Electronic Supporting Information

Long-lived charge-separated states produced in supramolecular complexes between anionic and cationic porphyrins

Nathan L. Bill,[a] Masatoshi Ishida,[b,c] Yuki Kawashima,[d] Kei Ohkubo,[d] Young Mo Sung,[b] Vincent M. Lynch,[a] Jong Min Lim,[b] Dongho Kim,*[b] Jonathan L. Sessler*[a] and Shunichi Fukuzumi*[d,e]

[a] *Department of Chemistry, 105 E. 24th Street-Stop A5300, The University of Texas at Austin, Austin, Texas 78712-1224, United States*

[b] *Department of Chemistry, Yonsei University, Seoul 120-749, Korea*

[c] *Education Center for Global Leaders in Molecular Systems for Devices, Kyushu University, Fukuoka, 819-0395, Japan*

[d] *Department of Material and Life Science, Graduate School of Engineering, Osaka University, ALCA, Japan Science and Technology (JST), Suita, Osaka 565-0871, Japan*

[e] *Department of Bioinspired Science, Ewha Womans University, Seoul 120-750, Korea*

* To whom correspondence should be addressed.

Email: fukuzumi@chem.eng.osaka-u.ac.jp (S.F.)

Email: sessler@cm.utexas.edu (J.L.S.)

Email: dongho@yonsei.ac.kr (D.K.)

Derivation of the Equilibrium Constants Used to Determine the Binding Affinity of the Supramolecular Complexes

UV/Vis Absorption Spectroscopy, [2-Zn^{2+}] is fixed:

$$K = [\mathbf{1\text{-}M^{4-}}/(\mathbf{2\text{-}Zn^{2+}})_2]/([\mathbf{2\text{-}Zn^{2+}}]^2[\mathbf{1\text{-}M^{4-}}]) \quad (1)$$

$$[\mathbf{1\text{-}M^{4-}}/(\mathbf{2\text{-}Zn^{2+}})_2] = K([\mathbf{2\text{-}Zn^{2+}}]_0 - 2[\mathbf{1\text{-}M^{4-}}/(\mathbf{2\text{-}Zn^{2+}})_2])^2([\mathbf{1\text{-}M^{4-}}] - [\mathbf{1\text{-}M^{4-}}/(\mathbf{2\text{-}Zn^{2+}})_2]) \quad (2)$$

$$\alpha = 2[\mathbf{1\text{-}M^{4-}}/(\mathbf{2\text{-}Zn^{2+}})_2]/[\mathbf{2\text{-}Zn^{2+}}]_0 = (A - A_0) / (A_\infty - A_0) \quad (3)$$

where A, A_0 and A_∞ represent the measured absorbance after the addition of a known aliquot of **1-M^{4-}**, the absorbance of **2-Zn^{2+}** at the start of the titration, and the absorbance of **1-M^{4-}/(2-Zn^{2+})$_2$** at the end of the titration when all of the free **2-Zn^{2+}** is bound to form **1-M^{4-}/(2-Zn^{2+})$_2$**, respectively.

From eqns (2) and (3), eqn (4) is obtained.

$$\alpha = K[\mathbf{2\text{-}Zn^{2+}}]_0(1 - \alpha)^2(2[\mathbf{1\text{-}M^{4-}}] - \alpha[\mathbf{2\text{-}Zn^{2+}}]_0) \quad (4)$$

Eqn (4) is rewritten by eqn (5).

$$\alpha/(1 - \alpha)^2 = K[\mathbf{2\text{-}Zn^{2+}}]_0 (2[\mathbf{1\text{-}M^{4-}}] - \alpha[\mathbf{2\text{-}Zn^{2+}}]_0) \quad (5)$$

Thus, a plot of $\alpha/(1 - \alpha)^2$ vs $2[\mathbf{1\text{-}M^{4-}}]_0 - \alpha[\mathbf{2\text{-}Zn^{2+}}]_0$ gives a linear correlation and from the slope K (M^{-2}) can be determined.

Fluorescence Spectroscopy, [1-M^{4-}] is fixed:

$$\alpha = [\mathbf{1\text{-}M^{4-}}/(\mathbf{2\text{-}Zn^{2+}})_2]/[\mathbf{1\text{-}M^{4-}}]_0 = (I_0 - I)/I_0 \quad (6)$$

From eqns (2) and (6), eqn (7) is obtained.

$$\alpha/(1 - \alpha) = K([\mathbf{2\text{-}Zn^{2+}}] - 2\alpha[\mathbf{1\text{-}M^{4-}}]_0)^2 \quad (7)$$

Supplemental figures

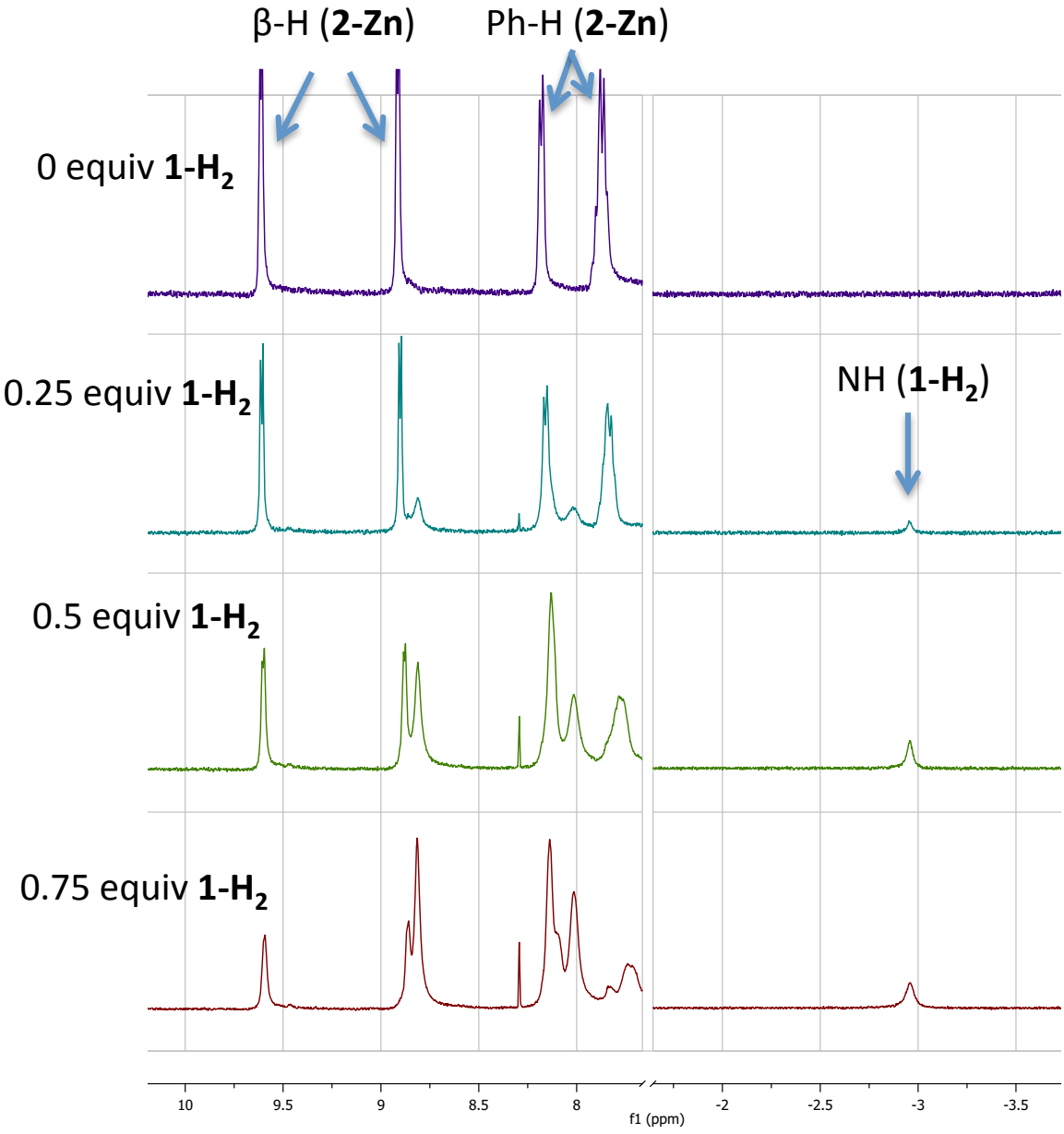

Fig. S1 Partial ^{1}H NMR spectra of **2-Zn•2ClO$_4$** (top, purple) and with increasing amounts of **1-H$_2$•4TBA** recorded in DMSO-d_6. In blue (second from top) there are 0.25 molar equiv**,** in green (third from top) there are 0.5 molar equiv and in red (bottom) there are 0.75 molar equiv of **1-H$_2$•4TBA**.

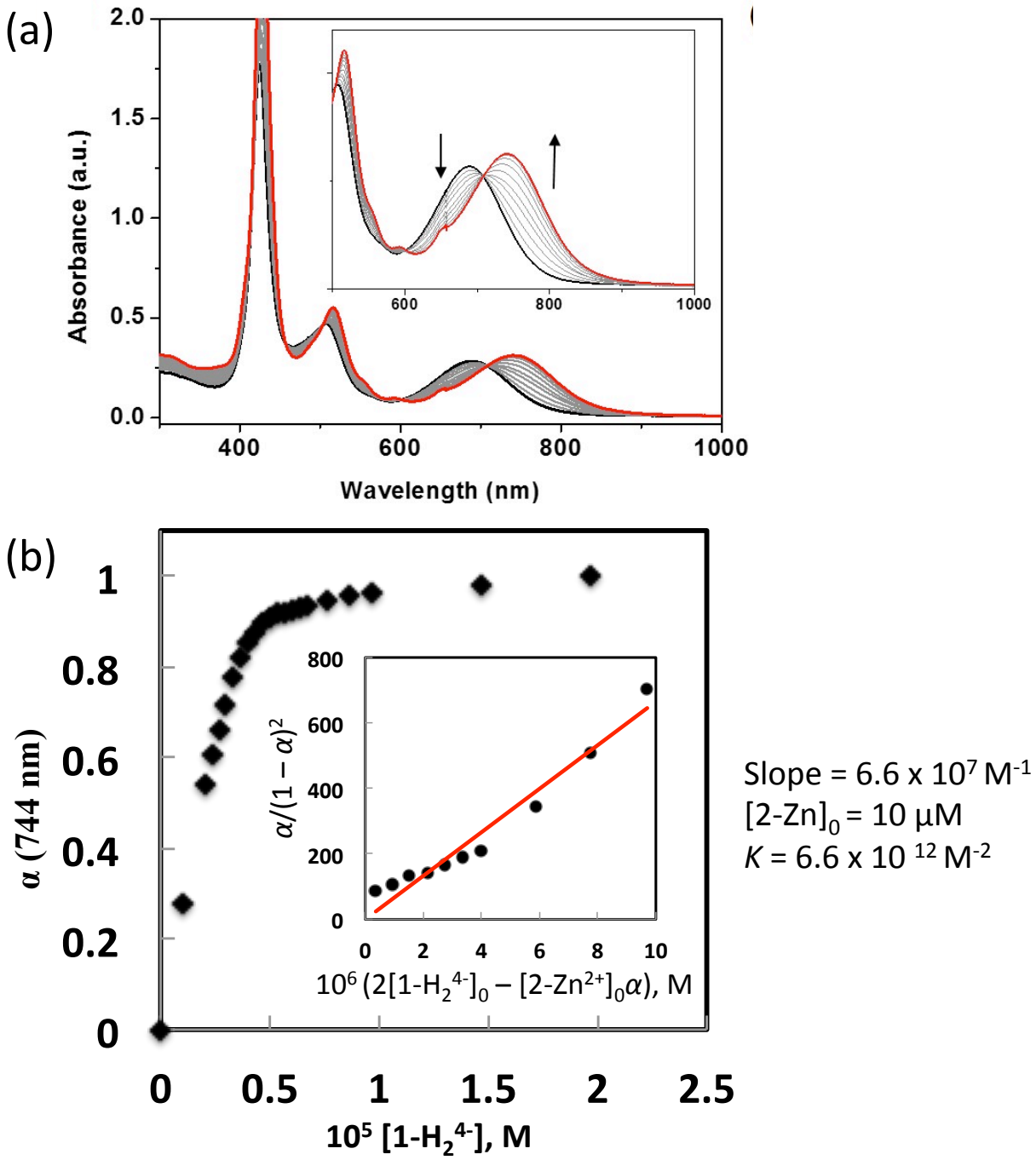

Fig. S2 (a) UV/vis absorption spectra of the titration **1-H_2•4TBA** into 10 μM solution of **2-Zn•2ClO_4** in PhCN at 298 K. (b) The linear fitting of the data to the 2:1 binding equations, detailed above.

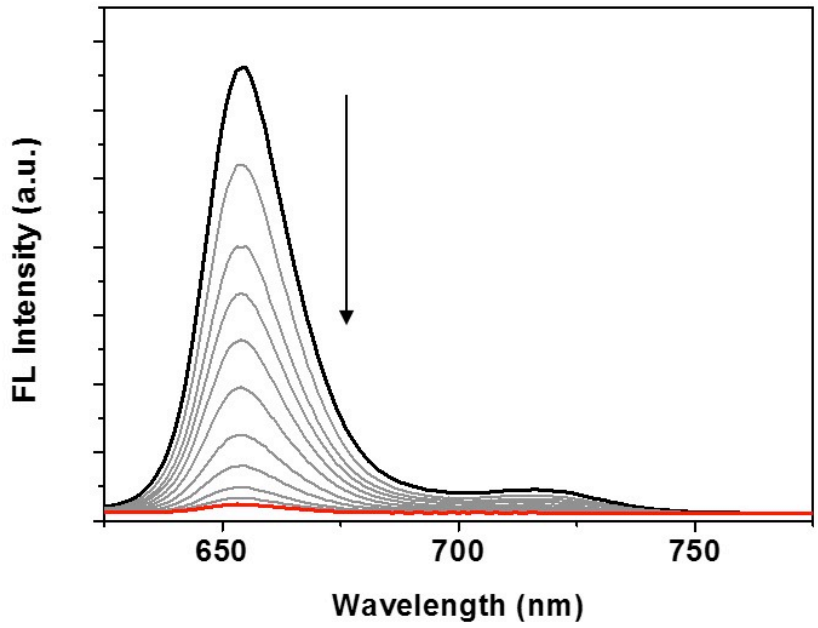

Fig. S3 Fluorescence spectral changes observed upon the treatment of a 50 μM PhCN solution of **1-H_2^{4-}** with **2-Zn^{2+}** at 298 K. The original spectrum is the bolded black line whereas the final spectrum is highlighted in red.

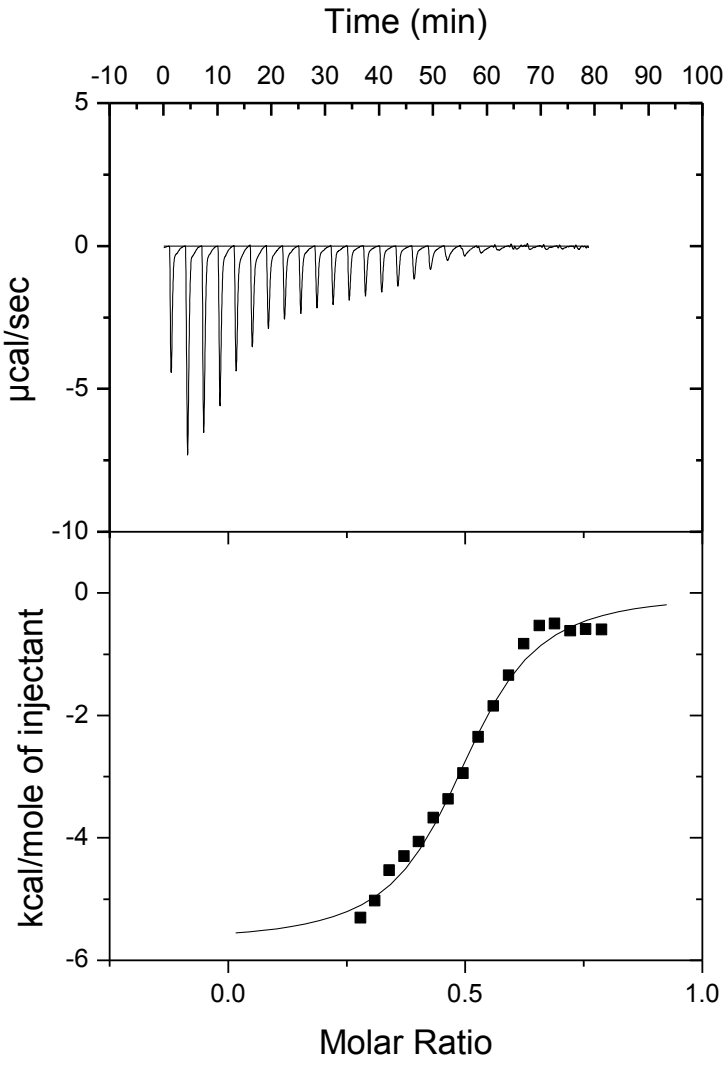

Fig. S4 ITC titration of **1-Zn**$^{4-}$ into **2-Zn**$^{2+}$ at 298 K in PhCN.

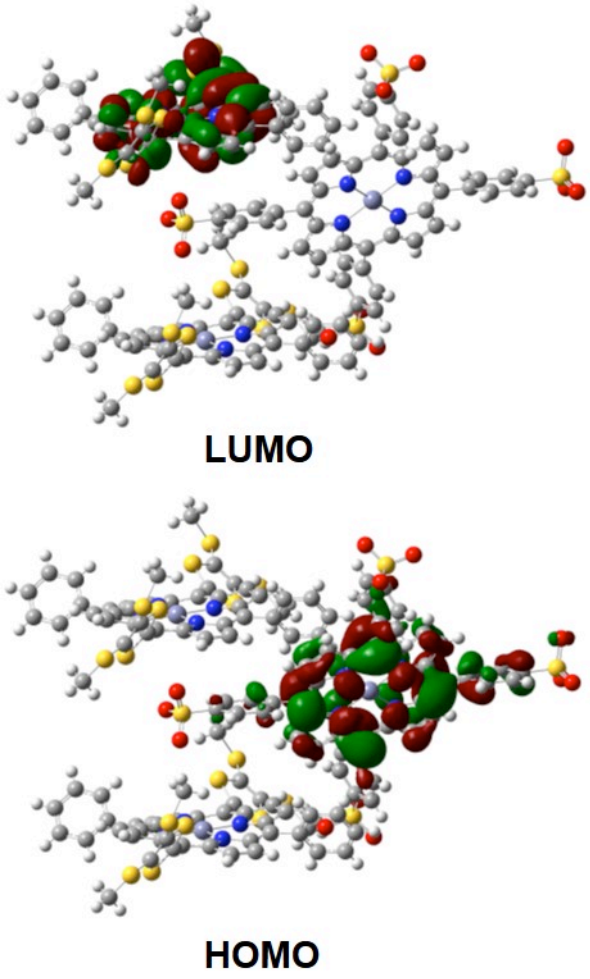

Fig. S5 Molecular orbital distributions of the supramolecular complex of **1-Zn**$^{4-}$**/(2-Zn**$^{2+}$**)**$_2$ analyzed by HF/LanL2DZ calculations based on the crystal structure.

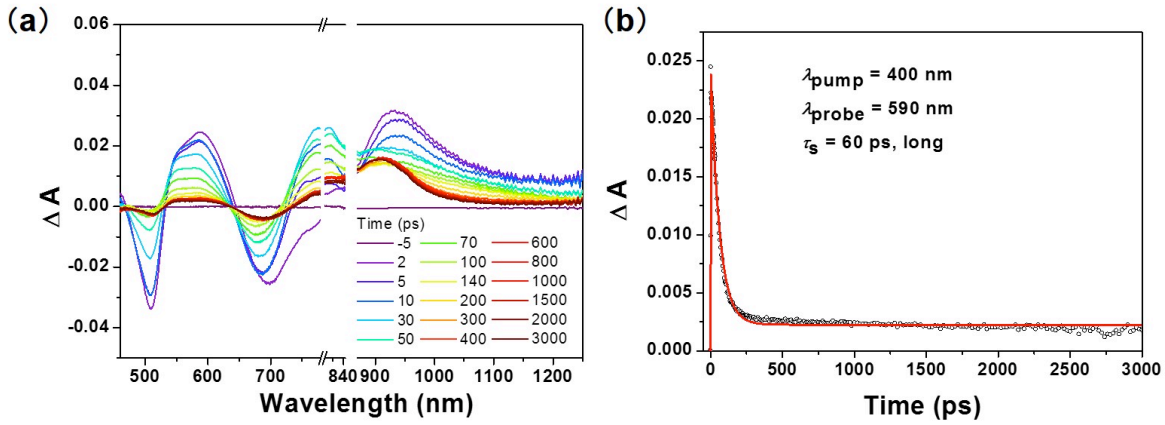

Fig. S6 (a) Femtosecond transient absorption spectra of the **1-Zn**$^{4-}$**/(2-Zn**$^{2+}$**)**$_2$ complex generated in situ in deaerated PhCN at 298 K recorded after laser excitation at 400 nm. (b) Time profile of the spectral trace at 585 nm.

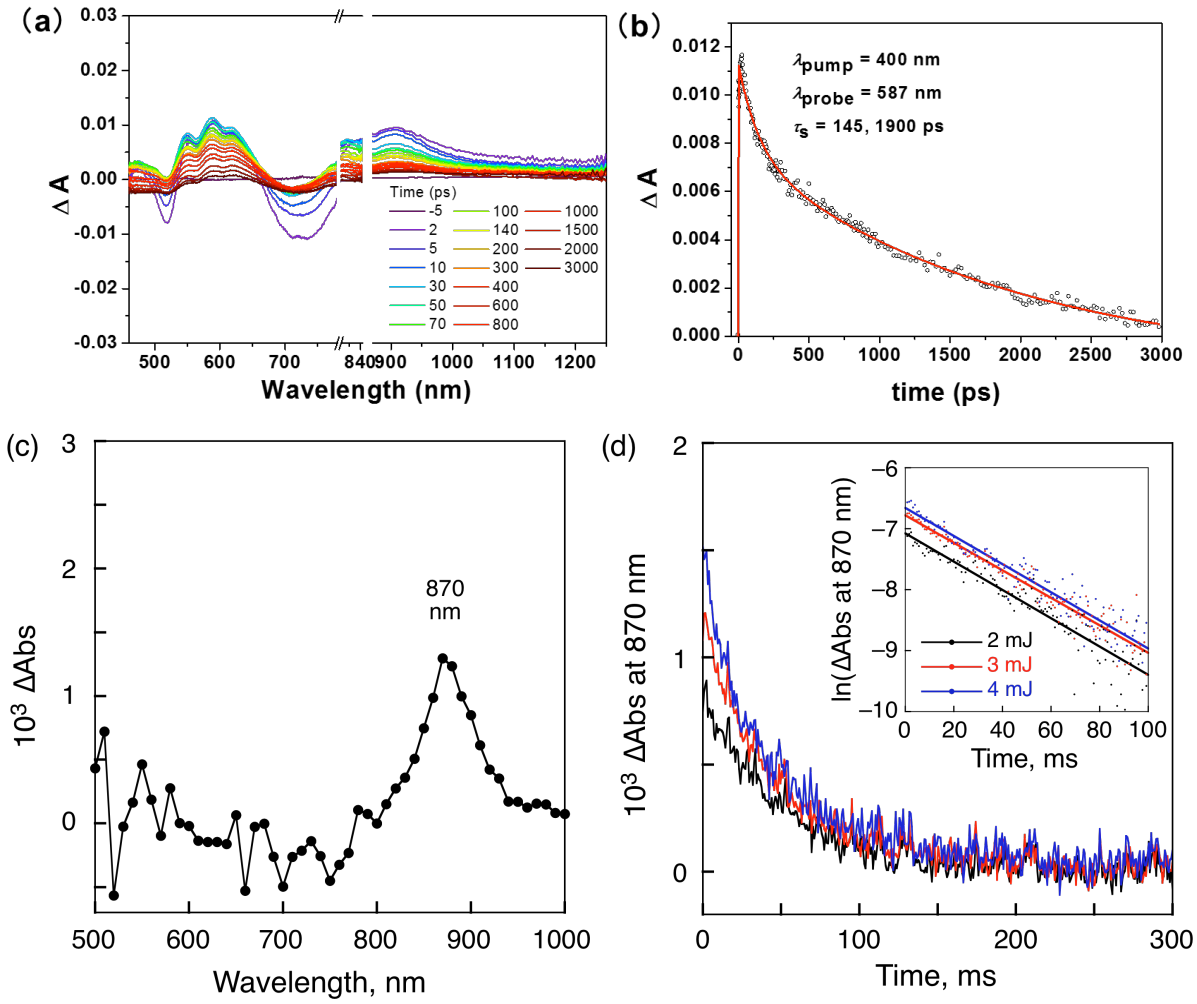

Fig. S7 (a) Femtosecond transient absorption spectra of the **1-Zn**$^{4-}$**/(2-Zn**$^{2+}$**)**$_2$ complex generated in situ in deaerated PhCN at 298 K recorded after laser excitation at 400 nm. (b) Time profile of the spectral trace at 585 nm. (c) Nanosecond transient absorption spectrum of **1-Zn**$^{4-}$**/(2-Zn**$^{2+}$**)**$_2$ complex generated in situ in deaerated PhCN at 298 K measured at 1ms after laser excitation at 400 nm. (d) Decay time profiles of absorbance at 870 nm; inset indicates the first-order plots with various laser power excitation (2-4 mJ).

Detailed X-ray experimental for $2[(C_{42}H_{30}N_4S_8)Zn(C_2H_5OH)]\bullet$ $[(C_{44}H_{24}N_4S_4O_{12})Zn]\bullet$ $2(C_2H_5OH)\bullet C_6H_{14}$: Crystals grew as long dark green needles by layering an MeCN solution of **1-Zn•4TBA** onto a THF solution of **2-Zn•$(ClO_4)_2$** with a small amount of MeOH to solubilize the compound. The data crystal was cut from a larger crystal and had approximate dimensions; 0.65 x 0.19 x 0.16 mm. The data were collected at -120 °C on a Nonius Kappa CCD diffractometer using a Bruker AXS Apex II detector and a graphite monochromator with MoKα radiation (λ = 0.71075 Å). Reduced temperatures were maintained by use of an Oxford Cryosystems 600 low-temperature device. A total of 1282 frames of data were collected using θ-scans with a scan range of 1.1° and a counting time of 44 seconds per frame. Details of crystal data, data collection and structure refinement are listed in Table S1. Data reduction were performed using SAINT V8.27B.[S1] The structure was solved by direct methods using SIR97[S2] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97.[S3] Structure analysis was aided by use of the programs PLATON98[S4] and WinGX.[S5]

Two molecules of solvent, one an ethanol molecule and one a molecule of n-hexane, were badly disordered. Attempts to model the disorder were unsatisfactory. The contributions to the scattering factors due to these solvent molecules were removed by use of the utility SQUEEZE[S6] in PLATON98.

In addition to that described above, one of the SO_3 groups and a coordinated ethanol molecule were also disordered. The disorder was modelled in basically the same fashion for both. For the SO_3 group, the variable x was assigned to the site occupancy factors for one component of the disorder. (1-x) was assigned to the alternate component. The geometry of the two groups was restrained to be approximately equal. A common isotropic displacement parameter was refined for the six oxygen atoms while refining x. The variable x refined to a value very close to 1/2. The site occupancy factors were subsequently fixed at 1/2 for the remainder of the refinement. These oxygen atoms were refined anisotropically with their displacement parameters restrained to be approximately isotropic.

The carbon atoms of the coordinated ethanol molecule were also disordered. The refinement of the disordered resulted in a site occupancy factor of 67(2)% for atoms C1a and C2a. No hydrogen atom was calculated for the oxygen atom of this molecule in the final refinement model.

The function, $\Sigma w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.0742*P)^2 + (0.0536*P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_W(F^2)$ refined to 0.174, with R(F) equal to 0.0666 and a goodness of fit, S, = 1.13. Definitions used for calculating R(F), $R_W(F^2)$ and the goodness of fit, S, are given in the footnotes below. The data were checked for secondary extinction but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[S7] All figures were generated using SHELXTL/PC.[S8] Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found in the .cif file uploaded separately.

Table S1 Crystal data and structure refinement for **1-Zn^{4-}•(2-Zn^{2+})$_2$**

Empirical formula	C140 H116 N12 O15 S20 Zn3	
Formula weight	3043.76	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.7122(5) Å	α= 101.781(3)°.
	b = 16.4862(9) Å	β= 102.522(3)°.
	c = 19.4020(10) Å	γ = 97.189(4)°.
Volume	3222.6(3) $Å^3$	
Z	1	
Density (calculated)	1.568 Mg/m^3	
Absorption coefficient	0.950 mm^{-1}	
F(000)	1570	
Crystal size	0.65 x 0.19 x 0.16 mm	
Theta range for data collection	1.11 to 25.00°.	
Index ranges	-12<=h<=12, -19<=k<=19, 0<=l<=23	
Reflections collected	10792	
Independent reflections	10792 [R(int) = 0.0000]	
Completeness to theta = 25.00°	95.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.864	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10792 / 100 / 846	
Goodness-of-fit on F^2	1.132	
Final R indices [I>2sigma(I)]	R1 = 0.0666, wR2 = 0.1555	
R indices (all data)	R1 = 0.1322, wR2 = 0.1738	
Largest diff. peak and hole	2.005 and -1.072 $e.Å^{-3}$	

Table S2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **1-Zn^{4-}•(2-Zn^{2+})$_2$**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
C1	7869(6)	8836(4)	2232(3)	28(2)
C2	8011(6)	9000(3)	1551(3)	25(1)
C3	8164(6)	9842(3)	1624(3)	27(2)
C4	8124(6)	10214(3)	2360(3)	27(2)
C5	8193(6)	11079(3)	2658(3)	28(2)
C6	8283(6)	11459(3)	3383(3)	31(2)
C7	8158(6)	12327(3)	3660(3)	31(2)
C8	8262(6)	12434(4)	4380(3)	34(2)
C9	8429(7)	11647(4)	4557(3)	36(2)
C10	8550(7)	11484(4)	5248(3)	42(2)
C11	8591(8)	10682(4)	5401(3)	47(2)
C12	8932(7)	10536(4)	6114(3)	45(2)
C13	8771(7)	9699(4)	6044(3)	44(2)
C14	8304(7)	9309(4)	5282(3)	44(2)
C15	7912(7)	8435(4)	4958(3)	39(2)
C16	7609(7)	8054(4)	4209(3)	40(2)
C17	7088(7)	7181(4)	3863(3)	38(2)
C18	7041(7)	7080(4)	3153(3)	37(2)
C19	7493(7)	7880(4)	3042(3)	35(2)
C20	7601(6)	8039(3)	2371(3)	29(2)
C21	8044(6)	11611(3)	2133(3)	32(2)
C22	7041(7)	12254(4)	1105(3)	42(2)
C23	8182(6)	12766(4)	1444(3)	32(2)
C24	4499(8)	11798(6)	327(5)	84(3)
C25	10067(7)	14184(4)	1893(4)	50(2)
C26	8572(8)	12194(4)	5870(3)	40(2)
C27	9516(7)	12923(4)	6091(3)	36(2)
C28	9472(7)	13560(4)	6672(3)	37(2)
C29	8494(8)	13478(4)	7022(4)	50(2)
C30	7536(8)	12773(4)	6801(4)	56(2)

C31	7588(8)	12130(4)	6228(4)	54(2)
C32	7812(7)	7868(4)	5453(3)	37(2)
C33	7208(7)	7130(4)	6401(3)	35(2)
C34	7936(6)	6641(4)	6056(3)	32(2)
C35	5265(9)	7423(5)	7076(5)	75(3)
C36	9081(7)	5300(4)	5607(3)	45(2)
C37	7356(6)	7277(4)	1755(3)	28(2)
C38	8235(7)	6727(4)	1768(3)	35(2)
C39	7972(8)	5992(4)	1222(4)	45(2)
C40	6848(8)	5796(4)	680(3)	43(2)
C41	5987(7)	6343(4)	666(3)	43(2)
C42	6245(6)	7082(4)	1200(3)	34(2)
C43	1521(6)	6711(4)	880(3)	29(2)
C44	2754(6)	7097(4)	1383(3)	28(2)
C45	3339(6)	6473(4)	1563(3)	28(2)
C46	2504(5)	5691(3)	1175(3)	21(1)
C47	2799(6)	4899(4)	1226(3)	26(1)
C48	2050(5)	4149(3)	796(3)	24(1)
C49	2343(6)	3341(4)	840(3)	33(2)
C50	1413(6)	2770(4)	311(3)	34(2)
C51	528(6)	3215(3)	-37(3)	24(1)
C52	-604(6)	2836(3)	-577(3)	26(1)
C53	4005(6)	4868(3)	1776(3)	24(1)
C54	5011(6)	4560(4)	1570(3)	36(2)
C55	6105(6)	4490(4)	2073(3)	38(2)
C56	6173(6)	4735(3)	2809(3)	24(1)
C57	5172(6)	5057(4)	3026(3)	30(2)
C58	4101(6)	5128(4)	2513(3)	31(2)
C59	-861(6)	1912(3)	-841(3)	26(2)
C60	-972(6)	1385(4)	-373(3)	34(2)
C61	-1163(6)	520(4)	-621(3)	37(2)
C62	-1292(5)	158(4)	-1356(3)	33(2)
C63	-1225(6)	675(4)	-1826(3)	33(2)
C64	-1005(6)	1545(4)	-1578(3)	32(2)
N1	7982(5)	9599(3)	2721(2)	30(1)
N2	8417(5)	11053(3)	3938(3)	36(1)

N3	8247(6)	9919(3)	4899(3)	48(2)
N4	7824(6)	8489(3)	3696(2)	39(2)
N5	1393(4)	5852(3)	747(2)	22(1)
N6	911(5)	4072(3)	267(2)	25(1)
S1	6674(2)	11401(1)	1459(1)	45(1)
S2	9099(2)	12461(1)	2168(1)	36(1)
S3	5961(2)	12427(1)	352(1)	62(1)
S4	8705(2)	13640(1)	1151(1)	44(1)
S5	6969(2)	8017(1)	6092(1)	46(1)
S6	8501(2)	7006(1)	5401(1)	39(1)
S7	6580(2)	6868(1)	7090(1)	58(1)
S8	8231(2)	5700(1)	6271(1)	47(1)
S9	7537(2)	4612(1)	3463(1)	33(1)
S10	-1601(2)	-952(1)	-1660(1)	52(1)
O4	-1786(10)	-1152(5)	-2427(3)	38(3)
O5	-386(8)	-1199(5)	-1280(5)	54(3)
O6	-2669(8)	-1252(5)	-1381(5)	75(4)
O4A	-3017(7)	-1180(5)	-1754(6)	80(4)
O5A	-1274(10)	-1123(5)	-2364(3)	30(3)
O6A	-839(9)	-1288(5)	-1131(4)	53(3)
Zn1	7906(1)	9762(1)	3793(1)	43(1)
Zn2	0	5000	0	26(1)
O1	8296(4)	4143(3)	3052(2)	49(1)
O2	8178(5)	5448(3)	3854(2)	53(1)
O3	7014(4)	4143(3)	3928(2)	50(1)
O1A	5812(5)	9771(3)	3546(3)	70(2)
C1A	5101(13)	10223(9)	3991(8)	84
C2A	4146(15)	10150(10)	3391(8)	105
C1AA	5150(30)	9005(18)	3417(15)	84
C2AA	4120(30)	9080(20)	2909(16)	105

Table S3 Bond lengths [Å] and angles [°] for **1-Zn^{4-}•(2-Zn^{2+})$_2$**.

C1-N1	1.386(7)	C17-H17	0.95
C1-C20	1.401(8)	C18-C19	1.422(8)
C1-C2	1.437(8)	C18-H18	0.95
C2-C3	1.352(7)	C19-N4	1.393(7)
C2-H2	0.95	C19-C20	1.405(8)
C3-C4	1.446(8)	C20-C37	1.498(8)
C3-H3	0.95	C21-S2	1.667(6)
C4-N1	1.358(7)	C21-S1	1.685(6)
C4-C5	1.410(7)	C22-C23	1.343(9)
C5-C6	1.395(8)	C22-S1	1.725(7)
C5-C21	1.470(8)	C22-S3	1.754(7)
C6-N2	1.371(7)	C23-S4	1.727(6)
C6-C7	1.456(8)	C23-S2	1.734(6)
C7-C8	1.349(8)	C24-S3	1.752(9)
C7-H7	0.95	C24-H24A	0.98
C8-C9	1.431(8)	C24-H24B	0.98
C8-H8	0.95	C24-H24C	0.98
C9-N2	1.384(7)	C25-S4	1.800(7)
C9-C10	1.402(8)	C25-H25A	0.98
C10-C11	1.416(8)	C25-H25B	0.98
C10-C26	1.494(8)	C25-H25C	0.98
C11-N3	1.377(7)	C26-C31	1.387(10)
C11-C12	1.430(8)	C26-C27	1.396(9)
C12-C13	1.344(8)	C27-C28	1.389(8)
C12-H12	0.95	C27-H27	0.95
C13-C14	1.436(8)	C28-C29	1.375(9)
C13-H13	0.95	C28-H28	0.95
C14-N3	1.368(8)	C29-C30	1.376(10)
C14-C15	1.418(8)	C29-H29	0.95
C15-C16	1.409(8)	C30-C31	1.387(9)
C15-C32	1.482(8)	C30-H30	0.95
C16-N4	1.380(7)	C31-H31	0.95
C16-C17	1.441(8)	C32-S6	1.677(6)
C17-C18	1.343(8)	C32-S5	1.682(7)

C33-C34	1.367(9)	C48-C49	1.421(8)
C33-S5	1.717(6)	C49-C50	1.364(8)
C33-S7	1.726(6)	C49-H49	0.95
C34-S6	1.702(6)	C50-C51	1.410(8)
C34-S8	1.737(6)	C50-H50	0.95
C35-S7	1.770(9)	C51-N6	1.386(7)
C35-H35A	0.98	C51-C52	1.397(8)
C35-H35B	0.98	C52-C43#1	1.408(8)
C35-H35C	0.98	C52-C59	1.473(7)
C36-S8	1.798(7)	C53-C54	1.349(8)
C36-H36A	0.98	C53-C58	1.383(7)
C36-H36B	0.98	C54-C55	1.386(8)
C36-H36C	0.98	C54-H54	0.95
C37-C42	1.373(8)	C55-C56	1.385(8)
C37-C38	1.388(9)	C55-H55	0.95
C38-C39	1.390(8)	C56-C57	1.363(8)
C38-H38	0.95	C56-S9	1.778(6)
C39-C40	1.369(9)	C57-C58	1.379(8)
C39-H39	0.95	C57-H57	0.95
C40-C41	1.368(10)	C58-H58	0.95
C40-H40	0.95	C59-C60	1.392(8)
C41-C42	1.383(8)	C59-C64	1.401(8)
C41-H41	0.95	C60-C61	1.383(8)
C42-H42	0.95	C60-H60	0.95
C43-N5	1.372(7)	C61-C62	1.397(8)
C43-C52#1	1.408(8)	C61-H61	0.95
C43-C44	1.442(8)	C62-C63	1.376(8)
C44-C45	1.337(8)	C62-S10	1.770(6)
C44-H44	0.95	C63-C64	1.388(8)
C45-C46	1.433(7)	C63-H63	0.95
C45-H45	0.95	C64-H64	0.95
C46-N5	1.385(6)	N1-Zn1	2.062(5)
C46-C47	1.398(8)	N2-Zn1	2.076(5)
C47-C48	1.382(7)	N3-Zn1	2.052(5)
C47-C53	1.501(8)	N4-Zn1	2.057(5)
C48-N6	1.387(7)	N5-Zn2	2.001(4)

N6-Zn2	2.009(5)	O1A-C1A	1.430(14)
S9-O2	1.433(4)	C1A-C2A	1.347(15)
S9-O1	1.443(5)	C1A-H1A1	0.99
S9-O3	1.458(5)	C1A-H1A2	0.99
S10-O6A	1.417(6)	C2A-H2A1	0.98
S10-O4	1.422(6)	C2A-H2A2	0.98
S10-O6	1.442(6)	C2A-H2A3	0.98
S10-O5A	1.465(6)	C1AA-C2AA	1.345(17)
S10-O4A	1.477(6)	C1AA-H1A3	0.99
S10-O5	1.497(6)	C1AA-H1A4	0.99
Zn1-O1A	2.193(6)	C2AA-H2A4	0.98
Zn2-N5#1	2.001(4)	C2AA-H2A5	0.98
Zn2-N6#1	2.009(5)	C2AA-H2A6	0.98
O1A-C1AA	1.32(3)		

N1-C1-C20	125.6(5)	C7-C8-C9	107.5(5)
N1-C1-C2	108.6(5)	C7-C8-H8	126.3
C20-C1-C2	125.8(5)	C9-C8-H8	126.3
C3-C2-C1	107.6(5)	N2-C9-C10	124.3(5)
C3-C2-H2	126.2	N2-C9-C8	109.9(5)
C1-C2-H2	126.2	C10-C9-C8	125.8(5)
C2-C3-C4	107.0(5)	C9-C10-C11	125.1(6)
C2-C3-H3	126.5	C9-C10-C26	118.2(5)
C4-C3-H3	126.5	C11-C10-C26	116.6(5)
N1-C4-C5	124.7(5)	N3-C11-C10	126.1(6)
N1-C4-C3	109.4(5)	N3-C11-C12	108.9(5)
C5-C4-C3	125.9(5)	C10-C11-C12	124.9(5)
C6-C5-C4	126.6(5)	C13-C12-C11	107.7(5)
C6-C5-C21	117.5(5)	C13-C12-H12	126.1
C4-C5-C21	115.6(5)	C11-C12-H12	126.1
N2-C6-C5	124.8(5)	C12-C13-C14	107.2(5)
N2-C6-C7	109.4(5)	C12-C13-H13	126.4
C5-C6-C7	125.7(5)	C14-C13-H13	126.4
C8-C7-C6	107.0(5)	N3-C14-C15	123.9(5)
C8-C7-H7	126.5	N3-C14-C13	109.2(5)
C6-C7-H7	126.5	C15-C14-C13	126.9(6)

C16-C15-C14	126.1(6)	S4-C25-H25C	109.5
C16-C15-C32	116.8(5)	H25A-C25-H25C	109.5
C14-C15-C32	117.1(5)	H25B-C25-H25C	109.5
N4-C16-C15	122.9(6)	C31-C26-C27	119.0(6)
N4-C16-C17	110.1(5)	C31-C26-C10	118.1(6)
C15-C16-C17	127.0(6)	C27-C26-C10	122.9(7)
C18-C17-C16	107.1(5)	C28-C27-C26	119.7(7)
C18-C17-H17	126.4	C28-C27-H27	120.2
C16-C17-H17	126.4	C26-C27-H27	120.2
C17-C18-C19	107.6(5)	C29-C28-C27	120.1(6)
C17-C18-H18	126.2	C29-C28-H28	119.9
C19-C18-H18	126.2	C27-C28-H28	119.9
N4-C19-C20	124.5(5)	C28-C29-C30	121.0(6)
N4-C19-C18	110.3(5)	C28-C29-H29	119.5
C20-C19-C18	125.2(5)	C30-C29-H29	119.5
C1-C20-C19	125.7(5)	C29-C30-C31	119.0(7)
C1-C20-C37	118.6(5)	C29-C30-H30	120.5
C19-C20-C37	115.6(5)	C31-C30-H30	120.5
C5-C21-S2	125.3(5)	C30-C31-C26	121.1(7)
C5-C21-S1	119.2(5)	C30-C31-H31	119.5
S2-C21-S1	115.3(3)	C26-C31-H31	119.5
C23-C22-S1	116.0(5)	C15-C32-S6	122.1(5)
C23-C22-S3	123.1(5)	C15-C32-S5	123.1(5)
S1-C22-S3	120.8(4)	S6-C32-S5	114.8(4)
C22-C23-S4	121.8(5)	C34-C33-S5	114.7(5)
C22-C23-S2	115.0(5)	C34-C33-S7	122.3(5)
S4-C23-S2	123.1(4)	S5-C33-S7	123.0(4)
S3-C24-H24A	109.5	C33-C34-S6	115.9(5)
S3-C24-H24B	109.5	C33-C34-S8	121.3(5)
H24A-C24-H24B	109.5	S6-C34-S8	122.8(4)
S3-C24-H24C	109.5	S7-C35-H35A	109.5
H24A-C24-H24C	109.5	S7-C35-H35B	109.5
H24B-C24-H24C	109.5	H35A-C35-H35B	109.5
S4-C25-H25A	109.5	S7-C35-H35C	109.5
S4-C25-H25B	109.5	H35A-C35-H35C	109.5
H25A-C25-H25B	109.5	H35B-C35-H35C	109.5

S8-C36-H36A	109.5	C48-C47-C46	123.7(5)
S8-C36-H36B	109.5	C48-C47-C53	118.5(5)
H36A-C36-H36B	109.5	C46-C47-C53	117.8(5)
S8-C36-H36C	109.5	C47-C48-N6	125.4(5)
H36A-C36-H36C	109.5	C47-C48-C49	124.2(5)
H36B-C36-H36C	109.5	N6-C48-C49	110.3(5)
C42-C37-C38	119.1(6)	C50-C49-C48	106.5(5)
C42-C37-C20	121.7(6)	C50-C49-H49	126.8
C38-C37-C20	119.1(5)	C48-C49-H49	126.8
C37-C38-C39	119.3(6)	C49-C50-C51	108.0(5)
C37-C38-H38	120.3	C49-C50-H50	126.0
C39-C38-H38	120.3	C51-C50-H50	126.0
C40-C39-C38	121.0(7)	N6-C51-C52	125.6(5)
C40-C39-H39	119.5	N6-C51-C50	110.0(5)
C38-C39-H39	119.5	C52-C51-C50	124.3(5)
C39-C40-C41	119.5(6)	C51-C52-C43#1	123.4(5)
C39-C40-H40	120.3	C51-C52-C59	118.5(5)
C41-C40-H40	120.3	C43#1-C52-C59	118.1(5)
C40-C41-C42	120.1(6)	C54-C53-C58	117.8(5)
C40-C41-H41	119.9	C54-C53-C47	121.2(5)
C42-C41-H41	119.9	C58-C53-C47	120.9(6)
C37-C42-C41	121.0(6)	C53-C54-C55	121.9(6)
C37-C42-H42	119.5	C53-C54-H54	119.1
C41-C42-H42	119.5	C55-C54-H54	119.1
N5-C43-C52#1	126.1(5)	C56-C55-C54	119.6(6)
N5-C43-C44	109.8(5)	C56-C55-H55	120.2
C52#1-C43-C44	124.1(5)	C54-C55-H55	120.2
C45-C44-C43	106.9(5)	C57-C56-C55	119.2(5)
C45-C44-H44	126.5	C57-C56-S9	120.3(4)
C43-C44-H44	126.5	C55-C56-S9	120.5(5)
C44-C45-C46	108.0(5)	C56-C57-C58	119.9(5)
C44-C45-H45	126.0	C56-C57-H57	120.1
C46-C45-H45	126.0	C58-C57-H57	120.1
N5-C46-C47	126.6(5)	C57-C58-C53	121.6(6)
N5-C46-C45	109.2(5)	C57-C58-H58	119.2
C47-C46-C45	124.2(5)	C53-C58-H58	119.2

C60-C59-C64	118.5(5)	C21-S1-C22	96.6(3)
C60-C59-C52	121.4(5)	C21-S2-C23	97.1(3)
C64-C59-C52	120.1(5)	C22-S3-C24	102.8(4)
C61-C60-C59	120.9(5)	C23-S4-C25	102.1(3)
C61-C60-H60	119.6	C32-S5-C33	97.3(3)
C59-C60-H60	119.6	C32-S6-C34	97.3(3)
C60-C61-C62	120.3(6)	C33-S7-C35	102.7(4)
C60-C61-H61	119.8	C34-S8-C36	101.6(3)
C62-C61-H61	119.8	O2-S9-O1	114.5(3)
C63-C62-C61	119.0(5)	O2-S9-O3	111.9(3)
C63-C62-S10	122.0(4)	O1-S9-O3	112.1(3)
C61-C62-S10	118.9(4)	O2-S9-C56	105.9(3)
C62-C63-C64	121.1(5)	O1-S9-C56	105.6(3)
C62-C63-H63	119.4	O3-S9-C56	106.1(3)
C64-C63-H63	119.4	O4-S10-O6	117.2(5)
C63-C64-C59	120.2(6)	O6A-S10-O4A	114.2(5)
C63-C64-H64	119.9	O5A-S10-O4A	110.7(4)
C59-C64-H64	119.9	O4-S10-O5	112.0(4)
C4-N1-C1	107.3(5)	O6-S10-O5	109.5(4)
C4-N1-Zn1	126.5(4)	O6A-S10-C62	108.6(4)
C1-N1-Zn1	126.1(4)	O4-S10-C62	107.5(4)
C6-N2-C9	106.3(5)	O6-S10-C62	106.3(4)
C6-N2-Zn1	124.3(4)	O5A-S10-C62	105.0(4)
C9-N2-Zn1	124.8(4)	O4A-S10-C62	103.6(4)
C14-N3-C11	106.8(5)	O5-S10-C62	103.2(4)
C14-N3-Zn1	127.6(4)	N3-Zn1-N4	88.61(19)
C11-N3-Zn1	125.3(4)	N3-Zn1-N1	167.8(2)
C16-N4-C19	104.8(5)	N4-Zn1-N1	89.62(18)
C16-N4-Zn1	126.2(4)	N3-Zn1-N2	89.76(19)
C19-N4-Zn1	125.2(4)	N4-Zn1-N2	167.7(2)
C43-N5-C46	106.0(4)	N1-Zn1-N2	89.39(18)
C43-N5-Zn2	127.2(4)	N3-Zn1-O1A	98.6(2)
C46-N5-Zn2	126.4(3)	N4-Zn1-O1A	98.2(2)
C51-N6-C48	105.2(4)	N1-Zn1-O1A	93.7(2)
C51-N6-Zn2	127.2(4)	N2-Zn1-O1A	94.2(2)
C48-N6-Zn2	127.6(4)	N5-Zn2-N5#1	180.000(1)

N5-Zn2-N6#1	90.06(17)	H1A1-C1A-H1A2	111.0
N5#1-Zn2-N6#1	89.94(17)	O1A-C1AA-C2AA	98(2)
N5-Zn2-N6	89.94(17)	O1A-C1AA-H1A3	112.1
N5#1-Zn2-N6	90.06(17)	C2AA-C1AA-H1A3	112.1
N6#1-Zn2-N6	180.000(1)	O1A-C1AA-H1A4	112.1
C1AA-O1A-C1A	99.8(15)	C2AA-C1AA-H1A4	112.1
C1AA-O1A-Zn1	110.6(13)	H1A3-C1AA-H1A4	109.8
C1A-O1A-Zn1	128.0(6)	C1AA-C2AA-H2A4	109.5
C2A-C1A-O1A	89.0(11)	C1AA-C2AA-H2A5	109.5
C2A-C1A-H1A1	113.8	H2A4-C2AA-H2A5	109.5
O1A-C1A-H1A1	113.8	C1AA-C2AA-H2A6	109.5
C2A-C1A-H1A2	113.8	H2A4-C2AA-H2A6	109.5
O1A-C1A-H1A2	113.8	H2A5-C2AA-H2A6	109.5

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z

Table S4 Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **1-Zn^{4-}•(2-Zn^{2+})$_2$.** The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C1	41(4)	23(3)	20(3)	5(3)	3(3)	12(3)
C2	33(4)	22(3)	18(3)	3(2)	5(3)	9(3)
C3	43(4)	24(3)	17(3)	6(3)	6(3)	11(3)
C4	43(4)	18(3)	22(3)	8(3)	3(3)	13(3)
C5	47(4)	14(3)	19(3)	5(2)	1(3)	9(3)
C6	55(5)	16(3)	21(3)	7(3)	6(3)	10(3)
C7	51(4)	17(3)	25(3)	7(3)	5(3)	6(3)
C8	57(5)	19(3)	27(3)	5(3)	9(3)	15(3)
C9	69(5)	20(3)	21(3)	4(3)	12(3)	10(3)
C10	78(6)	25(4)	22(3)	5(3)	11(3)	15(3)
C11	101(6)	18(4)	24(3)	1(3)	19(4)	16(4)
C12	89(6)	24(4)	18(3)	1(3)	10(3)	15(4)
C13	80(6)	30(4)	28(4)	14(3)	12(4)	16(4)
C14	86(6)	23(4)	25(4)	7(3)	15(4)	15(4)
C15	77(5)	23(4)	22(3)	7(3)	17(3)	19(3)
C16	75(5)	23(4)	29(4)	11(3)	17(3)	21(3)
C17	71(5)	20(3)	28(4)	10(3)	10(3)	22(3)
C18	67(5)	18(3)	22(3)	4(3)	1(3)	11(3)
C19	64(5)	23(4)	19(3)	5(3)	9(3)	17(3)
C20	46(4)	16(3)	23(3)	1(3)	3(3)	10(3)
C21	59(5)	17(3)	20(3)	3(2)	7(3)	13(3)
C22	67(5)	31(4)	26(4)	9(3)	3(3)	12(4)
C23	54(5)	31(4)	14(3)	7(3)	11(3)	19(3)
C24	62(6)	117(8)	70(6)	44(6)	-10(5)	19(6)
C25	59(5)	49(5)	42(4)	19(3)	13(4)	0(4)
C26	83(6)	21(4)	19(3)	7(3)	16(4)	16(4)
C27	54(5)	30(4)	23(3)	1(3)	11(3)	14(3)
C28	57(5)	27(4)	25(3)	1(3)	6(3)	8(3)
C29	82(6)	32(4)	31(4)	-7(3)	11(4)	20(4)
C30	91(6)	41(5)	41(4)	-2(4)	40(4)	10(4)

C31	91(7)	28(4)	41(4)	1(3)	22(4)	4(4)
C32	66(5)	22(4)	22(3)	5(3)	8(3)	14(3)
C33	60(5)	22(3)	26(3)	9(3)	14(3)	6(3)
C34	47(4)	26(4)	24(3)	10(3)	3(3)	10(3)
C35	95(7)	62(6)	73(6)	2(5)	43(5)	12(5)
C36	53(5)	40(4)	34(4)	9(3)	-8(3)	17(3)
C37	48(4)	22(3)	15(3)	7(2)	9(3)	5(3)
C38	55(5)	24(4)	26(3)	4(3)	11(3)	13(3)
C39	73(6)	32(4)	42(4)	11(3)	25(4)	25(4)
C40	78(6)	27(4)	28(4)	2(3)	24(4)	9(4)
C41	58(5)	34(4)	27(4)	4(3)	1(3)	-7(4)
C42	46(4)	28(4)	30(4)	8(3)	13(3)	4(3)
C43	44(4)	20(3)	20(3)	5(3)	2(3)	9(3)
C44	29(4)	22(3)	29(3)	2(3)	4(3)	5(3)
C45	28(4)	29(4)	23(3)	3(3)	-3(3)	9(3)
C46	20(3)	26(3)	15(3)	6(2)	-1(2)	7(3)
C47	33(4)	27(4)	20(3)	7(3)	5(3)	14(3)
C48	25(4)	26(3)	18(3)	3(3)	-3(3)	9(3)
C49	47(4)	21(3)	28(3)	6(3)	-4(3)	15(3)
C50	46(4)	18(3)	38(4)	8(3)	8(3)	15(3)
C51	35(4)	17(3)	19(3)	5(2)	2(3)	11(3)
C52	36(4)	21(3)	19(3)	6(3)	3(3)	10(3)
C53	30(4)	24(3)	17(3)	6(2)	-3(3)	13(3)
C54	47(5)	44(4)	15(3)	7(3)	-1(3)	19(3)
C55	33(4)	45(4)	38(4)	11(3)	4(3)	23(3)
C56	29(4)	17(3)	22(3)	3(2)	-3(3)	2(3)
C57	39(4)	32(4)	15(3)	4(3)	1(3)	7(3)
C58	32(4)	35(4)	25(3)	4(3)	8(3)	13(3)
C59	30(4)	19(3)	26(3)	1(3)	1(3)	8(3)
C60	54(5)	23(4)	19(3)	-4(3)	4(3)	9(3)
C61	58(5)	21(4)	35(4)	14(3)	11(3)	12(3)
C62	42(4)	20(3)	35(4)	1(3)	12(3)	0(3)
C63	48(4)	29(4)	18(3)	-3(3)	9(3)	4(3)
C64	37(4)	26(4)	30(4)	3(3)	7(3)	6(3)
N1	52(4)	17(3)	20(3)	6(2)	5(2)	11(2)
N2	71(4)	17(3)	23(3)	9(2)	9(3)	20(3)

N3	108(5)	20(3)	20(3)	9(2)	17(3)	22(3)
N4	82(4)	21(3)	19(3)	9(2)	12(3)	18(3)
N5	27(3)	18(3)	19(2)	4(2)	1(2)	6(2)
N6	34(3)	20(3)	18(2)	3(2)	0(2)	10(2)
S1	61(1)	33(1)	35(1)	17(1)	-7(1)	7(1)
S2	55(1)	27(1)	26(1)	10(1)	6(1)	10(1)
S3	80(2)	56(1)	46(1)	32(1)	-12(1)	9(1)
S4	74(1)	31(1)	30(1)	14(1)	14(1)	10(1)
S5	86(2)	27(1)	32(1)	10(1)	22(1)	23(1)
S6	64(1)	31(1)	28(1)	15(1)	13(1)	17(1)
S7	103(2)	36(1)	48(1)	16(1)	38(1)	13(1)
S8	76(2)	36(1)	36(1)	20(1)	13(1)	22(1)
S9	38(1)	25(1)	29(1)	5(1)	-6(1)	10(1)
S10	84(2)	19(1)	49(1)	0(1)	26(1)	-2(1)
O4	39(7)	29(5)	38(5)	2(4)	-2(4)	-1(4)
O5	111(7)	31(5)	40(5)	24(4)	45(5)	16(5)
O6	105(7)	44(5)	73(7)	-4(5)	54(6)	-18(5)
O4A	93(7)	45(5)	90(8)	0(5)	30(6)	-15(5)
O5A	31(7)	20(4)	30(4)	-2(3)	-4(4)	2(4)
O6A	123(7)	25(4)	30(5)	25(4)	35(5)	21(5)
Zn1	93(1)	18(1)	19(1)	6(1)	13(1)	18(1)
Zn2	36(1)	21(1)	19(1)	4(1)	0(1)	9(1)
O1	49(3)	67(3)	34(3)	8(2)	3(2)	36(3)
O2	61(3)	31(3)	49(3)	5(2)	-20(2)	8(2)
O3	49(3)	61(3)	44(3)	33(2)	0(2)	9(2)
O1A	75(4)	48(3)	85(4)	-8(3)	42(3)	5(3)

Table S5 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **1-Zn^{4-}•(2-Zn^{2+})$_2$**.

	x	y	z	U(eq)
H2	8000	8590	1126	30
H3	8277	10134	1261	33
H7	8028	12739	3387	38
H8	8231	12940	4709	41
H12	9220	10955	6558	53
H13	8935	9418	6427	53
H17	6826	6756	4094	46
H18	6757	6567	2790	45
H24A	4531	11206	131	126
H24B	3776	11965	15	126
H24C	4374	11871	820	126
H25A	9774	14324	2340	75
H25B	10448	14703	1787	75
H25C	10722	13822	1955	75
H27	10186	12983	5845	43
H28	10119	14054	6828	45
H29	8479	13913	7424	60
H30	6849	12728	7037	67
H31	6939	11637	6078	65
H35A	5595	8029	7185	113
H35B	4814	7301	7442	113
H35C	4659	7245	6593	113
H36A	8502	5185	5119	67
H36B	9362	4779	5696	67
H36C	9843	5719	5645	67
H38	9010	6851	2148	42
H39	8581	5620	1225	55
H40	6668	5285	316	52
H41	5210	6214	288	52
H42	5644	7460	1183	40

H44	3088	7683	1553	33
H45	4164	6537	1891	33
H49	3048	3222	1172	40
H50	1368	2177	196	40
H54	4968	4386	1067	43
H55	6803	4276	1913	45
H57	5212	5234	3529	36
H58	3414	5360	2671	37
H60	-915	1623	125	41
H61	-1207	170	-291	44
H63	-1332	433	-2327	40
H64	-953	1892	-1910	38
H1A1	4837	9925	4345	84
H1A2	5531	10811	4232	84
H2A1	4525	10176	2978	105
H2A2	3659	10612	3470	105
H2A3	3558	9611	3288	105
H1A3	4901	8885	3853	84
H1A4	5629	8571	3224	84
H2A4	3470	9293	3146	105
H2A5	3745	8525	2580	105
H2A6	4404	9468	2632	105

Table S6 Torsion angles [°] for 1-Zn^{4-}•(2-Zn^{2+})$_2$.

N1-C1-C2-C3	-1.9(7)	C13-C14-C15-C32	8.3(12)
C20-C1-C2-C3	175.4(6)	C14-C15-C16-N4	8.8(12)
C1-C2-C3-C4	0.3(7)	C32-C15-C16-N4	-171.2(6)
C2-C3-C4-N1	1.5(7)	C14-C15-C16-C17	-173.4(7)
C2-C3-C4-C5	-177.3(6)	C32-C15-C16-C17	6.6(11)
N1-C4-C5-C6	8.1(10)	N4-C16-C17-C18	2.6(8)
C3-C4-C5-C6	-173.3(6)	C15-C16-C17-C18	-175.4(7)
N1-C4-C5-C21	-166.5(6)	C16-C17-C18-C19	-1.5(8)
C3-C4-C5-C21	12.1(9)	C17-C18-C19-N4	-0.1(8)
C4-C5-C6-N2	5.2(11)	C17-C18-C19-C20	179.6(7)
C21-C5-C6-N2	179.7(6)	N1-C1-C20-C19	-4.8(11)
C4-C5-C6-C7	-170.2(6)	C2-C1-C20-C19	178.3(6)
C21-C5-C6-C7	4.3(10)	N1-C1-C20-C37	172.9(6)
N2-C6-C7-C8	2.0(7)	C2-C1-C20-C37	-4.0(10)
C5-C6-C7-C8	178.0(6)	N4-C19-C20-C1	-9.8(11)
C6-C7-C8-C9	-0.9(7)	C18-C19-C20-C1	170.5(6)
C7-C8-C9-N2	-0.4(8)	N4-C19-C20-C37	172.4(6)
C7-C8-C9-C10	-178.7(7)	C18-C19-C20-C37	-7.2(10)
N2-C9-C10-C11	-4.4(12)	C6-C5-C21-S2	60.0(8)
C8-C9-C10-C11	173.7(7)	C4-C5-C21-S2	-124.9(6)
N2-C9-C10-C26	178.8(7)	C6-C5-C21-S1	-116.3(6)
C8-C9-C10-C26	-3.1(11)	C4-C5-C21-S1	58.8(7)
C9-C10-C11-N3	-14.9(13)	S1-C22-C23-S4	179.1(4)
C26-C10-C11-N3	162.0(7)	S3-C22-C23-S4	-1.4(9)
C9-C10-C11-C12	168.9(8)	S1-C22-C23-S2	1.4(7)
C26-C10-C11-C12	-14.3(12)	S3-C22-C23-S2	-179.1(4)
N3-C11-C12-C13	-1.2(9)	C9-C10-C26-C31	118.0(8)
C10-C11-C12-C13	175.6(7)	C11-C10-C26-C31	-59.1(9)
C11-C12-C13-C14	-0.9(9)	C9-C10-C26-C27	-60.3(10)
C12-C13-C14-N3	2.8(9)	C11-C10-C26-C27	122.6(7)
C12-C13-C14-C15	-175.2(7)	C31-C26-C27-C28	1.4(10)
N3-C14-C15-C16	10.7(13)	C10-C26-C27-C28	179.7(6)
C13-C14-C15-C16	-171.6(8)	C26-C27-C28-C29	-0.8(9)
N3-C14-C15-C32	-169.3(7)	C27-C28-C29-C30	-0.9(10)

C28-C29-C30-C31	1.9(11)	C53-C47-C48-C49	0.2(9)
C29-C30-C31-C26	-1.2(11)	C47-C48-C49-C50	-177.5(6)
C27-C26-C31-C30	-0.4(11)	N6-C48-C49-C50	2.9(7)
C10-C26-C31-C30	-178.8(7)	C48-C49-C50-C51	-2.2(7)
C16-C15-C32-S6	49.6(9)	C49-C50-C51-N6	0.9(7)
C14-C15-C32-S6	-130.4(6)	C49-C50-C51-C52	-175.7(6)
C16-C15-C32-S5	-128.7(6)	N6-C51-C52-C43#1	-0.7(10)
C14-C15-C32-S5	51.3(9)	C50-C51-C52-C43#1	175.3(6)
S5-C33-C34-S6	1.3(7)	N6-C51-C52-C59	179.8(5)
S7-C33-C34-S6	-178.9(3)	C50-C51-C52-C59	-4.2(9)
S5-C33-C34-S8	-177.6(3)	C48-C47-C53-C54	64.0(8)
S7-C33-C34-S8	2.2(8)	C46-C47-C53-C54	-115.4(7)
C1-C20-C37-C42	-70.3(8)	C48-C47-C53-C58	-113.6(6)
C19-C20-C37-C42	107.6(7)	C46-C47-C53-C58	67.0(8)
C1-C20-C37-C38	113.8(7)	C58-C53-C54-C55	0.8(9)
C19-C20-C37-C38	-68.3(8)	C47-C53-C54-C55	-176.9(6)
C42-C37-C38-C39	0.0(9)	C53-C54-C55-C56	0.6(10)
C20-C37-C38-C39	176.0(6)	C54-C55-C56-C57	-1.4(9)
C37-C38-C39-C40	-1.3(10)	C54-C55-C56-S9	177.5(5)
C38-C39-C40-C41	1.6(10)	C55-C56-C57-C58	0.7(9)
C39-C40-C41-C42	-0.7(10)	S9-C56-C57-C58	-178.2(4)
C38-C37-C42-C41	0.9(9)	C56-C57-C58-C53	0.8(9)
C20-C37-C42-C41	-174.9(6)	C54-C53-C58-C57	-1.6(9)
C40-C41-C42-C37	-0.6(10)	C47-C53-C58-C57	176.2(5)
N5-C43-C44-C45	-1.7(7)	C51-C52-C59-C60	59.1(8)
C52#1-C43-C44-C45	178.5(6)	C43#1-C52-C59-C60	-120.4(7)
C43-C44-C45-C46	0.7(7)	C51-C52-C59-C64	-121.2(6)
C44-C45-C46-N5	0.4(7)	C43#1-C52-C59-C64	59.3(8)
C44-C45-C46-C47	179.8(6)	C64-C59-C60-C61	2.8(9)
N5-C46-C47-C48	6.1(10)	C52-C59-C60-C61	-177.5(6)
C45-C46-C47-C48	-173.2(6)	C59-C60-C61-C62	-2.2(10)
N5-C46-C47-C53	-174.5(5)	C60-C61-C62-C63	0.0(9)
C45-C46-C47-C53	6.2(9)	C60-C61-C62-S10	-177.4(5)
C46-C47-C48-N6	-0.8(10)	C61-C62-C63-C64	1.4(10)
C53-C47-C48-N6	179.8(5)	S10-C62-C63-C64	178.8(5)
C46-C47-C48-C49	179.6(6)	C62-C63-C64-C59	-0.7(10)

C60-C59-C64-C63	-1.4(9)	C52#1-C43-N5-Zn2	8.6(9)
C52-C59-C64-C63	178.9(6)	C44-C43-N5-Zn2	-171.2(4)
C5-C4-N1-C1	176.1(6)	C47-C46-N5-C43	179.2(6)
C3-C4-N1-C1	-2.7(7)	C45-C46-N5-C43	-1.4(6)
C5-C4-N1-Zn1	-2.6(9)	C47-C46-N5-Zn2	-7.6(8)
C3-C4-N1-Zn1	178.6(4)	C45-C46-N5-Zn2	171.8(4)
C20-C1-N1-C4	-174.4(6)	C52-C51-N6-C48	177.4(6)
C2-C1-N1-C4	2.9(7)	C50-C51-N6-C48	0.9(6)
C20-C1-N1-Zn1	4.3(9)	C52-C51-N6-Zn2	-2.2(9)
C2-C1-N1-Zn1	-178.4(4)	C50-C51-N6-Zn2	-178.7(4)
C5-C6-N2-C9	-178.2(6)	C47-C48-N6-C51	178.0(6)
C7-C6-N2-C9	-2.1(7)	C49-C48-N6-C51	-2.3(7)
C5-C6-N2-Zn1	-21.6(9)	C47-C48-N6-Zn2	-2.4(9)
C7-C6-N2-Zn1	154.5(4)	C49-C48-N6-Zn2	177.3(4)
C10-C9-N2-C6	179.9(7)	C5-C21-S1-C22	175.7(5)
C8-C9-N2-C6	1.6(8)	S2-C21-S1-C22	-1.0(4)
C10-C9-N2-Zn1	23.5(10)	C23-C22-S1-C21	-0.3(6)
C8-C9-N2-Zn1	-154.9(4)	S3-C22-S1-C21	-179.8(4)
C15-C14-N3-C11	174.5(7)	C5-C21-S2-C23	-174.8(5)
C13-C14-N3-C11	-3.5(9)	S1-C21-S2-C23	1.6(4)
C15-C14-N3-Zn1	-11.3(11)	C22-C23-S2-C21	-1.8(6)
C13-C14-N3-Zn1	170.7(5)	S4-C23-S2-C21	-179.5(4)
C10-C11-N3-C14	-173.9(8)	C23-C22-S3-C24	-162.2(6)
C12-C11-N3-C14	2.9(9)	S1-C22-S3-C24	17.3(6)
C10-C11-N3-Zn1	11.8(11)	C22-C23-S4-C25	168.7(6)
C12-C11-N3-Zn1	-171.5(5)	S2-C23-S4-C25	-13.8(5)
C15-C16-N4-C19	175.6(7)	C15-C32-S5-C33	177.1(6)
C17-C16-N4-C19	-2.6(8)	S6-C32-S5-C33	-1.2(4)
C15-C16-N4-Zn1	-25.7(10)	C34-C33-S5-C32	-0.1(6)
C17-C16-N4-Zn1	156.1(5)	S7-C33-S5-C32	-179.8(4)
C20-C19-N4-C16	-178.0(7)	C15-C32-S6-C34	-176.5(5)
C18-C19-N4-C16	1.7(8)	S5-C32-S6-C34	1.8(4)
C20-C19-N4-Zn1	23.0(10)	C33-C34-S6-C32	-1.9(6)
C18-C19-N4-Zn1	-157.3(5)	S8-C34-S6-C32	177.0(4)
C52#1-C43-N5-C46	-178.3(6)	C34-C33-S7-C35	-157.4(6)
C44-C43-N5-C46	1.9(6)	S5-C33-S7-C35	22.3(5)

C33-C34-S8-C36	175.0(5)	C4-N1-Zn1-N3	-94.6(10)
S6-C34-S8-C36	-3.9(5)	C1-N1-Zn1-N3	86.8(10)
C57-C56-S9-O2	-66.8(6)	C4-N1-Zn1-N4	-176.3(5)
C55-C56-S9-O2	114.3(5)	C1-N1-Zn1-N4	5.2(5)
C57-C56-S9-O1	171.4(5)	C4-N1-Zn1-N2	-8.6(5)
C55-C56-S9-O1	-7.5(6)	C1-N1-Zn1-N2	172.9(5)
C57-C56-S9-O3	52.2(5)	C4-N1-Zn1-O1A	85.6(5)
C55-C56-S9-O3	-126.7(5)	C1-N1-Zn1-O1A	-93.0(5)
C63-C62-S10-O6A	142.2(7)	C6-N2-Zn1-N3	-172.4(6)
C61-C62-S10-O6A	-40.4(7)	C9-N2-Zn1-N3	-20.0(5)
C63-C62-S10-O4	-1.7(7)	C6-N2-Zn1-N4	105.2(9)
C61-C62-S10-O4	175.7(6)	C9-N2-Zn1-N4	-102.4(10)
C63-C62-S10-O6	-128.0(7)	C6-N2-Zn1-N1	19.8(5)
C61-C62-S10-O6	49.4(7)	C9-N2-Zn1-N1	172.2(5)
C63-C62-S10-O5A	20.1(7)	C6-N2-Zn1-O1A	-73.8(5)
C61-C62-S10-O5A	-162.5(6)	C9-N2-Zn1-O1A	78.6(5)
C63-C62-S10-O4A	-96.1(7)	C43-N5-Zn2-N6#1	-4.6(5)
C61-C62-S10-O4A	81.3(7)	C46-N5-Zn2-N6#1	-176.4(5)
C63-C62-S10-O5	116.9(6)	C43-N5-Zn2-N6	175.4(5)
C61-C62-S10-O5	-65.8(6)	C46-N5-Zn2-N6	3.6(5)
C14-N3-Zn1-N4	-1.9(7)	C51-N6-Zn2-N5	-179.6(5)
C11-N3-Zn1-N4	171.3(7)	C48-N6-Zn2-N5	1.0(5)
C14-N3-Zn1-N1	-83.6(11)	C51-N6-Zn2-N5#1	0.4(5)
C11-N3-Zn1-N1	89.6(11)	C48-N6-Zn2-N5#1	-179.0(5)
C14-N3-Zn1-N2	-169.7(7)	N3-Zn1-O1A-C1AA	-89.7(14)
C11-N3-Zn1-N2	3.5(6)	N4-Zn1-O1A-C1AA	0.1(14)
C14-N3-Zn1-O1A	96.2(7)	N1-Zn1-O1A-C1AA	90.3(14)
C11-N3-Zn1-O1A	-90.6(6)	N2-Zn1-O1A-C1AA	179.9(14)
C16-N4-Zn1-N3	19.6(6)	N3-Zn1-O1A-C1A	31.9(9)
C19-N4-Zn1-N3	174.2(6)	N4-Zn1-O1A-C1A	121.8(9)
C16-N4-Zn1-N1	-172.5(6)	N1-Zn1-O1A-C1A	-148.1(9)
C19-N4-Zn1-N1	-17.9(6)	N2-Zn1-O1A-C1A	-58.4(9)
C16-N4-Zn1-N2	102.1(10)	C1AA-O1A-C1A-C2A	-75.1(15)
C19-N4-Zn1-N2	-103.2(9)	Zn1-O1A-C1A-C2A	158.9(8)
C16-N4-Zn1-O1A	-78.8(6)	C1A-O1A-C1AA-C2AA	77(2)
C19-N4-Zn1-O1A	75.8(6)	Zn1-O1A-C1AA-C2AA	-145.6(19)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z

References

(S1) *SAINT V8.27B,* Bruker AXS Inc, Madison, Wisconsin, USA, 2012.

(S2) A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. J. Spagna, *Appl. Cryst*., 1999, **32**, 115-119.

(S3) G. M. Sheldrick *Acta Cryst*., 2008, **A64**, 112.

(S4) A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, The Netherlands, 1998.

(S5) L. J. Farrugia, *J. Appl. Cryst*., 1999, **32**, 837.

(S6) P. v. d. Sluis and A. L. Spek, *Acta Cryst*., 1990, **A46**, 194.

(S7) *International Tables for X-ray Crystallography, Vol. C*, Tables 4.2.6.8 and 6.1.1.4, ed. A. J. C. Wilson, Boston, Kluwer Academic Press, 1992.

(S8) G. M. Sheldrick, *SHELXTL/PC (Version 5.03*), Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA, 1994.