Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Acetonitrile-induced structure fine-tuning of a trinuclear zinc complex showing multistimuli responsive luminescence

Han-Wen Zheng, Dong-Dong Yang, Qiong-Fang Liang, Xiang-Jun Zheng*

Beijing Key Laboratory of Energy Conversion and Storage Materials, College of Chemistry, Beijing Normal University, Beijing, 100875, China.

Corresponding author: Xiang-Jun Zheng

Tel.: +86-10-58805522; fax: +86-10-58802075.

E-mail address: xjzheng@bnu.edu.cn (X. -J. Zheng)

Contents

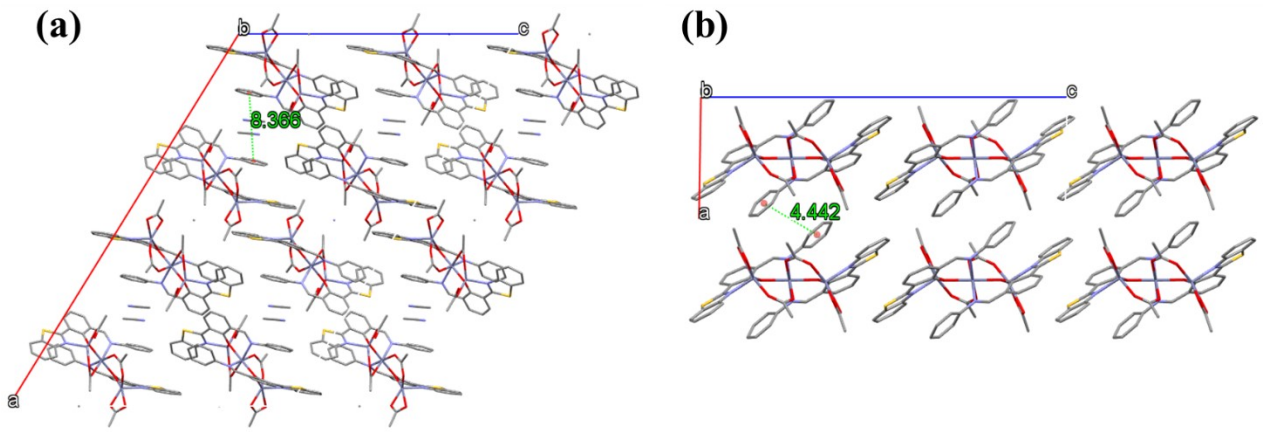


Fig. S1 The molecular packing in the (a) complex **1** and (b) complex **2** viewed along the b-axis direction.

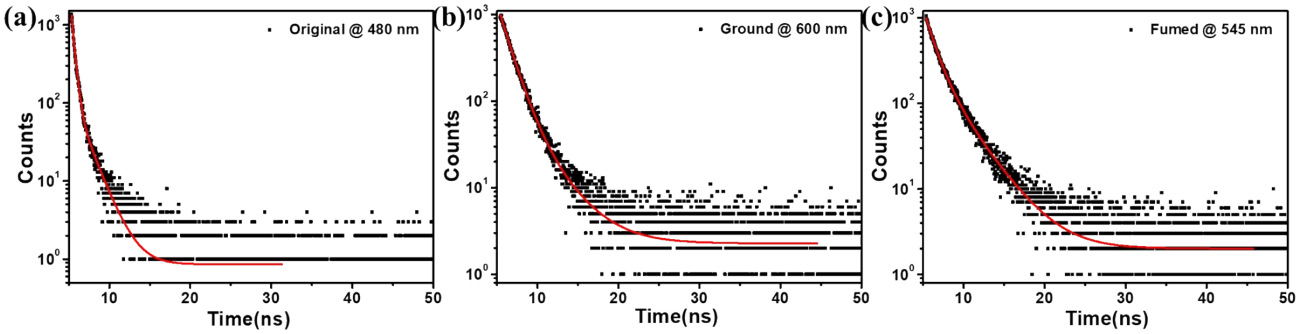


Fig. S2 Fluorescence decay curves and fit results of complex **1** in different states (excited at 371.8 nm): (a) Original sample monitored at 480 nm, (b) Ground sample monitored at 600 nm, (c) Fumed sample monitored at 545 nm.

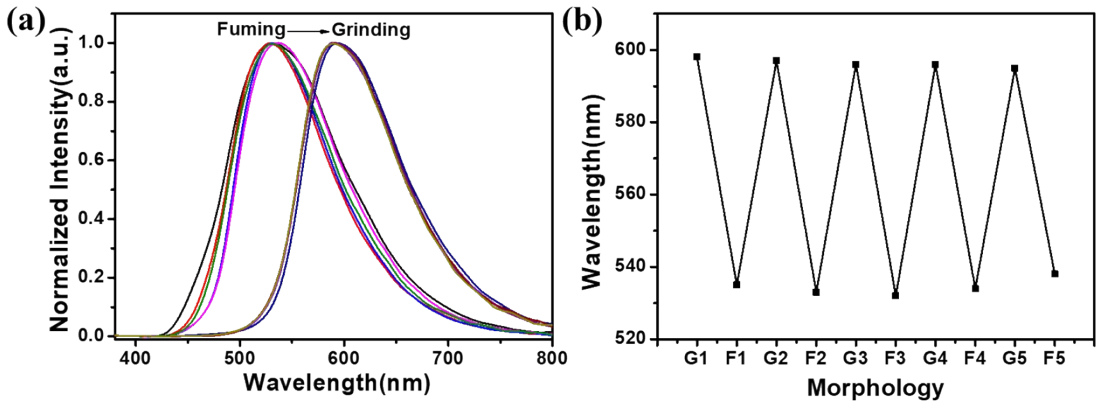


Fig. S3 (a) Fluorescence emission spectra, (b) emission switching characteristics of complex **1** upon repeating the grinding and fuming processes.

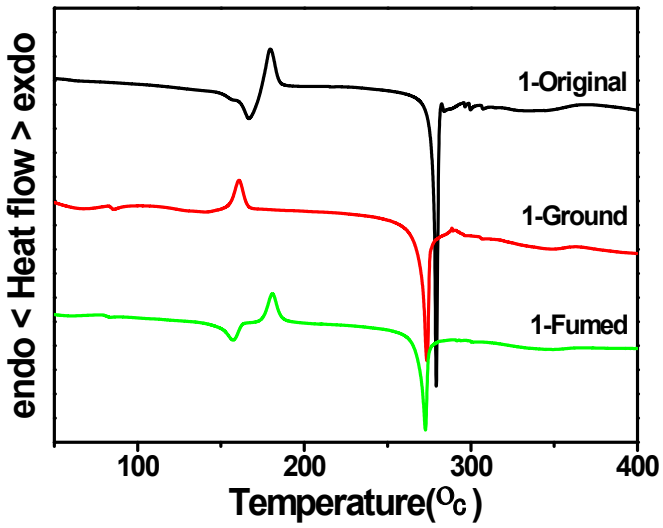


Fig. S4 DSC curves of complex **1** before and after grinding/fuming.

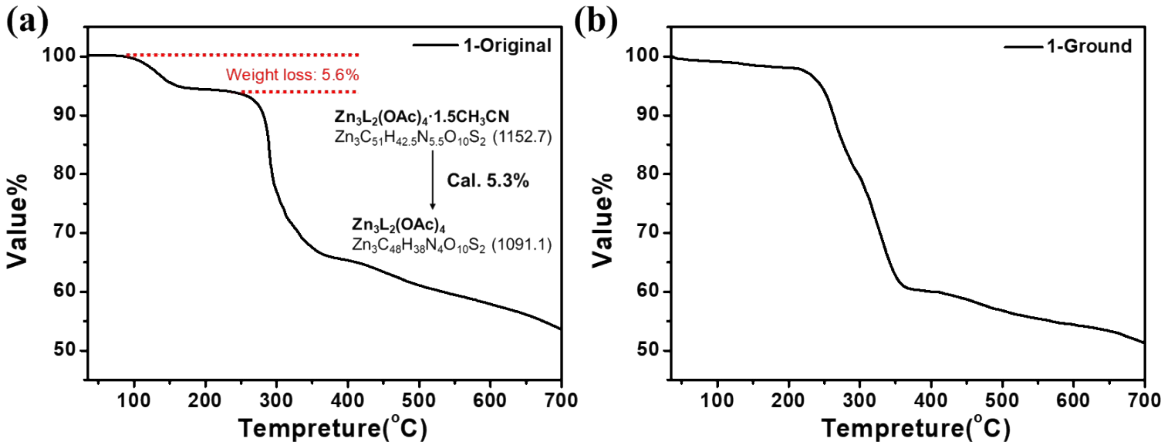


Fig. S5 TG curve of (a) Original and (b) Ground samples of complex **1**.

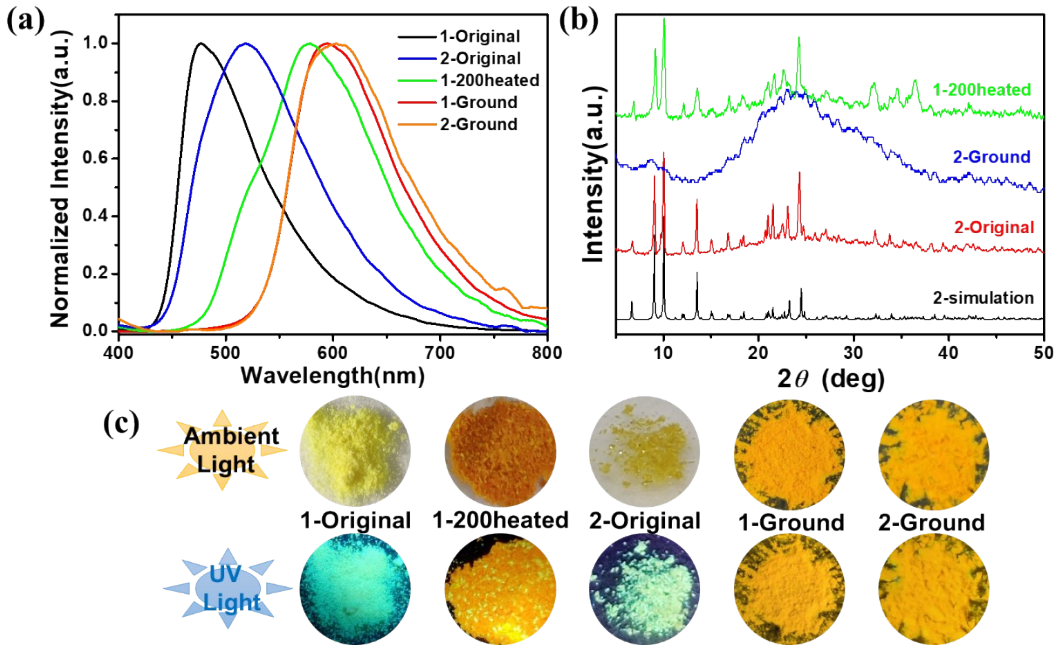


Fig. S6 (a) Fluorescence emission spectra (excited at 365 nm), (b) PXRD patterns, (c) photographs under ambient light and UV (365 nm) light of the **1**-Original/Ground, **1**-200heated and **2**-Original/Ground.

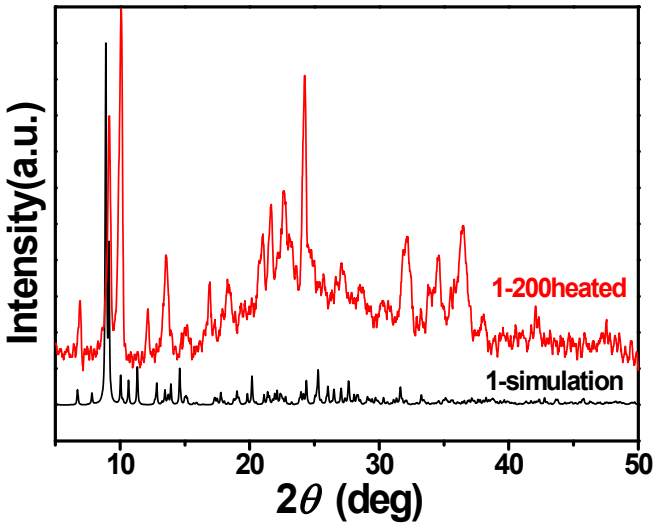


Fig. S7 PXRD patterns of complex **1**-simulation and **1**-200heated.

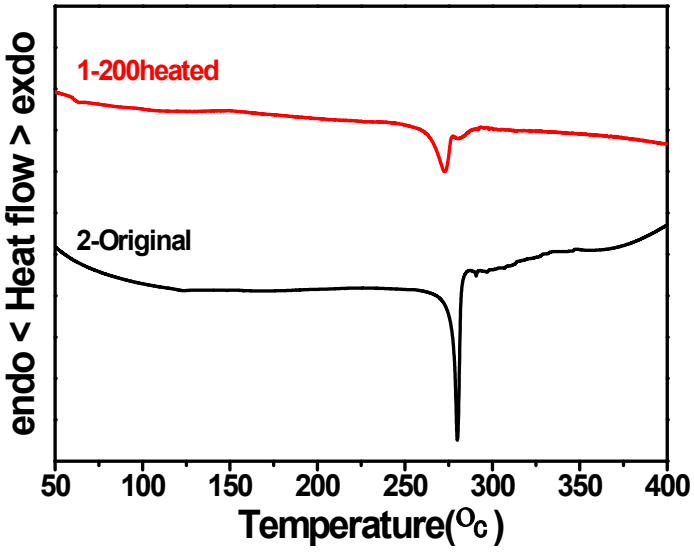


Fig. S8 DSC curves of complex **1**-200heated and **2**-Original.

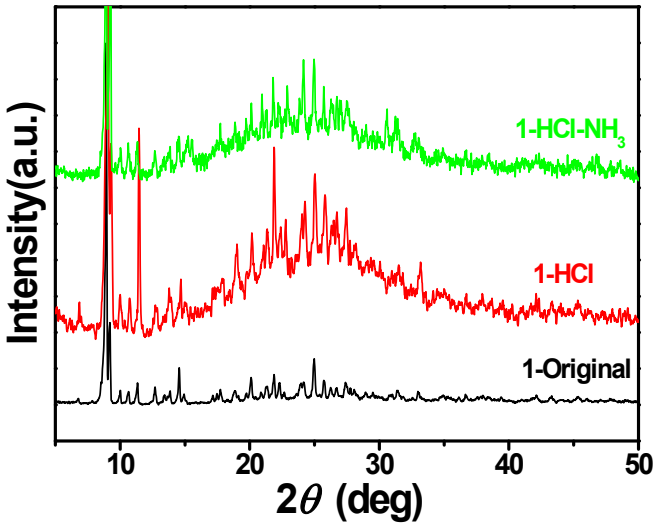


Fig. S9 PXRD patterns of original crystals of **1** before and after HCl/NH_3 vapor stimulation.

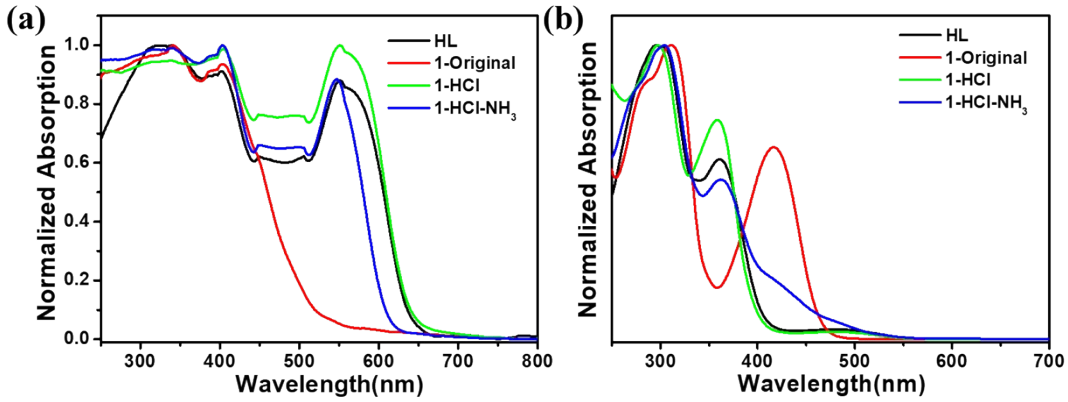


Fig. S10 UV–Vis absorption spectra of the original crystals of HL, **1** before and after exposing to HCl/NH_3 vapor, (a) in solid state, (b) in THF solution.

Table S1. Crystal data and structure refinement parameters of complexes **1** and **2**.

Compound	**$Zn_3L_2(OAc)_4 \cdot 1.5CH_3CN$ (1)**	**$Zn_3L_2(OAc)_4$ (2)**
Formula	$C_{102}H_{85}N_{11}O_{20}S_4Zn_6$	$C_{48}H_{38}N_4O_{10}S_2Zn_3$
Fw	2305.26	1091.05
T (K)	100.00(10)	99.99(17)
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/c	*P*2/c
a (Å)	41.3959(5)	8.80540(10)
b (Å)	10.39620(10)	9.76760(10)
c (Å)	26.5419(3)	26.3853(3)
α (°)	90	90
β (°)	121.6950(10)	90.9280(10)
γ (°)	90	90
V (Å^3)	9719.0(2)	2269.04(4)
Z	4	2
Calculated density (gcm^{-3})	1.575	1.597
F(000)	4712.0	1112.0
Reflections Collected/Unique	30569/9657	28988/4688
Goodness-of-fit on F^2	1.072	1.118
Final R indexes [I>=2σ(I)]	R_1 =0.0324,	R_1=0.0312,
	wR_2=0.0869	wR_2=0.0846
R indices	R_1 =0.0360,	R_1 =0.0336,
(all data)	wR_2=0.0890	wR_2=0.0859
CCDC number	2116595	2116596

Table S2. Selected Bond Distances (Å) and Angles (deg) of $[Zn_3L_2(OAc)_4] \cdot 1.5CH_3CN$ (**1**).

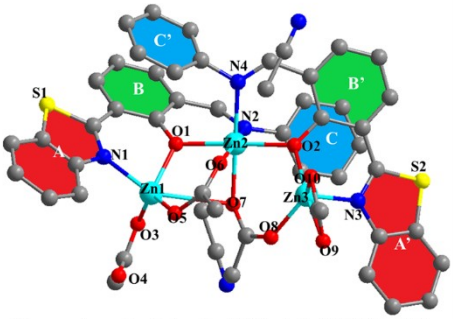
Zn1—O1	1.9835 (15)	Zn2—O1	2.0574 (14)
Zn1—O3	1.9276 (16)	Zn2—O2	2.0503 (14)
Zn1—O5	1.9365 (15)	Zn2—O6	2.1389 (15)
Zn1—N1	2.0701 (18)	Zn2—O7	2.0912 (15)
Zn2—N2	2.1742 (17)	Zn3—O8	1.9566 (15)
Zn2—N4	2.1295 (17)	Zn3—O9	2.4105 (17)
Zn3—O2	2.0092 (14)	Zn3—O10	1.9950 (16)
Zn3—N3	2.0397 (17)		
O1—Zn1—N1	86.40 (6)	O1—Zn2—O6	90.97 (6)
O3—Zn1—O1	102.90 (7)	O1—Zn2—O7	83.55 (6)
O3—Zn1—O5	126.95 (7)	O1—Zn2—N2	82.63 (6)
O3—Zn1—N1	110.45 (7)	O1—Zn2—N4	96.61 (6)
O5—Zn1—O1	115.82 (6)	O2—Zn2—O1	178.12 (6)
O5—Zn1—N1	106.95 (7)	O2—Zn2—O6	88.52 (6)
O2—Zn2—O7	94.61 (6)	O7—Zn2—N2	89.18 (6)
O2—Zn2—N2	97.76 (6)	O7—Zn2—N4	179.83 (9)
O2—Zn2—N4	85.23 (6)	N4—Zn2—O6	93.49 (6)
O6—Zn2—N2	172.67 (6)	N4—Zn2—N2	90.80 (7)
O7—Zn2—O6	86.55 (6)	O8—Zn3—O10	126.03 (7)
O2—Zn3—O9	163.17 (6)	O8—Zn3—N3	105.15 (7)
O2—Zn3—N3	88.02 (6)	O10—Zn3—O2	104.49 (6)
O2—Zn3—C48	134.35 (7)	O10—Zn3—O9	58.76 (6)
O8—Zn3—O2	106.95 (6)	O10—Zn3—N3	118.75 (7)
O8—Zn3—O9	86.28 (6)	N3—Zn3—O9	98.68 (6)
Zn1—O1—Zn2	107.55 (6)	C48—O10—Zn3	98.83 (14)
C1—O1—Zn1	123.53 (13)	C7—N1—Zn1	120.52 (14)
C1—O1—Zn2	128.80 (13)	C8—N1—Zn1	126.22 (15)
Zn3—O2—Zn2	111.08 (6)	C14—N2—Zn2	123.44 (14)
C21—O2—Zn2	125.59 (12)	C15—N2—Zn2	118.69 (13)
C21—O2—Zn3	123.33 (12)	C27—N3—Zn3	121.50 (14)
C42—O3—Zn1	117.54 (16)	C28—N3—Zn3	125.54 (14)
C44—O5—Zn1	120.87 (14)	C34—N4—Zn2	121.78 (14)
C44—O6—Zn2	133.75 (14)	C35—N4—Zn2	118.53 (13)

C46—O7—Zn2	133.51 (14)	O9—C48—Zn3	70.37 (13)
C46—O8—Zn3	128.67 (14)	O10—C48—Zn3	51.32 (11)
C48—O9—Zn3	80.69 (14)	C47—C48—Zn3	168.51 (17)

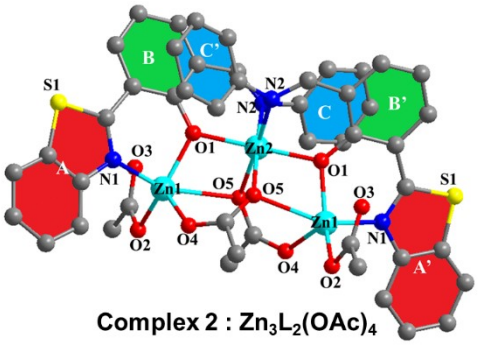
Table S3. Types of intramolecular and intermolecular interactions, corresponding bond distances and angles in complexes **1** and **2**.

compound	interactions	bond distances	angles
1	C5-H5···S1	2.574 Å	109.88°
	C5-H5···O3	2.464 Å	152.58°
	C16-H16···O7	2.486 Å	139.45°
	C25-H25···S2	2.578 Å	109.77°
	C32-H32···O9	2.527 Å	160.30°
	C40-H40···O4	2.496 Å	174.42°
	C45-H45B···N5	2.737 Å	165.91°
	C49-H49A···O7	2.668 Å	153.89°
	C51-H51B···O10	2.503 Å	158.88°
	π(C1-C6)···π(S1,C7,N1,C8,C9)	3.649 Å	
	π(S2,C27,N3,C28,C29)···π(S2,C27,N3,C28,C29)	3.677 Å	
	π(C1-C6)···π(C35-C40)	3.527 Å	
	π(C15-C20)···π(C21-C26)	3.698 Å	
	π(C21-C26)···π(C28-C33)	3.813 Å	
2	C3-H3···O2	2.483 Å	143.81°
	C5-H5···S1	2.593 Å	110.46°
	C21-H21B···π(C8-C13)	2.691 Å	128.88°
	π(S1,C7,N1,C8,C9)···π(S1,C7,N1,C8,C9)	3.990 Å	
	π(C1-C6)···π(C15-C20)	3.954 Å	

Table S4. The dihedral angles between different planes in complexes **1** and **2**.



Complex 1 : $[Zn_3L_2(OAc)_4]\cdot 1.5CH_3CN$



Complex 2 : $Zn_3L_2(OAc)_4$

	$[Zn_3L_2(OAc)_4]\cdot 1.5CH_3CN$ (1)	$Zn_3L_2(OAc)_4$ (2)
A/B	11.93	13.09
B/C	35.52	42.69
A/C	30.06	29.80
A'/B'	15.52	13.09
B'/C'	42.77	42.69
A'/C'	36.04	29.80

Table S5. Selected Bond Distances (Å) and Angles (deg) of $Zn_3L_2(OAc)_4$ (2).

Zn1—O1	1.9716 (13)	Zn2—O1	2.0455 (12)
Zn1—O2	1.9586 (15)	Zn2—O5	2.1076 (14)
Zn1—O4	1.9818 (15)	Zn2—O5^{i}	2.1076 (14)
Zn1—N1	2.0657 (16)	Zn2—N2^{i}	2.1327 (16)
Zn1—C22	2.554 (2)	Zn2—N2	2.1327 (17)
Zn2—O1^{i}	2.0455 (12)		
O1—Zn1—O4	107.00 (6)	O1^{i}—Zn2—O1	179.12 (7)
O1—Zn1—N1	87.59 (6)	O1^{i}—Zn2—O5	83.49 (5)
O2—Zn1—O1	142.60 (6)	O1^{i}—Zn2—O5^{i}	97.17 (5)
O2—Zn1—O4	103.15 (6)	O1—Zn2—O5	97.17 (5)
O2—Zn1—N1	106.96 (6)	O1—Zn2—O5^{i}	83.49 (5)
O4—Zn1—N1	102.62 (6)	O1^{i}—Zn2—N2^{i}	85.37 (6)
Zn1—O1—Zn2	105.71 (6)	O1^{i}—Zn2—N2	94.03 (6)
C1—O1—Zn1	123.87 (11)	O1—Zn2—N2^{i}	94.03 (6)
C22—O2—Zn1	102.01 (13)	O1—Zn2—N2	85.36 (6)
C24—O4—Zn1	127.78 (13)	O5—Zn2—O5^{i}	83.86 (8)
C7—N1—Zn1	122.61 (13)	O5—Zn2—N2^{i}	91.91 (6)

C8—N1—Zn1	124.64 (13)	O5^{i}—Zn2—N2^{i}	174.78 (6)
O2—C22—Zn1	48.61 (10)	O5—Zn2—N2	174.78 (6)
O3—C22—Zn1	73.89 (12)	O5^{i}—Zn2—N2	91.91 (6)
C21—C22—Zn1	164.96 (17)	N2^{i}—Zn2—N2	92.46 (9)
C14—N2—Zn2	121.85 (13)	C1—O1—Zn2	128.61 (12)
C15—N2—Zn2	120.55 (12)	C24—O5—Zn2	132.96 (14)

Symmetry code: (i) -*x*+1, *y*, -*z*+3/2.

Table S6. Detailed photophysical properties of complex **1** in different states.

	τ_1 (ns) [a]	A_1 [b]	τ_2 (ns) [a]	A_2 [b]
Original	0.35	0.71	1.62	0.29
Ground	1.34	0.78	3.40	0.22
Fumed	1.17	0.48	3.24	0.52