Two dual-emissive Zn(II) coordination polymers with tunable photoluminescence properties

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Experimental Section

All reactants were reagent grade and used as purchased without further purification. Elemental analyses for C, H, N were carried out on a German Elementary Vario EL III instrument. The FT-IR spectra were performed on a Nicolet Magna 750 FT-IR spectrometer using KBr pellets in the range of 4000-400 cm^{-1}. Thermogravimetric analyses were recorded on a NETZSCH STA 449C unit at a heating rate of 10℃ · min^{-1} under nitrogen atmosphere. The power X-ray diffraction (XRD) patterns were collected by a Rigaku DMAX2500 X-ray diffractometer using Cu Kα radiation (λ=0.154 nm). Fluorescent analysis of the complexes was performed on an Edinburgh Instruments FLS920 spectrofluorimeter equipped with both continuous (450 W) and pulse xenon lamps.

Synthesis of $[Zn_2(Hcpop)_2(dpe) (H_2O)]_n \cdot ndpe$ (1). A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.4 mmol, 118 mg), H_3cpop (0.05 mmol, 16 mg) and 6mL H_2O was stirred for 15 minutes, then a solution of dpe (0.15 mmol, 27mg) in 6ml n-pentenol was added with stirring at room temperature. After 15 minutes, the mixture was introduced in 20mL capped vial, which was heated to 85 ℃ for 72 hours. The resulting yellow rod-like crystals of **6** were filtered in 62% yield based on H_3cpop. Anal. Calcd for $C_{54}N_4O_{15}H_{38}Zn_2$ (Mr = 1113.62): cal: C, 58.24 %; H, 3.44%; N, 5.03%. found: C, 57.87%; H, 3.52%; N, 5.12%. Selected IR data (KBr pellet, cm^{-1}): 3650 (w), 3071 (w), 1617 (s), 1579 (s), 1504 (w), 1397 (m), 1365 (m), 1234 (m), 845 (m), 779 (w), 552 (m).

Synthesis of $[Zn_4(cpop)_2(dpe)_2(\mu\text{-OH})_2]_n \cdot ndpe$ (2). The preparation of **2** was similar to that of **1** except that the acetonitrile was used instead of n-pentenol. After cooling to room temperature, light yellow block-shaped crystals of **2** were obtained in 77% yield based on H_3cpop. Anal. Calcd for $C_{66}N_6O_{16}H_{46}Zn_4$ (Mr = 1440.74): cal: C, 55.02 %; H, 3.22%; N, 5.83%. found: C, 54.84%; H, 3.28%; N, 5.72%. Selected IR data (KBr pellet, cm^{-1}): 3394 (w), 3048 (w), 1612 (s), 1590 (s), 1504 (m), 1394 (m), 1259 (m), 1230 (m), 1207 (w), 842 (m), 791 (w), 553 (m).

Crystallographic Analyses

The intensity data were collected on a Rigaku Mercury CCD diffractometer equipped with a graphite-monochromated Mo Kα radiation (λ=0.71073 Å) at room temperature. All absorption corrections were performed by using the multiscan program. The structure were solved by direct methods and refined by full-matrix least squares on F^2 with the SHELXTL-97 program.[1] Crystallographic data for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Center with CCDC reference numbers 871847 and 834613 for complexes **1-2**.

Thermal Gravimetric Analysis (TGA)

To examine the thermal stability of the complex **1** and **2**, the thermal gravimetric analysis (TGA) experiments were carried out in the temperature range of 30-800 ℃ under a flow of nitrogen with heating rate of 10 ℃·min^{-1} (Fig. S6). A total loss of 1.72% was observed for **1** in the temperature range of 30-190 ℃, which can be attributed to the loss of one coordinated aqua molecule (calcd

1.62%), and the decomposition of the residue was observed at about 240 ℃.TGA for **2** shows no obvious weight loss between 30 and about 300℃. On further heating, the framework gradually decomposes.

X-ray Diffractometer Analysis (XRD)

For complex **1** and **2**, the positions of diffraction peaks of the experimental are consistent with the simulated XRD patterns well, indicating the phase purity of the as-synthesized simple (Fig. S7).
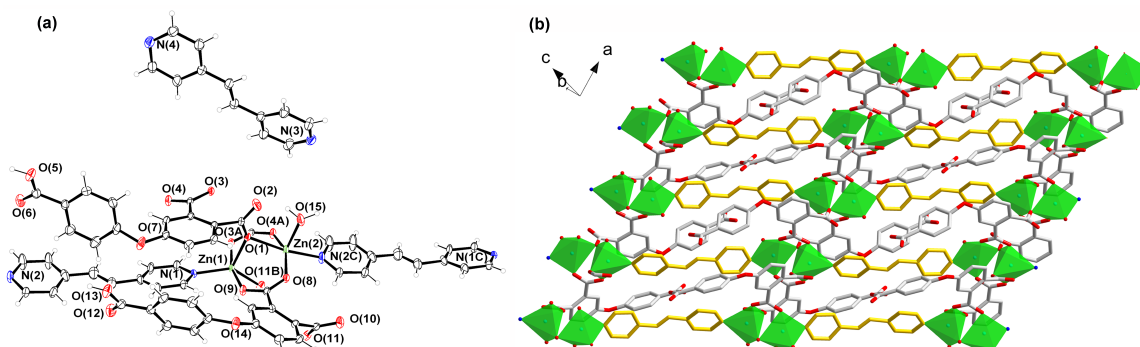

Fig. S1 (a) The coordination environment of Zn(II) atoms in complex **1**. Symmetry transformations used to generate equivalent atoms: A= -x, -y, 1-z, B= -x-1, y, 1-z, C=x-1, y, 1+z. (b) 2D (4, 4)-connected network constructed from 1D chains of **1**.
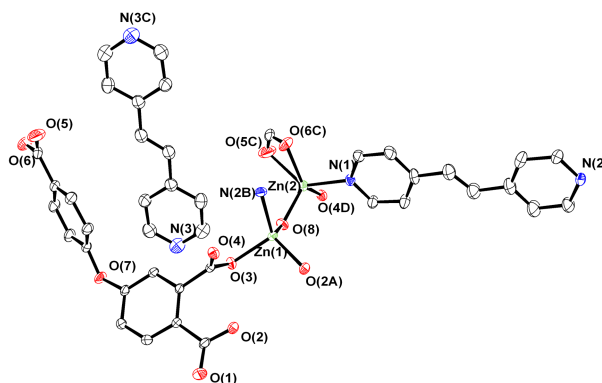

Fig. S2 The coordination environment of Zn(II) atoms in complex **2** (the hydrogen atoms are omitted for clarity). Symmetry transformations used to generate equivalent atoms: A= 1-x, 1-y, -z, B= 1+x, 3/2-y, 1/2+z, C= 1-x, 1-y, 1-z-, D= x-1, y, z.
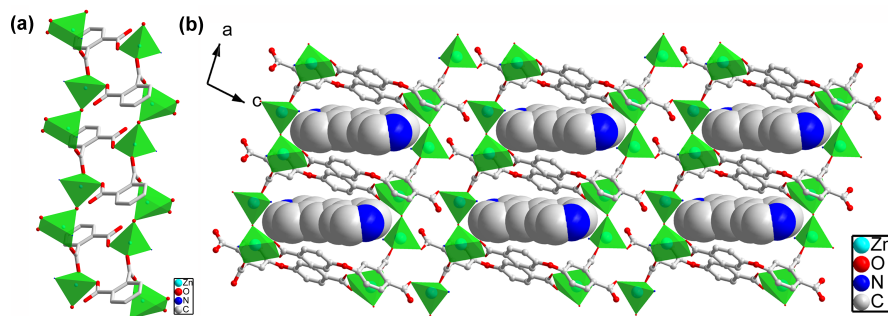
Fig. S3 (a) View of 1D double chain based on binuclear Zn_2 clusters in **2**. (b) The drawing of cavities in complex **2**, the uncoordinated dpe ligands reserved in these cavities represent as space-filling mode.
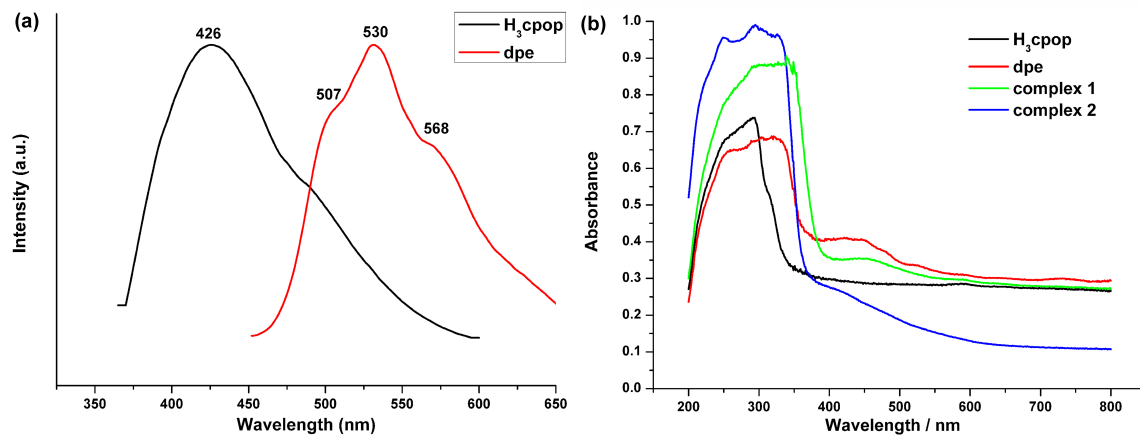

Fig. S4 (a) Normalized emission spectra of ligands H_3cpop and dpe at room temperature. (b) UV/Vis spectra of H_3cpop, dpe and complexes **1-2** at room temperature.
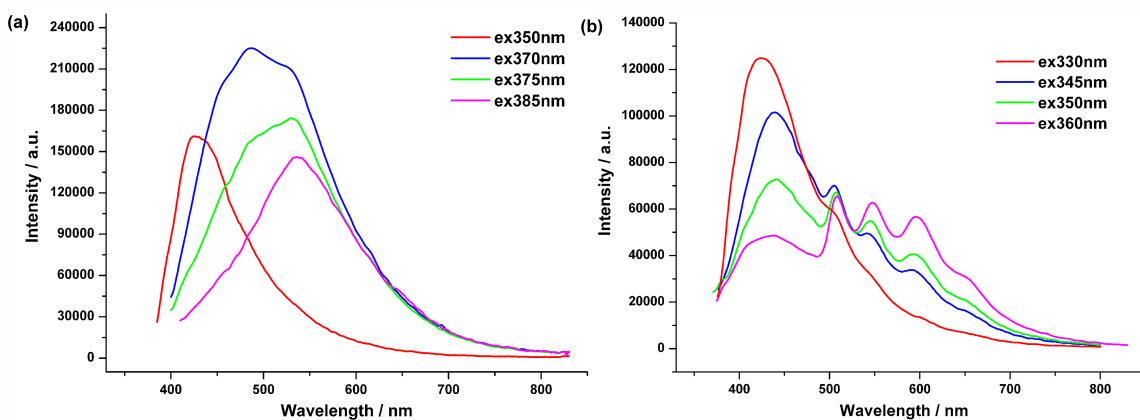

Fig. S5 Solid-state PL spectra of **1** (a) and **2** (b) by variation of excitation length under the same metrical condition at 10 K.
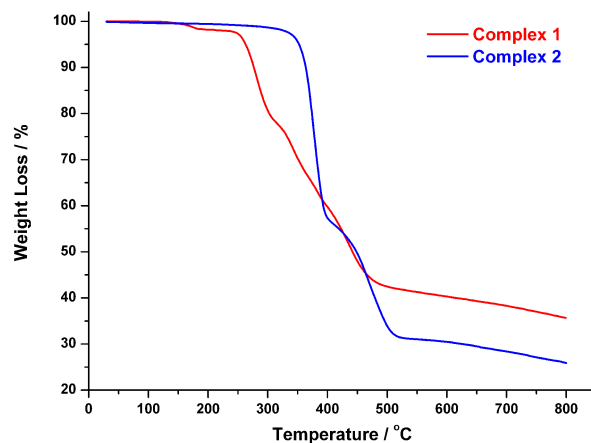

Fig. S6 TGA curves for complexes **1** and **2**

(a)

(b)
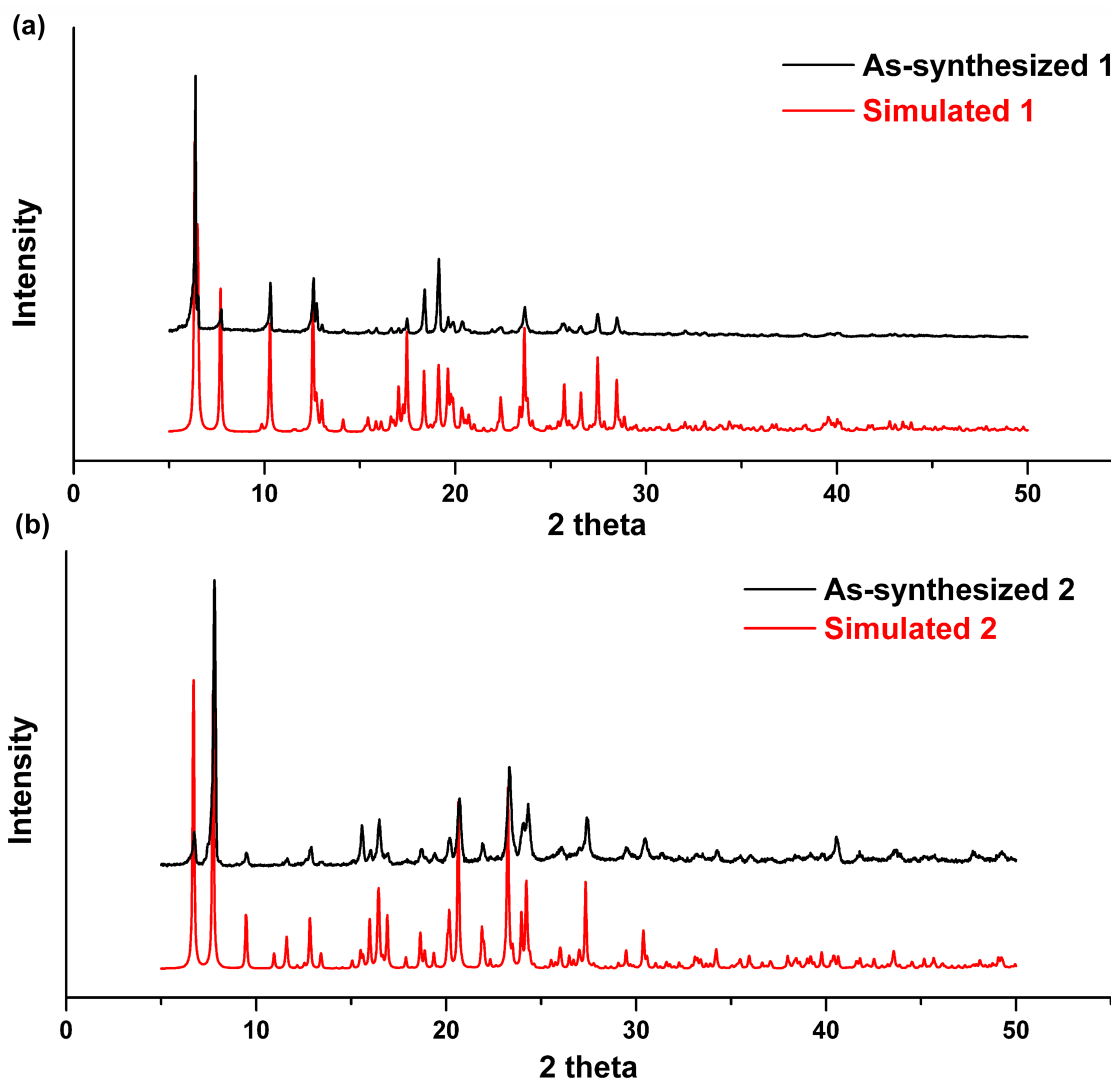
Fig. S7 Powder X-ray diffraction patterns of the simulated and as-synthesized samples of **1** and **2.**

Table S1. Selected Hydrogen-bond Lengths (Å) and Angles (°) for **1**[a]

	D—H	H...A	D...A	D—H...A
O13—H13A...N4[i]	0.92	1.75	2.593 (4)	152.6
O5—H5A...N3[ii]	0.91	1.66	2.563 (4)	173.7

[a]Symmetry codes: (i) 1-x, 1-y, -z; (ii) 1+x, y, -1+z.

Table S2. Luminescence Lifetimes of Complexes **1** and **2**[a]

Complex **1**[b]		Complex **2**[c]	
λ_{em}/nm	τ/ns	λ_{em}/nm	τ/ns
450	0.58/3.20/16.9	430	0.50/2.93
540	2.59/0.43/8.04	515	0.69/3.44/11.1
		550	0.84/4.11/13.9
		595	1.04/2.59/14.3

[a]Measurements were performed at room temperature. [b]Lifetimes determined following excitation at

350 nm and 397 nm, respectively. [c]Lifetimes determined following excitation at 360 nm.

Table S3. Quantum yield of complexes 1 and 2 at room temperature (298K) and 10K

Complex 1	$\Phi_{f,ex\ 350}$/ %	$\Phi_{f,ex\ 370}$/ %	$\Phi_{f,ex\ 375}$/ %	$\Phi_{f,ex\ 385}$/ %
298K	2.09	2.34	2.39	2.60
10K	6.28	14.59	11.14	8.74
Complex 2	$\Phi_{f,ex\ 330}$/ %	$\Phi_{f,ex\ 345}$/ %	$\Phi_{f,ex\ 350}$/ %	$\Phi_{f,ex\ 360}$/ %
298K	2.02	2.81	3.25	4.59
10K	9.44	9.72	8.98	8.90

Table S4. Crystallographic data and structure refinement details for **1** and **2**

complexes	1	2
chemical formula	$C_{54}N_4O_{15}H_{38}Zn_2$	$C_{66}N_6O_{16}H_{46}Zn_4$
formula weight	1113.62	1440.64
crystal system	Triclinic	Monoclinic
space group	P-1	$P2_1/c$
a (Å)	11.697(2)	7.778(2)
b (Å)	14.521(3)	22.865(7)
c (Å)	14.760(3)	16.384(5)
α (°)	73.646(4)	90.00
β (°)	73.937(5)	99.471(5)
γ (°)	87.731(7)	90.00
V(Å^3)	2309.7(8)	2876(2)
Z	2	4
T/K	298(2)	298(2)
D_C (g cm^{-3})	1.601	1.665
μ(mm^{-1})	1.12	1.73
$F(000)$	1140	1464
θ range (°)	2.0–25.0	2.2–27.5
Collected reflections	7862	6562
unique reflections	5471	5846
parameters	676	415
Gof on F^2	0.935	1.014
$R_1{}^a$ ($I > 2\sigma(I)$)	0.0450	0.0393

$wR_2{}^b$ (all data)	0.1000		0.1131

$^a R_1 = \Sigma||F0| - |Fc||/\Sigma|F0|.$ $^b wR2 = [\Sigma w(Fo^2 - Fc^2)^2/\Sigma w(F0)^2]^{1/2}.$

Table S5. Selected Bond Lengths (Å) and Bond Angles (°) for **1** and **2**

1			
Zn1—O11^i	2.001 (2)	Zn2—O4^{ii}	2.002 (2)
Zn1—N1	2.002 (2)	Zn2—O8	2.013 (2)
Zn1—O1	2.066 (2)	Zn2—O15	2.056 (3)
Zn1—O9	2.095 (2)	Zn2—N2^{iii}	2.073 (3)
Zn1—O3^{ii}	2.100 (2)	Zn2—O1	2.263 (2)
O11^i—Zn1—N1	137.65 (11)	O4^{ii}—Zn2—O8	155.48 (9)
O11^i—Zn1—O1	107.25 (9)	O4^{ii}—Zn2—O15	103.14 (11)
N1—Zn1—O1	114.92 (10)	O8—Zn2—O15	97.78 (11)
O11^i—Zn1—O9	85.09 (9)	O4^{ii}—Zn2—N2^{iii}	93.66 (10)
N1—Zn1—O9	95.06 (10)	O8—Zn2—N2^{iii}	98.73 (10)
O1—Zn1—O9	84.20 (9)	O15—Zn2—N2^{iii}	90.85 (12)
O11^i—Zn1—O3^{ii}	87.28 (9)	O4^{ii}—Zn2—O1	83.63 (8)
N1—Zn1—O3^{ii}	100.75 (9)	O8—Zn2—O1	86.47 (8)
O1—Zn1—O3^{ii}	83.65 (9)	O15—Zn2—O1	82.78 (9)
O9—Zn1—O3^{ii}	163.06 (8)	N2^{iii}—Zn2—O1	172.30 (11)

Symmetry codes: (i) -1-x, -y, 1-z, (ii) -x, -y, 1-z, (iii) -1+x, y, 1+z

2			
Zn1—O8	1.9508 (18)	Zn2—O8	1.9265 (17)
Zn1—O2^i	1.9738 (18)	Zn2—O4^{iii}	1.9982 (17)
Zn1—O3	2.0173 (17)	Zn2—O6^{iv}	2.101 (3)
Zn1—N2^{ii}	2.052 (2)	Zn2—O5^{iv}	2.300 (3)
N1—Zn2	2.057 (2)	O8—Zn2—O6^{iv}	109.74 (10)
O8—Zn1—O2^i	115.78 (8)	O4^{iii}—Zn2—O6^{iv}	137.00 (10)
O8—Zn1—O3	97.82 (8)	N1—Zn2—O6^{iv}	92.87 (10)
O2^i—Zn1—O3	103.96 (8)	O8—Zn2—O5^{iv}	111.44 (9)

O8—Zn1—N2^{ii}	107.96 (8)	O4^{iii}—Zn2—O5^{iv}	90.26 (9)
O2^{i}—Zn1—N2^{ii}	118.40 (9)	N1—Zn2—O5^{iv}	133.89 (10)
O3—Zn1—N2^{ii}	110.82 (8)	O6^{iv}—Zn2—O5^{iv}	58.71 (11)
O8—Zn2—O4^{iii}	109.13 (8)	O8—Zn2—O6^{iv}	109.74 (10)
O8—Zn2—N1	112.26 (8)	O4^{iii}—Zn2—O6^{iv}	137.00 (10)
O4^{iii}—Zn2—N1	88.95 (8)		

Symmetry codes: (i) 1-x, 1-y, -z, (ii) 1+x, 3/2-y, 1/2+z, (iii) -1+x, y, z, (iv) 1-x, 1-y, 1-z, (v) -1+x, 3/2-y, -1/2+z, (vi) 1+x, y, z.

Table S6. List of π-π interactions in complexes **1** and **2**[a].

Complex **1**					
Ring A	Ring B	Cg-Cg (Å)	Dihedral angel (°)	CgA_Perp(Å)	Slippage(Å)
R1	R2	3.8306	10.02	3.552	1.434
R3	R3^{i}	3.8684	0.00	3.591	1.439

R1 = N(1)-C(33)-C(32)-C(31)-C(35)-C(34)   R2 = C(1)-C(2)-C(3)-C(4)-C(5)-C(6)
R3 = N(3)-C(45)-C(44)-C(43)-C(47)-C(46)
Symmetry codes: (i) -x, 1-y, 1-z.

Complex **2**					
Ring A	Ring B	Cg-Cg (Å)	Dihedral angel (°)	CgA_Perp(Å)	Slippage(Å)
R1	R2^{i}	4.3922	8.58	3.981	1.856

R1 = N(1)-C(18)-C(17)-C(16)-C(20)-C(19)   R2 = N(2)-C(25)-C(24)-C(23)-C(27)-C(26)
Symmetry codes: (i) x, 1/2-y, -1/2+z.

[a]Cg-Cg = Distance between ring Centroids, CgA_Perp = Perpendicular distance of Cg(A) on ring B, Slippage = Distance between Cg(A) and Perpendicular Projection of Cg(B) on Ring A.

Reference

1 G. M. Sheldrick, SHELXS-97, Programs for X-ray Crystal Structure Solution; University of Göttingen: Germany, 1997.