## **Electronic Supplementary Information**

# A simple zinc(II) complex that features multi-functional luminochromism

## induced by reversible ligand dissociation

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#### A. Methods

**Materials.** TPA-tpy hybrid ligand **L1**,<sup>[51]</sup> and reference zinc(II) complex Zn(**L1**)Cl<sub>2</sub><sup>[52]</sup> were synthesized according to previous reports. Hexane, toluene, diethyl ether, tetrahydrofurane (THF), 1,4-dioxane, chlorobenzene, 1,2-dichlorobenzene, acetone, 3-pentanone, ethyl acetate, acetonitrile, benzyl alcohol, methanol, *N*,*N*-dimethylformamide (DMF) were purchased from Kanto Chemical Co., Inc. Cyclohexane, *i*-butanol, *s*-butanol, dimethyl sulfoxide (DMSO) and zinc dichloride were supplied by Nacalai Tesque, Inc. 1,2-dichloroethane, benzonitrile, *n*-butanol, *t*-butanol, *n*-propanol, 35%w aqueous hydrochloric acid, sulfuric acid, 42%w aqueous tetrafluoroboric acid and zinc sulfate heptahydrate were purchased from Wako Pure Chemical Industries, Ltd. Zinc diacetate, zinc ditetrafluoroborate hydrate and cadmium diacetate hydrate was purchased from Sigma-Aldrich Co. LLC. Anisol, chloroform, dichloromethane, *i*-propanol, were supplied by Tokyo Chemical Industry Co., Ltd., Shin-Etsu Chemical Co., Ltd., Asahi Glass Co., Ltd. and Daishin Chemical, Co., Ltd., respectively. All solvents were used as received.

**Instruments.** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on Bruker US500 spectrometer. Highresolution electrospray ionization time-of-flight mass spectrometry (HR-ESI-TOF-MS) was performed on a Waters LCT Premier XE spectrometer. UV/vis absorption spectra were obtained on a JASCO V-570 spectrometer. Steady-state PL and excitation spectra were recorded on a HITACHI F-4500 or a JASCO FP-8600 spectrometer. Absolute fluorescence quantum yields were measured on Hamamatsu Photonics C9920-02G. Fluorescence lifetime measurements were conducted using Hamamatsu Photonics Quantaurus-Tau C11367-02.

**Synthesis of complex C1.** Tpy ligand **L1** 50 mg (0.10 mmol) and zinc acetate 9.6 mg (0.050 mmol) were added to 50 mL ethanol and the reaction mixture was stirred for 1 h at room temperature, then the mixture was evaporated. To the crude was added acetone (7 mL), and the suspension was sonicated and filtered to obtain a product solid. Yield: 19 mg (26%). <sup>1</sup>H NMR (500 MHz, chloroform-d<sub>1</sub>):  $\delta$  9.05 (d, 2H), 8.28 (s, 2H), 8.21 (d, 2H), 8.01 (t, 2H), 7.60 (m, 4H), 7.35 (t, 4H), 7.19 (m, 6H), 7.14 (t, 2H), 1.91 (s, 6H) (Fig. S1); <sup>13</sup>C NMR (125 MHz, methanol-d<sub>4</sub>):  $\delta$  181.3, 156.4,

152.2, 150.4, 149.9, 148.3, 142.1, 131.0, 130.0, 129.3, 128.3, 127.1, 125.9, 123.6, 122.6, 122.5, 120.1, 22.8 (Fig. S1); UV/vis (chloroform): HR-ESI-TOF-MS (*m/z*): [M − OAc]<sup>+</sup> calcd. for C<sub>35</sub>H<sub>27</sub>N<sub>4</sub>O<sub>2</sub>Zn<sup>+</sup>, 599.1425; found, 599.1450 (Fig. S2).

Synthesis of  $[Zn(L1)_2](BF_4)_2$ . L1 39 mg (0.082 mmol) and zinc tetrafluoroborate 20 mg (0.084 mmol) were added to 20 mL methanol and the reaction mixture was stirred for 1 h at room temperature, then the mixture was evaporated. To the crude was added methanol (2 mL), and the suspension was sonicated, filtered, and washed with a small amount of methanol to obtain product  $[Zn(L1)_2](BF_4)_2$ . Yield: 26 mg (27%). <sup>1</sup>H NMR (500 MHz, methanol-d<sub>4</sub>) :  $\delta$  7.14 (m, 16H), 7.34 (m, 12H), 7.82 (d, 4H), 8.10 (m, 8H), 8.80 (d, 4H), 9.05 (s, 4H) (Fig. S8); <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>):  $\delta$  150.1, 149.2, 147.8, 147.7, 146.2, 141.3, 129.9, 129.5, 127.7, 127.6, 125.4, 124.7, 123.4, 123.3, 120.9, 120.0 (Fig. S9). HR-ESI-TOF-MS (*m*/*z*): [M – BF<sub>4</sub>]<sup>+</sup> calcd. for C<sub>66</sub>H<sub>48</sub>N<sub>8</sub>BF<sub>4</sub>Zn<sup>+</sup>, 1103.3334; found, 1103.3335 (Fig. S10).

Synthesis of  $Zn_2(L1)_2(\mu-O_2SO_2)_2$ . To L1 (31 mg, 0.065 mmol) was added a saturated methanol solution of zinc sulfate (30 mg in 30 mL, 0.10 mmol), and the reaction mixture was stirred for 1 h at room temperature, then the product was precipitated. The suspension was sonicated, filtered, and washed with a large amount of methanol to obtain product  $Zn_2(L1)_2(\mu-O_2SO_2)_2$ . Yield: 53 mg (89%). <sup>1</sup>H NMR (500 MHz, methanol-d<sub>4</sub>) :  $\delta$  9.30 (d, 4H), 8.88 (s, 4H), 8.79 (d, 4H), 8.33 (t, 4H), 8.04 (d, 4H), 7.87 (t, 4H), 7.40 (m, 8H), 7.20 (m, 16H) (Fig. S11). <sup>13</sup>C NMR could not be acquired because of its low solubility. ESI-TOF-MS (*m/z*): [M – SO<sub>4</sub>]<sup>2+</sup> calcd. for C<sub>66</sub>H<sub>48</sub>N<sub>8</sub>O<sub>4</sub>SZn<sub>2</sub><sup>2+</sup>, 588.11; found, 588.10 (Fig. S12). HR-MS could not be determined because of its complicated isotope pattern. Single crystal of Zn<sub>2</sub>(L1)<sub>2</sub>( $\mu$ -O<sub>2</sub>SO<sub>2</sub>)<sub>2</sub>·2MeOH suitable for X-ray diffraction analysis was obtained by slow evaporation from methanol (Fig. S13 and Table S5).

**Single crystal X-ray diffraction analysis.** Single crystals of **C1·MeOH** and  $Zn_2(L1)_2(\mu-O_2SO_2)_2 \cdot 2MeOH$  suitable for X-ray diffraction analysis were obtained by vapor diffusion from methanol and diethyl ether. Sets of X-ray diffraction data for **C1·MeOH** and  $Zn_2(L1)_2(\mu-O_2SO_2)_2 \cdot 2MeOH$  were collected at 93 K on a Rigaku Saturn724 (Varimax dual) diffractometer with

multi-layer mirror monochromated MoK $\alpha$  radiation ( $\lambda = 0.71075$  Å). Lorentz-polarization and numerical absorption corrections were performed with the program Crystal Clear 2.0. The structure of **C1·MeOH** and Zn<sub>2</sub>(**L1**)<sub>2</sub>( $\mu$ -O<sub>2</sub>SO<sub>2</sub>)<sub>2</sub>·2MeOH were solved by direct methods using SIR-2004 program and refined against *F*<sup>2</sup> using SHELXL-97. Crystallographic data for the structures of **C1·MeOH** and Zn<sub>2</sub>(**L1**)<sub>2</sub>( $\mu$ -O<sub>2</sub>SO<sub>2</sub>)<sub>2</sub>·2MeOH were deposited to the Cambridge Crystallographic Data Centre (CCDC 1436043 and 1463881). The crystallographic data as cif files are also included as Supporting Information. Single-crystal X-ray diffractions of **C1·MeOH** and Zn<sub>2</sub>(**L1**)<sub>2</sub>( $\mu$ -O<sub>2</sub>SO<sub>2</sub>)<sub>2</sub>·2MeOH were supported by "Nanotechnology Platform" (project No.12024046) of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

Powder X-ray diffraction analysis. Microcrystals of crystal-solvent-free C1 suitable for powder X-ray diffraction analysis were obtained by sonication of **C1** in acetone and drying of **C1** in vacuum. The powder crystals were installed in a 0.4 mm glass capillary. The synchrotron powder diffraction experiments of C1 with an Imaging Plate (IP) as a detector were carried out at SPring-8, BL02B2 beam line.<sup>[S3]</sup> The powder data of crystal-solvent-free **C1** were collected at 100K using N<sub>2</sub> gas flow low temperature device. Indexing was carried out using the program DICVOL06.<sup>[54]</sup> The first 19 peaks of the powder pattern were completely indexed on the basis of a monoclinic cell. The space group was uniquely determined as C2/c from the reflection conditions. The crystal structure of C1 has been determined by the structure solution system based on genetic algorithm (GA).<sup>[55]</sup> Rietveld analysis<sup>[56]</sup> was employed for the final refinement, with chemically equivalent distances being equal and displacement parameters were refined as isotropic. The reliability factors of final Rietveld refinement were  $R_{wp} = 2.2\%$  and  $R_{I} = 4.8\%$  with d > 0.94 Å d-spacing range which are satisfactory for accurate structure solution. Crystallographic data for the structure of **C1** were deposited to the Cambridge Crystallographic Data Centre (CCDC 1436485). The crystallographic data as a cif file are also included as Supporting Information. The synchrotron radiation experiments were performed at SPring-8 with approval of the Japan Synchrotron Radiation Research Institute (JASRI: Proposal No 2015A0074).

**Solution sample preparation.** For UV/vis absorption spectroscopy, a quartz cell with an optical path of 1 mm was employed for  $1.0 \times 10^{-4}$  mol L<sup>-1</sup> samples. On the other hand, one with an optical path of 1 cm were used for samples with concentrations of <  $1.0 \times 10^{-4}$  mol L<sup>-1</sup>. For fluorescent spectroscopy, a quartz cell with an optical path of 1 cm was used for all samples. All optical measurements were carried out at room temperature under air otherwise specified. For acid sensing in acetone, water content ratio in sample solution was controlled at < 0.01% (v/v).

**DFT calculation methods.** Starting from the initial geometry taken from the crystal structures, the molecular structures of ligand **L1** and complex **C1** were initially optimized at the B3LYP /6-31+G\* level of theory under the gas phase. It was confirmed that the optimized geometries did not have negative frequencies. After the geometry optimization, the excited states (S1–S10) were examined by the TD-B3LYP/6-31+G\* level of theory under the same solvent conditions to simulate the absorption spectra. All calculations were performed by Gaussian 09 revision C.01.<sup>[57]</sup> The calculated frontier molecular orbitals were plotted using a GaussView 5.0 program package with an isovalue of 0.02 atomic unit (Fig. 3c). Therein, the positive and negative wavefunctions were in brown and green, respectively.

## B. Crystallographic data for polymorphous C1

Empirical formula	$C_{38}H_{34}N_4O_5Zn$						
<i>Fw</i> / g mol <sup>-1</sup>	692.09						
Crystal system	monoclinic						
Space group	<i>P</i> 2 <sub>1</sub> /c						
Crystal size / mm	$0.150 \times 0.030 \times 0.030$						
Temperature / K	93						
<i>a /</i> Å	9.217(4)						
<i>b /</i> Å	33.638(14)						
<i>c /</i> Å	10.663(5)						
α/°	90						
ß/°	100.141(7)						
γ/ °	90						
V/ų	3254(2)						
Ζ	4						
$D_{calcd}$ g/cm <sup>-3</sup>	1.412						
λ/Å	0.71075						
$\mu/\text{mm}^{-1}$	0.806						
<b>Reflections collected</b>	21605						
Independent reflections	6347						
Parameters	437						
R <sub>int</sub>	0.1351						
$R_1 (l > 2.00 \sigma(l))^{a}$	0.0766						
$wR_2$ (All reflections) <sup>b</sup>	0.2784						
GoF <sup>c</sup>	0.978						

Table S1. Crystallographic data for C1·MeOH

 ${}^{a}R_{1} = \Sigma ||F^{\circ}| - |F^{\circ}| / \Sigma |F^{\circ}| \ (I > 2\sigma(I)). \ {}^{b}wR_{2} = [\Sigma(w(F^{\circ 2} - F^{\circ 2})^{2} / \Sigma w(F^{\circ 2})^{2})^{1/2} \ (I > 2\sigma(I)). \ {}^{c}GoF = [\Sigma(w(F^{\circ 2} - F^{\circ 2})^{2} / \Sigma (N^{c} - N^{o})^{2}).$ 

Table S2. Crystallographic data for C1

Empirical formula	$C_{37}H_{30}N_4O_4Zn$
<i>Fw</i> / g mol <sup>-1</sup>	660.04
Crystal system	monoclinic
Space group	C2/c
Cylinder size / mm	3 × 0.4
Temperature / K	100
a / Å	8.5635(3)
<i>b /</i> Å	34.049(1)
<i>c</i> / Å	10.7218(3)
α/°	90
$\beta$ / °	102.222(3)
γ/°	90
V/ų	3055.39(17)
Ζ	4
$D_{calcd}$ g/cm <sup>-3</sup>	1.435
λ/Å	0.79683
$\mu/mm^{-1}$	1.155
2 $oldsymbol{ heta}_{ ext{fixed}}$	0.01-79.29
Data collection mode	transmission
Specimen mounting	capillary
Data points	7929
Parameter	230
Restraints	224
$R_{p}$	0.016
R <sub>wp</sub>	0.022
$R_{exp}$	0.010
$R_{Bragg}$	0.048
R(F)	0.040
<i>R</i> ( <i>F</i> <sup>2</sup> )	0.048

# C. Identification of complex C1



**Fig. S1.** <sup>1</sup>H NMR of **C1** in chloroform-d<sub>1</sub> at a concentration of  $1.0 \times 10^{-4}$  M.



**Fig. S2.** <sup>13</sup>C NMR of **C1** in methanol- $d_4$  at a concentration of  $1.0 \times 10^{-4}$  M.



Fig. S3. High-resolution ESI-TOF-MS of C1 dissolved in dichloromethane.

#### D. Van't Hoff plot for complex C1

Here we consider the equilibrium reaction (1)

$$C1 \leftrightarrow Zn(OAc)_2 + L1$$
 (1)

Initially complex **C1** is dissolved in 2-butanol, the concentration of which is  $C_0$  (= 5.00 × 10<sup>-5</sup> M). Then, **C1** is dissociated into ligand **L1** and zinc acetate according to scheme (1). [**C1**], [**L1**], and [Zn(OAc)<sub>2</sub>] denote the concentrations of **C1**, **L1**, and zinc acetate, respectively, in the sample solution reaching the equilibrium. In this scheme, eqs. (2) and (3) are applicable:

$$C_0 = [C1] + [L1]$$
 (2)  
[Zn(OAc)<sub>2</sub>] = [L1] (3)

The concentration fractions for [C1] and [L1], *a* and *b*, are defined as follows.

$$a = \frac{[\mathbf{C1}]}{[\mathbf{C1}] + [\mathbf{L1}]}$$
(4)  
$$b = \frac{[\mathbf{L1}]}{[\mathbf{C1}] + [\mathbf{L1}]}$$
(5)  
$$a + b = 1$$
(6)

Then, the dissociation constant,  $K_d$ , can be represented as eq. (7), using eqs. (2)-(6).

$$K_{d} = \frac{[\mathbf{L1}][\mathrm{Zn}(\mathrm{OAc})_{2}]}{[\mathbf{C1}]} = \frac{[\mathbf{L1}]^{2}}{[\mathbf{C1}]} = \frac{b^{2}C_{0}}{a} = \frac{(1-a)^{2}C_{0}}{a}$$
(7)

The absorbance at a certain wavelength of the sample solution (*A*) is represented as a sum of absorbances contributed by C1 ( $A_{C1}$ ) and L1 ( $A_{L1}$ ), as eq. (8):

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$$A = A_{\rm C1} + A_{\rm L1} \tag{8}$$

 $A_{C1}$  and  $A_{L1}$  can be obtained from eqs. (9) and (10):

$$A_{C1} = \varepsilon_{C1}[C1]l = a\varepsilon_{C1}C_0l \qquad (9)$$
$$A_{L1} = \varepsilon_{L1}[L1]l = b\varepsilon_{L1}C_0l = (1-a)\varepsilon_{L1}C_0l \qquad (10)$$

where  $\varepsilon_{C1}$ ,  $\varepsilon_{L1}$ , and l is the molar extinction coefficients of C1 and L1, and the optical path (= 1 cm).  $\varepsilon_{L1}$  may be determined by measuring the UV/vis spectrum of L1 at a certain concentration. On the other hand,  $\varepsilon_{C1}$  may be determined by measuring the spectrum of a concentrated solution of C1: a thicker concentration prevents dissociation into L1 and zinc(II) acetate. If the dissociation is still significant, the measurement is conducted at a lower temperature, which also suppress the dissociation. Therefore, *a* can be obtained from eqs. (8)-(10) as eq. (11):

$$a = \frac{A - \varepsilon_{L1} C_0 l}{\varepsilon_{C1} C_0 l - \varepsilon_{L1} C_0 l} \tag{11}$$

Eqs. (7) and (11) indicate that  $K_d$  can be determined by measuring A. We extracted A at 412 nm at different temperatures (T) from temperature-dependent UV/vis spectra in Fig. 2f, and the  $K_d$  values are collected in Table S3, which also contains a set of concentration information.  $\ln K_d - T^2$  <sup>1</sup> plot (van't Hoff plot) are shown in Fig. S4, which provides the standard dissociation enthalpy and entropy ( $\Delta H_d^\circ$  and  $\Delta S_d^\circ$ ) for eq. (1) according to eq. (12).

$$\ln K_{\rm d} = \frac{\Delta S_{\rm d}^{\circ}}{R} - \frac{\Delta H_{\rm d}^{\circ}}{RT} \qquad (12)$$

<i>Т /</i> К	273	283	293	303	313	323
[ <b>C1</b> ] / 10 <sup>-5</sup> M	4.848	4.712	4.533	4.362	4.140	4.000
[ <b>L1</b> ] / 10 <sup>-5</sup> M	0.152	0.288	0.467	0.638	0.860	1.000
[ <b>C1</b> ]/[ <b>L1</b> ] ratio	32.0	16.4	9.70	6.84	4.82	4.00
<i>K</i> <sub>d</sub> / M	4.74×10 <sup>-8</sup>	1.76×10-7	4.82×10-7	9.32×10-7	1.79×10-6	2.52×10-6

Table S3. Equilibrium parameters for eq. (1) in 2-butanol



**Fig. S4.** Van't Hoff plot for equilibrium  $C1 \leftrightarrow L1 + Zn(OAc)_2$  in 2-butanol.

### E. Photophysical properties of complex C1 and ligand L1 in various solvents

Solvent	<i>E</i> r	$\lambda_{abs}^{L}$	λ <sub>PL</sub> L / nm	$\lambda_{abs}^{C}$	λ <sub>PL</sub> C / nm	$E_{\rm ss}^{\rm L}$	$E_{\rm ss}^{\rm C}$	$\Phi_{\rm f}^{\sf L}$ $d$	⊅ <sub>f</sub> C	τ <sub>f</sub> L / 10 ns	τ <sub>f</sub> C / 10 ns	k <sub>r</sub> <sup>L</sup> / 10 <sup>8</sup> s <sup>-1</sup>	k <sub>r</sub> <sup>C</sup> / 10 <sup>8</sup> s <sup>-1</sup>	k <sub>nr</sub> ∟ / 10 <sup>8</sup> s <sup>-1</sup>	k <sub>nr</sub> <sup>C</sup> / 10 <sup>8</sup> s <sup>-1</sup>
hexane	1 88	360	395	_a	_a	2 460	_a	0.51 -	а	11	_a	46	_a	4.5	_a
cvclohexane	2 02	360	395	_a	_a	2 460	_a	0.53 -	а	12	_a	44	_a	3.9	_a
1 4-dioxane	2 21	360	435	395	500	4 790	5 320	077 0	86	3.6	50	21	17	0.64	0.28
toluene	2.38	365	420	395	485	3 590	4 700	0 47 0	57	21	4.0	22	14	2.5	11
diethyl ether	4 20	360	425	_b	_b	4 250	_b	0.88 -	_b	27	_b	3.3	_b	0.44	b
anisole	4 33	365	450	395	530	5 180	6 4 5 0	0.61 0	82	3.1	52	2.0	16	13	0.35
chloroform	4 89	360	455	410	525	5 800	5 340	0.84 0	88	3.6	5.5	2.3	1.6	0.44	0.22
chlorobenzene	5.62	360	445	415	450	5 310	1 870	0.67 0	79	34	53	2.0	1.5	10	0.40
ethyl acetate	6.02	360	455	410	545	5,800	6 040	0.75 0	92	3.2	54	2.3	17	0.78	0.15
THF	7 58	360	455	_b	_b	5 800	_ <sup>b</sup>	0.78 -	b	3.2	_b	2.0	_b	0.69	_b
dichloromethane	8.93	360	470	405	570	6 500	7 150	0.82 0	71	47	66	17	11	0.38	0 44
1.2-dichlorobenzene	9.93	365	455	415	550	5.420	5.910	0.50 0.	.81	3.8	6.2	1.3	1.3	1.3	0.31
1 2-dichloroethane	10.4	360	470	420	570	6 500	6 270	0.89.0	58	44	57	2.0	1.0	0.25	0.74
<i>t</i> -butanol	12.5	360	470	400	550	6,500	6.820	0.87 0.	.50	4.9	5.5	1.8	0.91	0.27	0.91
benzvl alcohol	12.7	370	505	420	590	7.230	6.860	0.11 0.4	.41	2.5	4.7	0.4	0.87	3.6	1.3
<i>i</i> -butanol	16.6	360	490	410	565	7.370	6.690	0.81 0.	.28	5.2	3.8	1.6	0.74	0.37	1.9
3-pentanone	17.0	360	470	400	575	6 500	7 610	0.21.0	26	4.5	3.6	0.5	0.72	1.8	21
<i>n</i> -butanol	17.5	360	490	415	570	7.370	6.550	0.70 0.1	.21	4.6	3.2	1.5	0.66	0.65	2.5
2-butanol	17.9	365	480	405	560	6,560	6.830	0.97 0.4	44	5.3	4.6	1.8	1.0	0.06	1.2
<i>i</i> -propanol	19.9	360	490	410	570	7.370	6.850	0.90 0.	25	5.8	3.2	1.6	0.78	0.17	2.3
<i>n</i> -propanol	20.5	360	495	410	575	7,580	7.000	0.67 0.	.14	4.2	1.8	1.6	0.78	0.79	4.8
acetone	20.6	360	480	405	590	6,940	7,740	0.68 0.	.00	4.2	1.9	1.6	0.00	0.76	5.3
benzonitrile	25.2	365	480	420	605	6,560	7.280	0.48 0.	35	4.1	3.7	1.2	0.95	1.3	1.8
methanol	32.7	360	535	420	660	9.090	8,660	0.40 0.	.01	0.57	0.33	7.0	0.30	11	30
acetonitrile	35.9	360	500	410	635	7,780	8.640	0.65 0.	.02	4.9	1.0	1.3	0.20	0.71	9.8
DMF	36.7	360	495	410	605	7.580	7.860	0.78 0.	.00	5.1	0.94	1.5	0.00	0.43	11
DMSO	46.5	365	500	415	635	7 400	8 350	0.81 0	00	64	0.94	13	0.00	0.30	11

Table S4. Photophysical parameters of complex C1 and ligand L1 in various solvents

<sup>a</sup>no datum because of poor solubility. <sup>b</sup>no datum because of complete dissociation into L1 + Zn(OAc)<sub>2</sub>.  $\epsilon_{f}$ : relative permittivity.  $\lambda_{abs}$ : absorption maximal wavelength.  $\lambda_{PL}$ : PL maximal wavelength.  $E_{SS}$ : Stokes shift.  $\Phi_{f}$ : PL quantum yield. q: PL lifetime.  $k_{r}$ : radiative decay rate constant.  $k_{nr}$ : non-radiative decay rate constant. L and C in superscript denote ligand L1 and complex C1, respectively.

### F. UV/vis spectral change of complex C1 dissolved in dichloromethane/acetone



**Fig. S5.** UV/vis spectra of **C1** dissolved in a mixture of dichloromethane and acetone at various mixing ratios. Concentration of **C1** =  $1.0 \times 10^{-5}$  mol L<sup>-1</sup>.

### G. White luminescence of C1



**Fig. S6.** PL spectra for **C1** featuring white luminescence. (a) 3-pentanone  $(1.0 \times 10^{-4} \text{ mol } \text{L}^{-1})$ . (b) THF / 2-propanol (1:5 v/v)  $(1.0 \times 10^{-4} \text{ mol } \text{L}^{-1})$ .





**Fig. S7. (a)** UV/vis spectral change upon addition of aqueous HBF<sub>4</sub>. That of referential  $[Zn(L1)_2](BF_4)_2$  is overlaid. **(b)** UV/vis spectral change upon addition of aqueous H<sub>2</sub>SO<sub>4</sub>. That of referential  $Zn_2(L1)_2(\mu-O_2SO_2)_2$  is overlaid.

# I. Identification of referential complexes



Fig. S8. <sup>1</sup>H NMR spectrum of  $[Zn(L1)_2](BF_4)_2$  in methanol-d<sub>4</sub>.



Fig. S9. <sup>13</sup>C NMR spectrum of  $[Zn(L1)_2](BF_4)_2$  in DMSO-d<sub>6</sub>.



**Fig. S10**. HR-ESI-TOF-MS of  $[Zn(L1)_2](BF_4)_2$  in methanol.



Fig. S11. <sup>1</sup>H NMR spectrum of  $Zn_2(L1)_2(\mu$ -O<sub>2</sub>SO<sub>2</sub>)<sub>2</sub> in methanol-d<sub>4</sub>.



Fig. S12. ESI-TOF-MS of  $Zn_2(L1)_2(\mu$ -O $_2SO_2)_2$  in methanol and acetonitrile.



**Fig. S13**. ORTEP drawings of  $Zn_2(L1)_2(\mu-O_2SO_2)_2 \cdot 2MeOH$  with thermal ellipsoid sets at the 50% probability level. Hydrogen atoms are omitted for clarity.

Empirical formula	$C_{68}H_{56}N_8O_{10}S_2Zn_2$
<i>Fw</i> / g mol <sup>-1</sup>	1340.12
Crystal system	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> /c
Crystal size / mm	$0.040 \times 0.030 \times 0.030$
Temperature / K	93
<i>a /</i> Å	18.840(5)
<i>b /</i> Å	15.678(4)
c / Å	20.073(6)
$\alpha / \circ$	90
ß/°	97.206(4)
γ/ °	90
V/ų	5882(3)
Ζ	4
$D_{calcd}$ g/cm <sup>-3</sup>	1.513
λ/Å	0.71075
$\mu/mm^{-1}$	0.958
<b>Reflections collected</b>	35289
Independent reflections	12124
Parameters	815
R <sub>int</sub>	0.1783
$R_1$ (/>2.00 $\sigma$ (/)) $^{\circ}$	0.0986
wR <sub>2</sub> (All reflections) <sup>b</sup>	0.199
GoF	1.020

**Table S5.** Crystallographic data for  $Zn_2(L1)_2(\mu$ -O<sub>2</sub>SO<sub>2</sub>)<sub>2</sub>·2MeOH

 ${}^{a}R_{1} = \Sigma ||F^{\circ}| - |F^{c}|| / \Sigma |F^{\circ}| \ (I > 2\sigma(I)). \ {}^{b}wR_{2} = [\Sigma(w(F^{\circ 2} - F^{\circ 2})^{2} / \Sigma w(F^{\circ 2})^{2})^{1/2} \ (I > 2\sigma(I)). \ {}^{c}GoF = [\Sigma(w(F^{\circ 2} - F^{\circ 2})^{2} / \Sigma (N^{r} - N^{p})^{2}).$ 

### J. References for Supporting Information

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