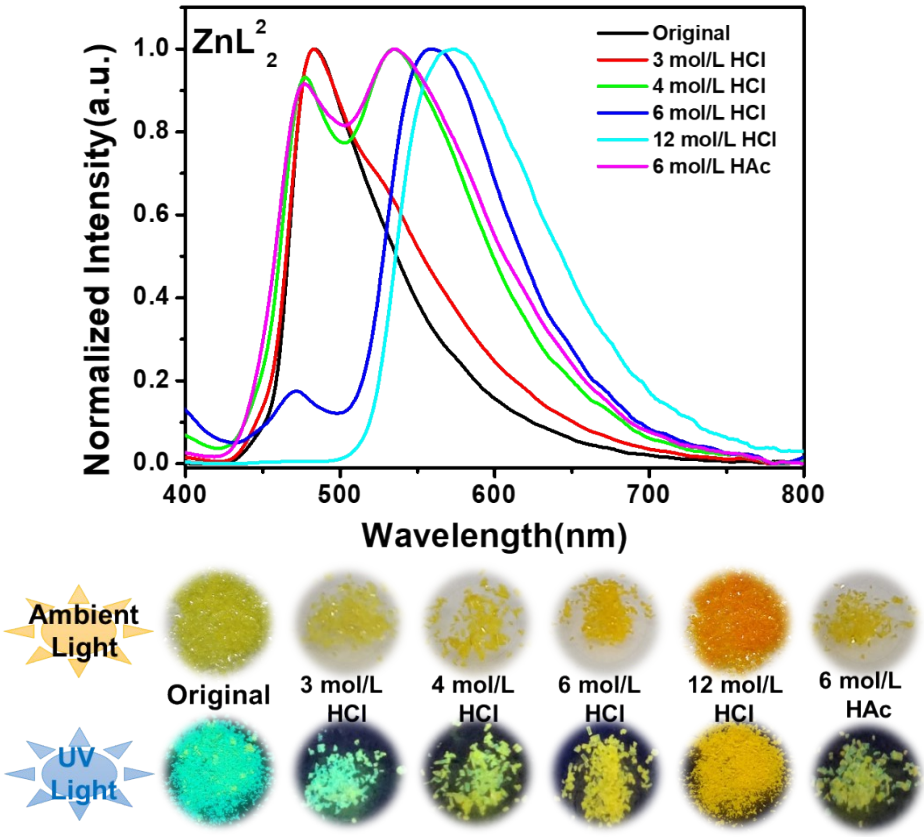


Figure S18. Fluorescence emission spectra of the original crystals of ZnL^2_2 and the samples exposed to HCl (different concentration)/HAc vapor (excited at 365 nm), photographs of the under ambient light and UV (365 nm) light.

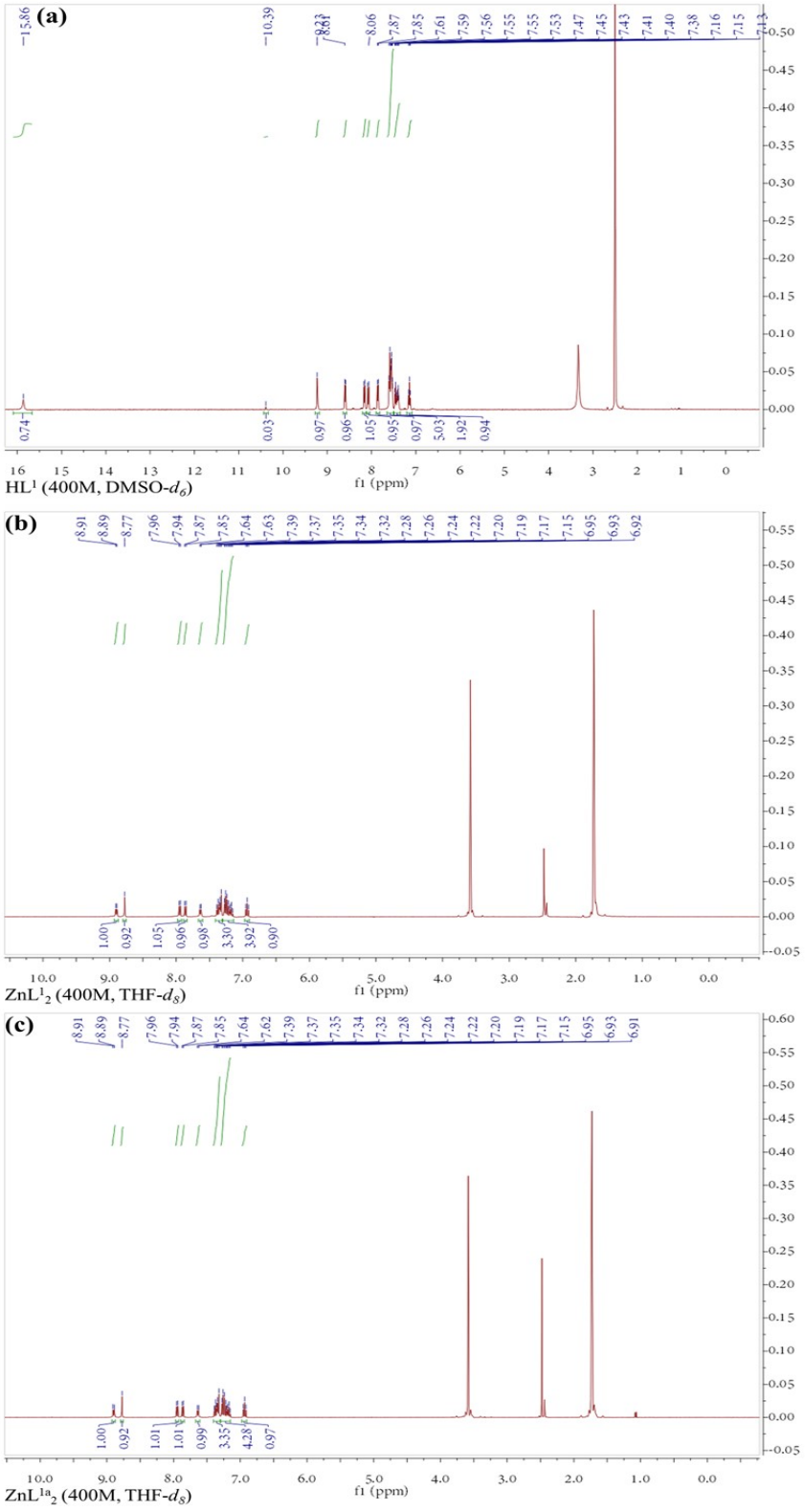


Figure S19. ^{1}HNMR of (a) **HL^1** in DMSO-d_6, (b) **ZnL$^1_2$** and **ZnL$^{1a}_2$** in THF-d_8.

Table S1. Crystal data and structure refinement parameters of **ZnL^1_2, ZnL^{1a}_2 and ZnL^2_2**.

Compound	**ZnL^1_2**	**ZnL^{1a}_2**	**ZnL^2_2**
Formula	$C_{40}H_{26}N_4O_2S_2Zn$	$C_{40}H_{26}N_4O_2S_2Zn$	$C_{42}H_{30}N_4O_2S_2Zn$
Fw	724.14	724.21	752.19
T (K)	100.00(10)	100.00(10)	99.99(10)
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a (Å)	11.4929(5)	13.1878(3)	9.16130(17)
b (Å)	12.7136(5)	15.1875(3)	14.4849(3)
c (Å)	13.8590(4)	16.8527(4)	14.8515(3)
α (°)	66.694(4)	90	118.3611(19)
β (°)	89.324(3)	108.139(2)	94.9008(16)
γ (°)	65.169(4)	90	96.0026(15)
V (Å^3)	1658.66(13)	3207.68(13)	1704.06(6)
Z	2	4	2
Calculated density (gcm^{-3})	1.450	1.500	1.466
F(000)	744.0	1488.2	776.0
Reflections Collected/Unique	20225/6587	23215/6393	23231/6862
Goodness-of-fit on F^2	1.058	1.026	1.068
Final R indexes [I>=2σ(I)]	R_1 =0.0437, wR_2=0.1169	R_1=0.0381, wR_2=0.1037	R_1=0.0352, wR_2=0.0944
R indices (all data)	R_1 =0.0499, wR_2=0.1211	R_1 =0.0423, wR_2=0.1086	R_1 =0.0372, wR_2=0.0963
CCDC number	2099170	2099171	2055758

Table S2. Selected Bond Distances (Å) and Angles (deg) of **ZnL^1_2, ZnL^{1a}_2 and ZnL^2_2**.

	ZnL^1_2	**ZnL^{1a}_2**	**ZnL^2_2**
Zn1—O1	1.9173 (17)	1.9306 (15)	1.9308 (12)
Zn1—O2	1.9142 (17)	1.9045 (15)	1.9428 (12)
Zn1—N2	2.015 (2)	1.9845 (18)	2.0080 (14)
Zn1—N4	2.009 (2)	2.0187 (18)	2.0006 (14)
O2—Zn1—O1	120.67 (7)	119.62 (6)	124.30 (5)
N2—Zn1—O1	96.01 (8)	96.60 (7)	95.06 (5)
N2—Zn1—O2	116.80 (8)	126.20 (7)	108.65 (6)
N2—Zn1—N4	116.03 (8)	114.49 (7)	127.70 (6)
N4—Zn1—O1	113.46 (8)	103.45 (7)	109.97 (6)
N4—Zn1—O2	95.37 (8)	95.35 (7)	94.24 (5)
C1—O1—Zn1	126.15 (15)	122.85 (13)	124.38 (10)
C21—O2—Zn1	126.59 (15)	125.22 (13)	——
C14—N2—Zn1	120.55 (17)	119.70 (15)	120.60 (12)
C15—N2—Zn1	122.68 (16)	119.61 (14)	121.62 (11)
C34—N4—Zn1	121.74 (16)	120.27 (15)	——
C35—N4—Zn1	119.93 (16)	117.82 (14)	120.62 (12)
C36—N4—Zn1	——	——	120.61 (11)
C22—O2—Zn1	——	——	123.48 (11)

Table S3. Types of intermolecular interactions and corresponding bond distances and angles in **ZnL^1_2, ZnL^{1a}_2 and ZnL^2_2**.

compound	interactions	bond distances	angles
ZnL^1_2	C_9-H_9···π(C_{15}-C_{20})	2.760 Å	141.47°
	C_{31}-H_{31}···π(S_1,C_7,N_1,C_8,C_{13})	2.745 Å	145.92°
	C_{38}-H_{38}···π(C_8-C_{13})	2.914 Å	129.63°
	π(C_{21}-C_{26})···π(S_2,C_{27},N_3,C_{28},C_{33})	3.593 Å	
	π(C_1-C_6)···π(C_1-C_6)	3.571 Å	
	π(C_{21}-C_{26})···π(C_{28}-C_{33})	3.826 Å	
ZnL^{1a}_2	C_{23}-H_{23}···π(S_1,C_7,N_1,C_8,C_{13})	2.942 Å	154.85°
	C_{34}-H_{34}···π(S_1,C_7,N_1,C_8,C_{13})	2.894 Å	156.06°
	C_{39}-H_{39}···π(C_{21}-C_{26})	2.828 Å	139.52°
	π(C_{15}-C_{20})···π(S_2,C_{27},N_3,C_{28},C_{33})	3.616 Å	
ZnL^2_2	C_3-H_3···π(S_2,C_{28},N_3,C_{29},C_{34})	2.936 Å	170.33°
	C_{17}-H_{17}···π(C_{22}-C_{27})	2.931 Å	142.06°
	C_{24}-H_{24}···π(C_8-C_{13})	2.824 Å	162.18°
	C_{38}-H_{38}···π(C_{16}-C_{21})	2.856 Å	131.00°

$\pi(C_{37}\text{-}C_{42})\cdots\pi(S_1,C_7,N_1,C_8,C_{13})$	3.880 Å
$\pi(C_{16}\text{-}C_{21})\cdots\pi(C_{16}\text{-}C_{21})$	3.925 Å

Table S4. The dihedral angles between different planes in **ZnL^1_2, ZnL^{1a}_2 and ZnL^2_2**.

	ZnL^1_2	**ZnL^{1a}_2**	**ZnL^2_2**
A/B	7.10	8.06	2.69
B/C	55.98	27.83	74.22
A/C	59.37	35.49	71.76
A'/B'	3.91	10.44	12.09
B'/C'	50.23	61.02	84.88
A'/C'	50.09	57.56	78.48

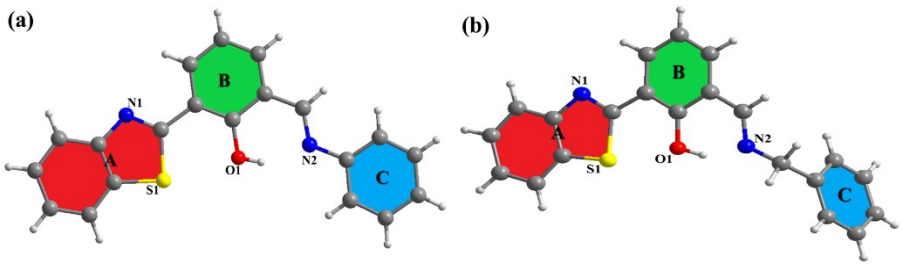
Table S5. Detailed photophysical properties of Zn (II) complexes in different states.

	τ_1 (ns) [a]	A_1 [b]	τ_2 (ns) [a]	A_2 [b]
ZnL^1_2-Original	0.85	0.33	3.78	0.67
ZnL^1_2-Ground	1.28	0.80	3.28	0.20
ZnL^1_2-Fumed	1.34	1.00	-	-
ZnL^{1a}_2-Original	2.28	1.00	-	-
ZnL^{1a}_2-Ground	1.75	1.00	-	-
ZnL^{1a}_2-Fumed	2.58	1.00	-	-
ZnL^2_2-Original	0.86	0.87	2.75	0.13
ZnL^2_2-High ground	1.67	0.39	3.97	0.61
ZnL^2_2-Fumed	0.46	0.31	2.52	0.69

Table S6. Crystal data and structure refinement parameters of **HL[1]** and **HL[2]**.

Compound	**HL[1]**	**HL[2]**
Formula	$C_{20}H_{14}N_2OS$	$C_{21}H_{16}N_2OS$
Fw	330.39	344.42
T (K)	100.00(10)	150.00(10)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
a (Å)	10.8786(5)	4.81310(10)
b (Å)	14.3556(6)	22.3451(3)
c (Å)	11.6830(11)	15.3199(2)
α (°)	90	90
β (°)	120.899(4)	93.7770(10)
γ (°)	90	90
V (Å^3)	1565.57(19)	1644.06(5)
Z	4	4
Calculated density (gcm^{-3})	1.402	1.391
F(000)	688.0	720.0
Reflections Collected/Unique	9713/3132	15079/3385
Goodness-of-fit on F^2	1.091	1.049
Final R indexes [I>=2σ(I)]	R_1 =0.0671, wR_2=0.1696	R_1 =0.0423, wR_2=0.1112
R indices (all data)	R_1 =0.0744, wR_2=0.1745	R_1 =0.0452, wR_2=0.1145
CCDC number	2099172	2046924

Table S7. The dihedral angles between different planes in **HL[1] and HL[2]**.



	A/B	**B/C**	**A/C**
HL[1]	5.76	7.15	11.70
HL[2]	2.10	85.16	83.93