

Two multifunctional stimuli-responsive materials with room-temperature phosphorescence and their applications in multiple dynamic encryption

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Materials and instrumentation

All solvents and metal ions ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) in the present work were available from commercial sources and used without further purification. 1-(3-carboxybenzyl)-4,4'-bipyridinium chloride (Hcbbbc) was purchased from the Jinan Henghua Trading Company in China. Single crystal X-ray diffraction data were collected by XtaLAB Synergy-DW area-detector diffractometer using mirror optics monochromated Cu-K α radiation ($\lambda = 1.54184 \text{ \AA}$) at low temperature (100 K). Fourier transform infrared (FT-IR) spectra were recorded on an Avatar 360 FT-IR spectrometer using KBr pellets in 4000-400 cm^{-1} . X-ray powder diffraction (PXRD) pattern was collected using a SHIMADZU XRD-7000 diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) at 25°C. Elemental analyses (CHN) were conducted using a Vario EL elemental analyzer. Thermogravimetric data (TGA) were obtained using a Mettler TGA instrument in the range of 25–500°C under nitrogen flow with a heating rate of 10°C min^{-1} . Solid-state UV-Vis diffuse reflectance spectra were recorded on a TU-1901 spectrophotometer with an integrating sphere at room temperature in the range of 250–800 nm. The UV light was generated by a hand-held UV lamp (365 nm). Electron paramagnetic resonance (EPR) signals were recorded with a Bruker E500 system. The fluorescence spectra were recorded on an FS5 fluorescence spectrophotometer with a quartz cuvette (path length of 1 cm), and the lifetime was measured on an FLS980 instrument.

Synthesis of $\{[\text{Zn}(\text{cbbpy})(\text{HBTC})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}\}_n$ (1). A mixture of Hcbbpy (32.6 mg, 0.1 mmol) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (29.7 mg, 0.1 mmol) was added to a mixture of CH_3CN (5 mL) and 4 mL NaOH (0.05 mol/L) in a 15 mL glass bottle and then stirred for 30 min. Another H_3BTC (21.1 mg, 0.1 mmol) was added into 4 mL NaOH (0.05 mol/L) then stirred for 30 min. After putting the two kinds of solution together and stirred 10 min, the resulting solution was filtrated and slowly evaporated in the air at room temperature. After 7 days, colorless block crystals were collected by filtration, and dried in the air (48% yield based on Hcbbpy). Elemental analysis: calcd for $\text{C}_{27}\text{H}_{24}\text{N}_2\text{O}_{10}\text{Zn}$: C, 53.55; H, 4.02; N, 4.65%. Found: C, 53.43; H, 3.94; N, 4.38%. IR (KBr, cm^{-1}): 3431 s, 1708 m, 1619 s, 1431 m, 1366 s, 1252 m, 1186 w, 758 w, 715 w, 682 w.

Synthesis of $[\text{Cd}(\text{cbbpy})(\text{HBTC})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ (2). Synthesis of **2** was similar to that of **1** except that $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (29.7 mg, 0.1 mmol) was replaced by $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (30.1 mg, 0.1 mmol). Colorless block-shaped crystals were collected by filtration, the yield was 56% (based on Hcbbpy). Calculated for $\text{C}_{27}\text{H}_{24}\text{N}_2\text{O}_{10}\text{Cd}$: C 49.98, H 3.73, N 4.32%. Found: C 55.34, H 3.12, N 7.86%. IR (KBr pellet, cm^{-1}): 3463 s, 1614 s, 1386 m, 1349 m, 1138 w, 1069 w, 677 w, 608 w, 635 w.

X-ray Diffraction Analysis.

Crystallographic data of complexes **1**, **1T**, **1Q** and **2** were collected on the XtaLAB Synergy-DW diffractometer with Cu K α radiation ($\lambda = 1.54184 \text{ \AA}$, powered at 4 kW) at 100 K. The crystal structures were solved and refined using the Olex2 program and all hydrogen atoms were added automatically. Absorption corrections were applied by using the program SADABS. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions. Crystal data and structure refinement parameters were summarized in Table S1. Selected bond distances (Å) and angles (deg) were displayed in Table S3.

Computational Details

Vienna Ab Initio Simulation Package (VASP) was employed for density of states (DOS) theory calculations, for which the GGA-type PBE functional was used. The experimental crystal structure was used for calculations with the following parameters: the cut-off for the kinetic energy of the plane-waves was set to 450 eV. Γ -Centered Gamma $3 \times 2 \times 2$ grids were used for the Brillouin zone sampling in the crystal calculations.

Gaussian 09 software was employed for analyzing the molecule frontier orbitals to further demonstrate the mechanism of photochromism. The single point energy of the singlet and triplet ground states has been performed with a PBE0 functional with def2SVP basis set.

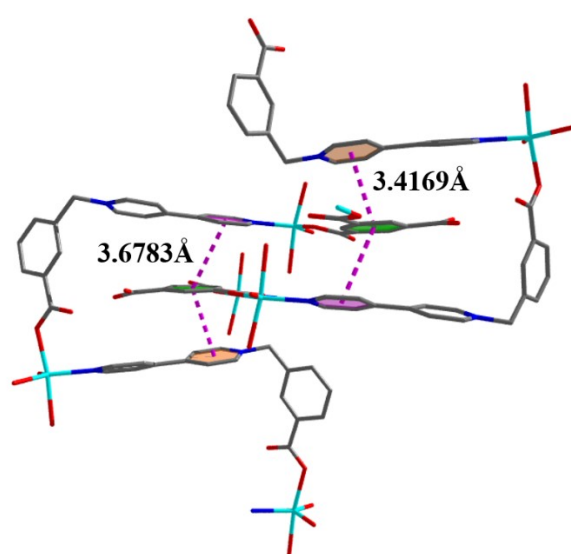


Figure S1. The π - π stacking interactions of complex 1.

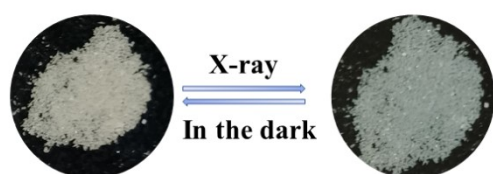


Figure S2. Photographs of the complex 2 before and after X-ray irradiation.

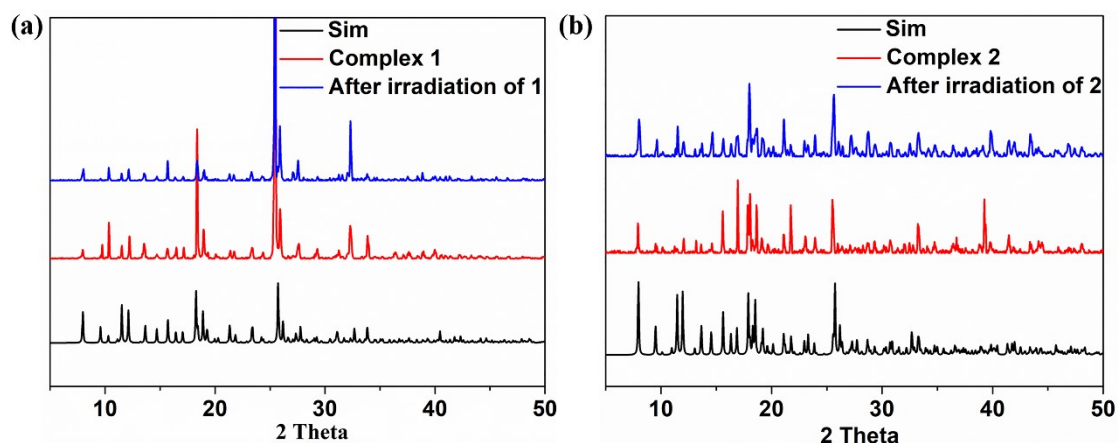


Figure S3. The PXRD of **1** (a) and **2** (b) before and after irradiation by UV light.

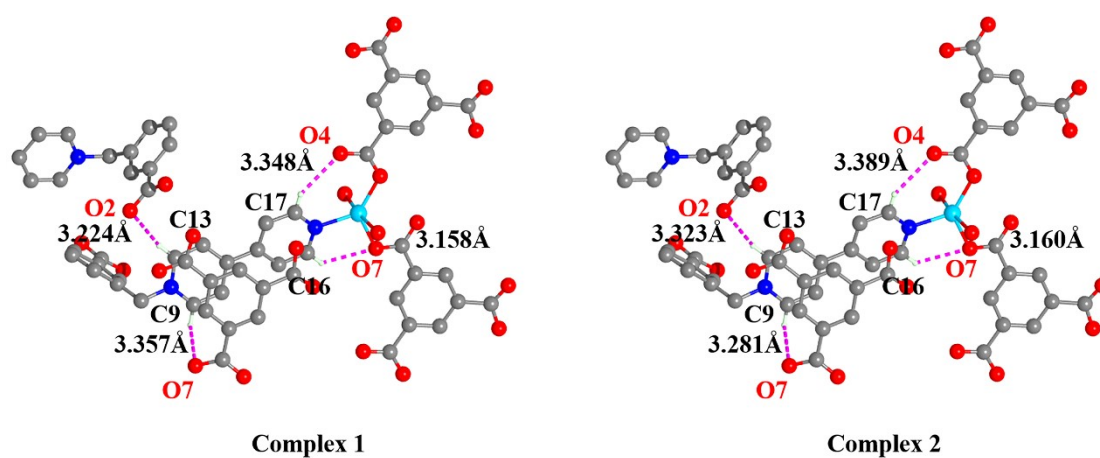


Figure S4. Possible electron transfer pathways by hydrogen bonding of **1** and **2**. (Hydrogen bonding is demonstrated with purple dashed lines with C...O (Å) distances provided)

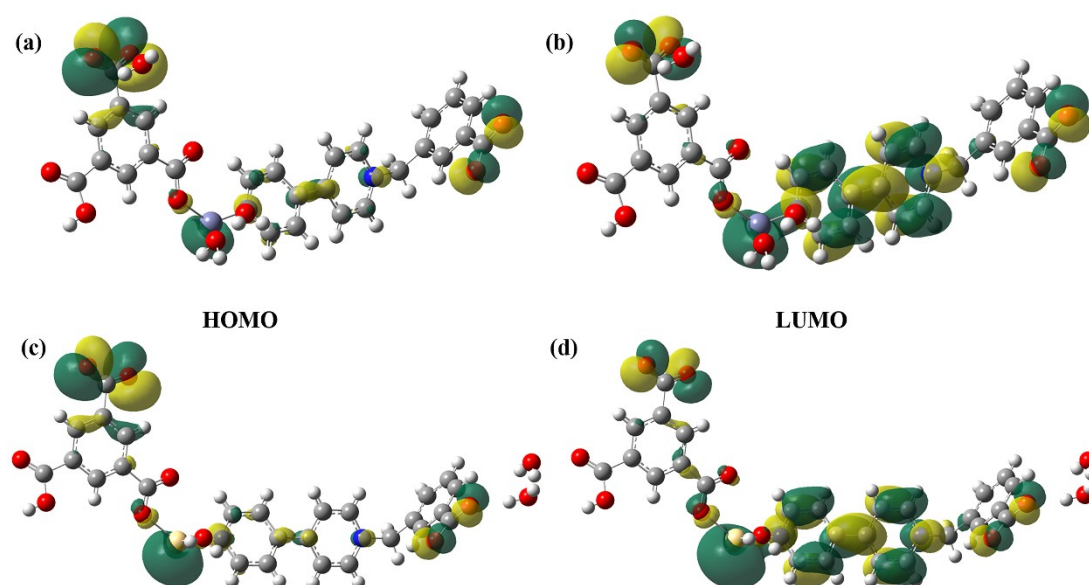


Figure S5. Electron distribution of the HOMO and the LUMO for complexes **1** and **2**.

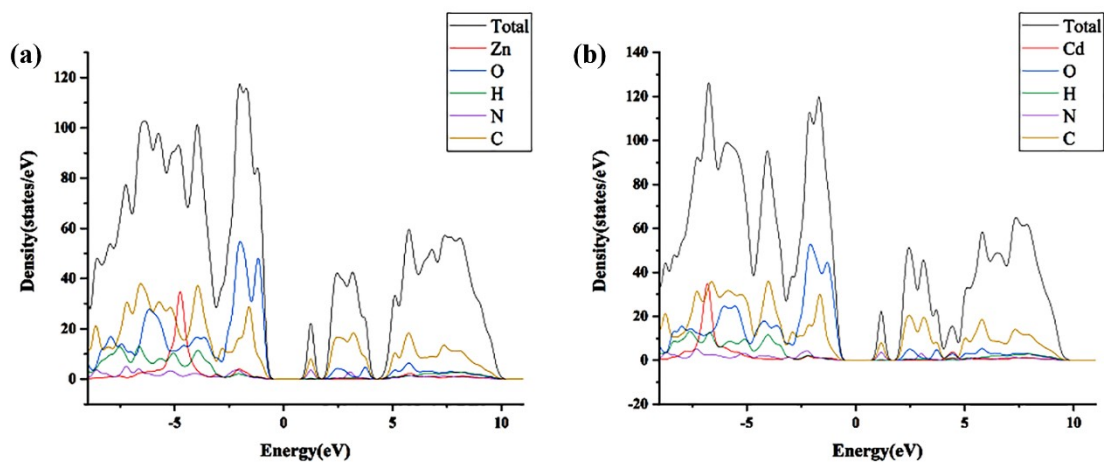


Figure S6 Total and partial DOS for 1 (a) and 2 (b). The Fermi level is located at 0 eV.

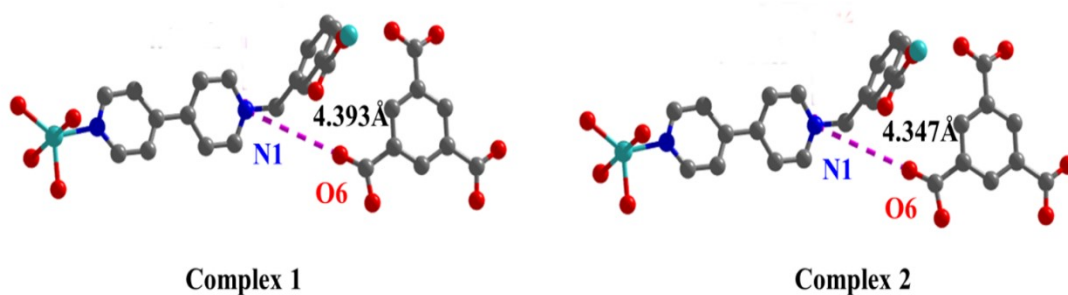


Figure S7. Possible electron transfer pathways of 1 and 2 by X-ray.

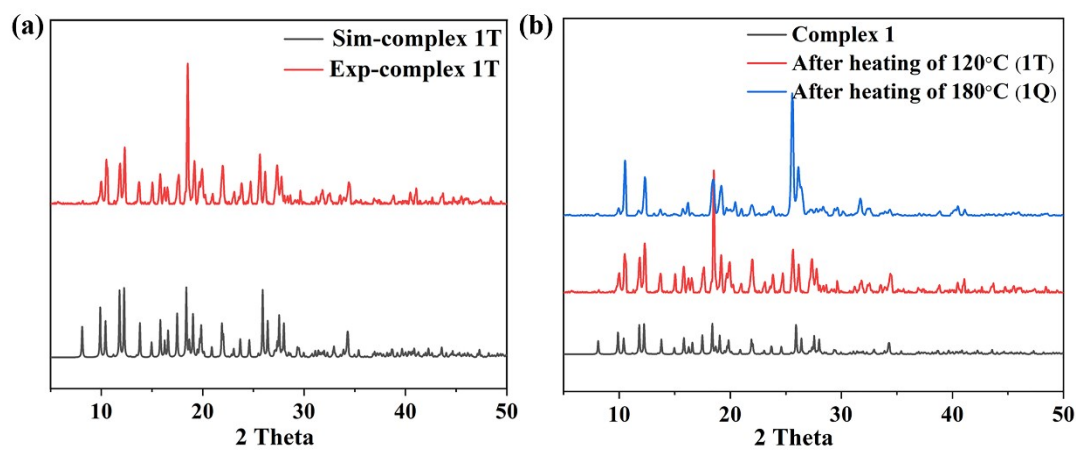


Figure S8. PXRD patterns of complexes 1, 1T and 1Q.

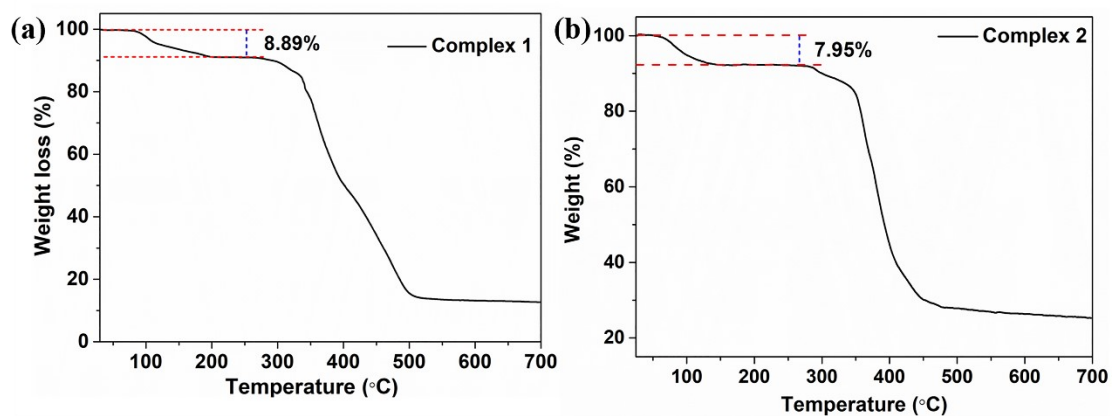


Figure S9. The TGA of **1** (a) and **2** (b).

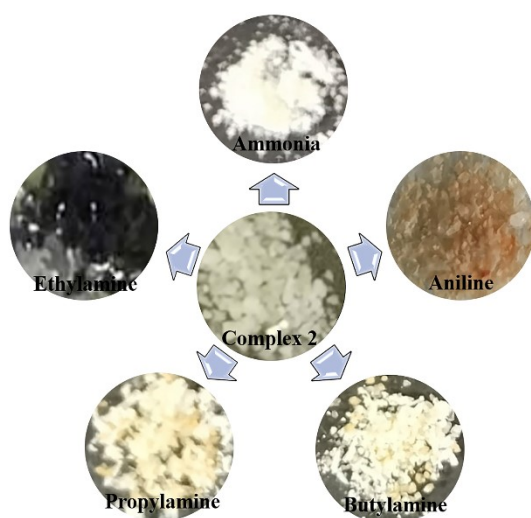


Fig. S10 Photographs of **2** before and after treated with amine vapors.

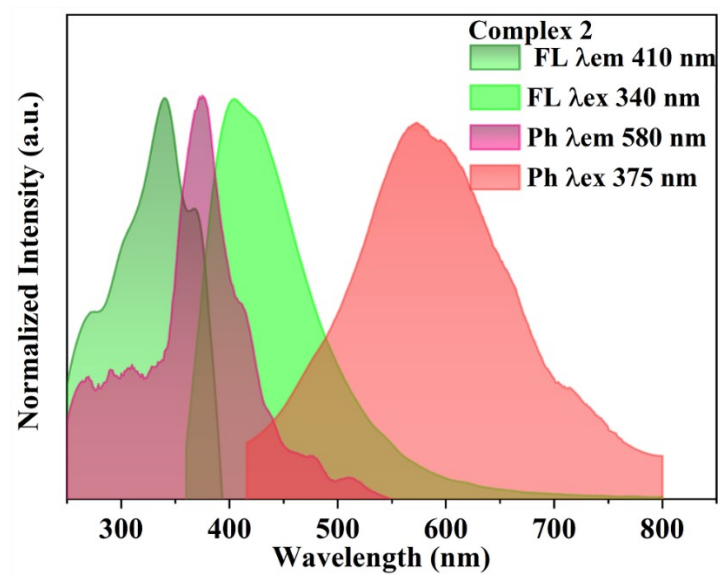


Figure S11. Fluorescence and phosphorescence excitation and emission spectra of complex **2** at room temperature.

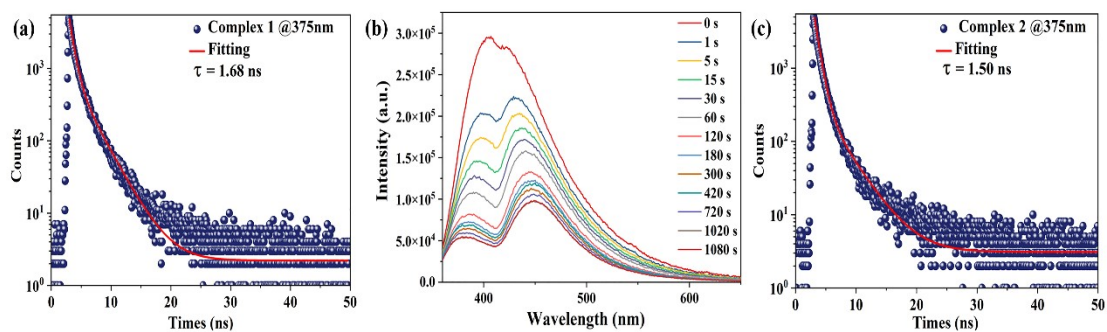


Figure S12 FL lifetime decay curve of **1** (405 nm) (a) and **2** (410 nm) (c) at room temperature. (b) Steady-state emission spectra of **2** ($\lambda_{\text{exc}} = 340$ nm) at different irradiation time at room temperature.

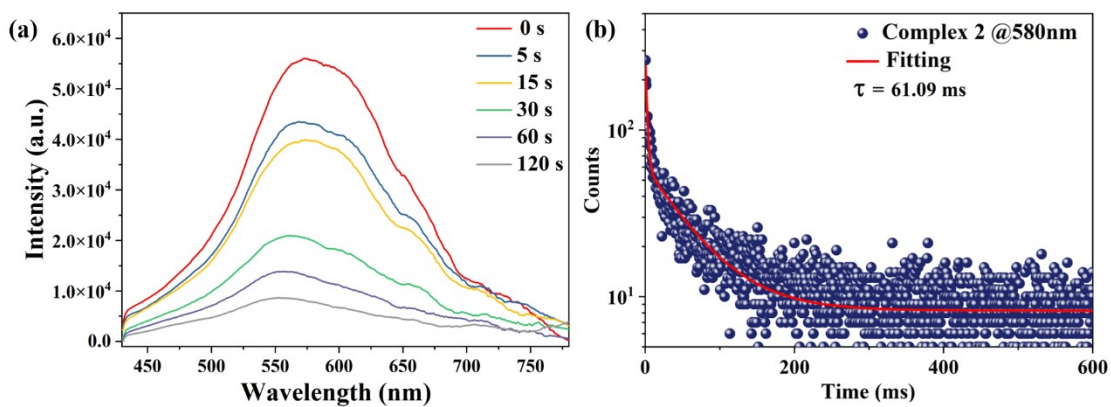


Figure S13. (a) Time-dependent luminescence (phosphorescence) spectra for complex **2** before and after irradiation ($\lambda_{\text{exc}} = 375$ nm). (b) Long-lived RTP lifetime decay curve of **1** at 580 nm.

Table S1 Crystal data and structure refinement for **1**, **1T**, **1Q** and **2**.

Complex	1	1T	1Q	2
Formula	C ₂₇ H ₂₀ N ₂ O ₉ Zn·2(H ₂ O)	C ₂₇ H ₁₈ N ₂ O ₈ Zn·H ₂ O	C ₂₇ H ₁₈ N ₂ O ₈ Zn·0.5(H ₂ O)	C ₂₇ H ₂₀ CdN ₂ O ₉ ·2(H ₂ O)
M _r	617.85	581.82	572.81	664.88
T (K)	100	100	100	100
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁
a (Å)	9.7060 (1)	9.6470 (2)	9.64805 (18)	9.90680 (18)
b (Å)	13.8370 (2)	13.7384 (3)	13.6870 (3),	13.8370 (3)
c (Å)	18.4275 (3)	17.8760 (4)	17.7021 (4)	18.5919 (3)
α (°)	90	90	90	90
β (°)	90	90	90	90
γ (°)	90	90	90	90
V (Å ³)	2474.85(6)	2369.18 (9)	2337.61 (8)	2548.57 (8)
Z	4	4	2	4
D _x /Mg m ⁻³	1.658	1.631	1.628	1.733
F(000)	1272	1192	1172	1344
μ(mm ⁻¹)	2.01	1.99	2.00	7.48
GOF	1.08	1.12	1.06	1.11
R ₁ [I > 2σ(I)]	0.028	0.041	0.035	0.030
wR ₂ [I > 2σ(I)]	0.072	0.104	0.089	0.080
R _{int}	0.039	0.040	0.046	0.051
CCDC	2176982	2176984	2176983	2176985

Table S2 Hydrogen-bonding geometry in complexes **1** and **2**.

	C-H···A (symmetry code)	C···A (Å)	∠C-H···A (°)	Potential electron acceptor
1	C9-H9···O1	3.572	171.89	N1 ⁺
	C9-H9···O7	3.357	120.10	
	C13-H13···O2	3.225	163.79	
2	C9-H9···O1	3.642	165.49	N1 ⁺

	C9-H9···O7	3.281	115.07	
	C13-H13···O2	3.323	162.18	

Table S3 Selected bond distances (Å) and angles (°) for **1**, **1T**, **1Q** and **2**.

Complex 1			
Zn1—O7 ⁱ	2.007 (2)	Zn1—O3	1.956 (2)
Zn1—O9	2.233 (2)	Zn1—N2	2.058 (2)
Zn1—O1 ⁱⁱ	2.155 (2)		
O7 ⁱ —Zn1—O9	89.20 (9)	O3—Zn1—O7 ⁱ	123.35 (9)
O7 ⁱ —Zn1—O1 ⁱⁱ	85.61 (10)	O3—Zn1—O9	86.76 (9)
O7 ⁱ —Zn1—N2	100.99 (9)	O3—Zn1—O1 ⁱⁱ	90.88 (10)
O1 ⁱⁱ —Zn1—O9	171.88 (8)	O3—Zn1—N2	135.23 (9)
N2—Zn1—O9	88.11 (9)	N2—Zn1—O1 ⁱⁱ	99.00 (9)

Symmetry codes: (i) $x+1, y, z$; (ii) $-x+2, y+1/2, -z+3/2$;

Complex 1T			
Zn1—O7 ⁱ	1.982 (3)	Zn1—O3	1.914 (3)
Zn1—O1 ⁱⁱ	2.075 (4)	Zn1—N2	2.034 (4)
O7 ⁱ —Zn1—O1 ⁱⁱ	89.69 (14)	O3—Zn1—O1 ⁱⁱ	97.97 (15)
O7 ⁱ —Zn1—N2	101.80 (14)	O3—Zn1—N2	132.66 (15)
O3—Zn1—O7 ⁱ	118.86 (14)	N2—Zn1—O1 ⁱⁱ	105.87 (15)

Complex 1Q			
Zn1—N2 ⁱ	2.051 (3)	Zn1—O3	1.920 (3)
Zn1—O1	2.028 (3)	Zn1—O7 ⁱⁱ	1.952 (3)
O1—Zn1—N2 ⁱ	109.97 (12)	O3—Zn1—O7 ⁱⁱ	119.16 (12)
O3—Zn1—N2 ⁱ	128.76 (13)	O7 ⁱⁱ —Zn1—N2 ⁱ	98.55 (12)
O3—Zn1—O1	102.49 (13)	O7 ⁱⁱ —Zn1—O1	91.98 (12)

Complex 2			
Cd1—N2	2.256 (3)	Cd1—O3	2.162 (3)
Cd1—O1 ⁱ	2.308 (4)	Cd1—O7 ⁱⁱ	2.237 (3)

Cd1—O9	2.393 (3)		
N2—Cd1—O1 ⁱ	100.80 (13)	O3—Cd1—O1 ⁱ	91.35 (15)
N2—Cd1—O9	86.56 (12)	O3—Cd1—O7 ⁱⁱ	121.81 (12)
O1 ⁱ —Cd1—O9	168.81 (13)	O3—Cd1—O9	87.85 (13)
O3—Cd1—N2	142.00 (13)	O7 ⁱⁱ —Cd1—N2	95.40 (13)
O7 ⁱⁱ —Cd1—O1 ⁱ	83.92 (16)	O7 ⁱⁱ —Cd1—O9	87.02 (14)