## **Electronic Supplementary Information (ESI+)**

Reversible single-crystal-to-single-crystal conversion of a photoreactive coordination network for rewritable optical memory storage

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**General procedure.** Reagents and solvents were purchased from TCI Co., Ltd., and Sigma-Aldrich Co. All the chemicals were used without any further purification. Infrared (IR) samples were prepared as KBr pellets, and spectra were obtained in the 4000–400 cm<sup>-1</sup> range using a Nicolet Avatar 360 FT-IR spectrophotometer. PXRD patterns were obtained using a PANalytical X'Pert PRO MPD system (PW3040/60). Thermal analyses were performed with a Perkin\_Elmer TGA-7 thermogravimetric analyser at a heating rate of 10 °C/min and a flow rate of 100 cm<sup>3</sup>/min (N<sub>2</sub>). <sup>1</sup>H NMR spectra were recorded in *d*<sub>6</sub>-DMSO on a Bruker ADVANCE III spectrometer (400MHz). High-resolution mass spectra (HRMS) were obtained by ESI. UV-vis absorption spectra were obtained with a Shimadzu UV-3600 spectrophotometer. The fluorescence spectra were obtained with an Edinburgh FLS920 spectrofluorometer. The confocal fluorescence microscopy images were taken with an Olympus FluoView FV 1000 confocal laser-scanning microscope. Scanning electron microscopy (SEM) images were taken on a Hitachi S-4700 field emission scanning electron microscope.

**Preparation of 4,4'-di(4-pyridyl)-stilbene (4,4'-dpsb)**: A 100 mL round-bottom flask was charged with 4,4'-diiodostilbene (4.32 g, 10 mmol), 4-pyridylboronic acid (2.95 g, 24 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.14 g, 2 mol%) and caesium carbonate (8.15 g, 25 mmol) in 40 mL of DMF. The solution was heated at 100°C for a period of 24 h. The resulting mixture was poured onto water and extracted with dichloromethane. The organic layer was washed with NaOH solution and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The organic solution was evaporated in vacuo to give a solid which was recrystallized from dichloromethane to give pure 4,4'-dpsb as yellow powder. Yield: 2.74 g (82% yield based on 4,4'-diiodostilbene). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  8.63 (d, *J* = 5.2 Hz, 4H), 7.87 (d, *J* = 8.4 Hz, 4H), 7.77 (m, 8H), 7.45 (s, 2H). HRMS (ESI, *m/z*) calcd. for C<sub>24</sub>H<sub>18</sub>N<sub>2</sub> [M+H]<sup>+</sup> 335.1548, found 335.1546.

**Preparation of**  $[Zn(1,4-pda)(4,4'-dpsb)]_n$  (1): To a 50 mL Teflon-lined autoclave was loaded a mixture of  $Zn(NO_3)_2$ ·6H<sub>2</sub>O (0.149g, 0.5 mmol), 1,4-H<sub>2</sub>pda (0.096g, 0.5 mmol), 4,4'-dpsb (0.167 g, 0.5 mmol) and H<sub>2</sub>O (25 mL). The Teflon-lined autoclave was sealed and heated in an oven to 175°C for 3 days, and then cooled to ambient temperature at a rate of 5°C h<sup>-1</sup> to form light-yellow

crystals of **1**, which were washed with ethanol and dried in air. Yield: 0.254g (86% yield based on Zn). IR (KBr, cm<sup>-1</sup>): 1615s, 1591s, 1559s, 1430s, 1381s, 1235m, 1182w, 1109m, 1041m, 965s, 850w, 783s, 696s, 643m, 498m. <sup>1</sup>H NMR (400 MHz, *d*<sub>6</sub>-DMSO): δ 8.64 (d, *J* = 6.0 Hz, 4H), 7.87 (d, *J* = 8.4 Hz, 4H), 7.78 (m, 8H), 7.46 (s, 2H), 7.18 (s, 4H), 3.52 (s, 4H).

Preparation of  $[Zn(1,4-pda)(tppcb)_{0.5}]_n$  (1a): Single crystals of 1 (0.118 g) were irradiated by 20 W LED lamp ( $\lambda = 365$  nm) for about 30 min to form crystals of 1a in a quantitative yield (based on 1). IR (KBr, cm<sup>-1</sup>): 1616s, 1591s, 1556s, 1430s, 1379s, 1241m, 1184w, 1110m, 1043m, 965s, 851w, 783s, 717s, 645m, 498m. <sup>1</sup>H NMR (400 MHz, *d*<sub>6</sub>-DMSO):  $\delta$  8.55 (d, *J* = 6.0 Hz, 4H), 7.63 (m, 8H), 7.43 (d, *J* = 8.4 Hz, 4H), 7.18 (s, 4H), 4.72 (s, 2H), 3.52 (s, 4H).

**Regeneration of 1**: Single crystals of **1a** (0.059 g) were irradiated by a 50 W low pressure Hg lamp ( $\lambda = 254$  nm) for about 30 min to form crystals of **1** in a quantitative yield (based on **1a**). IR (KBr, cm<sup>-1</sup>): 1615s, 1590s, 1556s, 1430s, 1381s, 1235m, 1183w, 1109m, 1041m, 965s, 850w, 783s, 696s, 644m, 498m. <sup>1</sup>H NMR (400 MHz, *d*<sub>6</sub>-DMSO):  $\delta$  8.64 (d, *J* = 6.0 Hz, 4H), 7.87 (d, *J* = 8.4 Hz, 4H), 7.77 (m, 8H), 7.45 (s, 2H), 7.18 (s, 4H), 3.52 (s, 4H).

**X-ray diffraction crystallography**. Single-crystal X-ray diffraction data for **1**, **1a** and regenerated **1** were collected on a Bruker SMART APEX II CCD diffractometer equipped with graphite-monochromated Mo-K $\alpha$  ( $\lambda = 0.71073$  Å) by using the  $\Phi/\omega$  scan technique. Absorption correction was based on symmetry equivalent reflections using the SADABS program.<sup>1</sup> The crystal structures of **1**, **1a** and regenerated **1** were solved by direct methods and refined on  $F^2$  by full-matrix least-squares methods with the *SHELXL-2014* program.<sup>2</sup> All non-hydrogen atoms refined anisotropically. All H atoms were introduced at the calculated positions and included in the structure-factor calculations.

1 G. M. Sheldrick, *A program for the Siemens Area Detector Absorption correction*, University of Göttingen, Göttingen, Germany, 1997.

2 G. M. Sheldrick, Acta Cryst., 2015, C71, 3-8.

Compound	1	1a	regenerated 1
chemical formula	$C_{34}H_{26}N_2O_4Zn$	$C_{34}H_{26}N_2O_4Zn$	$C_{34}H_{26}N_2O_4Zn$
formula weight	591.96	591.96	591.96
crystal system	triclinic	triclinic	triclinic
space group	PError!	PError!	PError!
<i>a</i> (Å)	9.2972(19)	9.3272(19)	9.1552(18)
<i>b</i> (Å)	10.943(2)	11.065(2)	10.954(2)
c (Å)	14.517(3)	14.204(3)	14.582(3)
α (°)	97.63(3)	94.76(3)	97.65(3)
β (°)	104.80(3)	106.97(3)	104.66(3)
γ (°)	98.88(3)	98.35(3)	98.55(3)
$V(Å^3)$	1387.7(6)	1375.0(5)	1376.6(6)
Ζ	2	2	2
$D_c (g/cm^3)$	1.417	1.430	1.428
F(000)	612	612	612
$\mu$ (MoKa,cm <sup>-1</sup> )	0.928	0.936	0.935
total no. of reflns	25374	23515	9634
no. of unique reflns	6316	6311	5361
no. of obsd. reflns	5448	4630	4202
$R_{ m int}$	0.0259	0.0352	0.0355
$R_1^a$	0.0368	0.0487	0.0493
$wR_2^b$	0.0991	0.1215	0.1460
$GOF^c$	1.031	1.038	1.060
CCDC number	1543279	1543280	1543281

Table S1. Summary of Crystallographic Data for 1, 1a and regenerated 1.

 ${}^{a}R = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|. \ {}^{b}wR = \{ \sum w(F_{o}^{2} - F_{c}^{2})^{2} / \sum w(F_{o}^{2})^{2} \}^{1/2}. \ {}^{c}GOF = \{ \sum w[(F_{o}^{2} - F_{c}^{2})^{2}] / (n-p) \}^{1/2}, \ {}^{b}wR = \{ \sum w[(F_{o}^{2} - F_{c}^{2})^{2}] / (n-p) \}^{1/2}. \ {}^{c}WR = \{ \sum w[(F_{o}^{2} - F_{c}^{2})^{2}] / (n-p) \}^{1/2}. \ {}^{c}WR = \{ \sum w[(F_{o}^{2} - F_{c}^{2})^{2}] / (n-p) \}^{1/2}. \ {}^{c}WR = \{ \sum w[(F_{o}^{2} - F_{c}^{2})^{2}] / (n-p) \}^{1/2}. \ {}^{c}WR = \{ \sum w[(F_{o}^{2} - F_{c}^{2})^{2}] / (n-p) \}^{1/2}. \ {}^{c}WR = \{ \sum w[(F_{o}^{2} - F_{c}^{2})^{2}] / (n-p) \}^{1/2}. \ {}^{c}WR = \{ \sum w[(F_{o}^{2} - F_{c}^{2})^{2}] / (n-p) \}^{1/2}. \ {}^{c}WR = \{ \sum w[(F_{o}^{2} - F_{c}^{2})^{2}] / (n-p) \}^{1/2}. \ {}^{c}WR = \{ \sum w[(F_{o}^{2} - F_{c}^{2})^{2}] / (n-p) \}^{1/2}. \ {}^{c}WR = \{ \sum w[(F_{o}^{2} - F_{c}^{2})^{2}] / (n-p) \}^{1/2}. \ {}^{c}WR = \{ \sum w[(F_{o}^{2} - F_{c}^{2})^{2}] / (n-p) \}^{1/2}. \ {}^{c}WR = \{ \sum w[(F_{o}^{2} - F_{c}^{2})^{2}] / (n-p) \}^{1/2}. \ {}^{c}WR = \{ \sum w[(F_{o}^{2} - F_{c}^{2})^{2}] / (n-p) \}^{1/2}. \ {}^{c}WR = \{ \sum w[(F_{o}^{2} - F_{c}^{2})^{2}] / (n-p) \}^{1/2}. \ {}^{c}WR = \{ \sum w[(F_{o}^{2} - F_{c}^{2})^{2}] / (n-p) \}^{1/2}. \ {}^{c}WR = \{ \sum w[(F_{o}^{2} - F_{c}^{2})^{2}] / (n-p) \}^{1/2}. \ {}^{c}WR = \{ \sum w[(F_{o}^{2} - F_{c}^{2})^{2}] / (n-p) \}^{1/2}. \ {}^{c}WR = \{ \sum w[(F_{o}^{2} - F_{c}^{2})^{2}] / (n-p) \}^{1/2}. \ {}^{c}WR = \{ \sum w[(F_{o}^{2} - F_{c}^{2})^{2}] / (n-p) \}^{1/2}. \ {}^{c}WR = \{ \sum w[(F_{o}^{2} - F_{c}^{2})^{2}] / (n-p) \}^{1/2}. \ {}^{c}WR = \{ \sum w[(F_{o}^{2} - F_{c}^{2})^{2}] / (n-p) \}^{1/2}. \ {}^{c}WR = \{ \sum w[(F_{o}^{2} - F_{c}^{2})^{2}] / (n-p) \}^{1/2}. \ {}^{c}WR = \{ \sum w[(F_{o}^{2} - F_{c}^{2})^{2}] / (n-p) \}^{1/2}. \ {}^{c}WR = \{ \sum w[(F_{o}^{2} - F_{c}^{2})^{2}] / (n-p) \}^{1/2}. \ {}^{c}WR = \{ \sum w[(F_{o}^{2} - F_{c}^{2})^{2} / (n-p) \}^{1/2}. \ {}^{c}WR = \{ \sum w[(F_{o}^{2} - F_{c}^{2})^{2} / (n-p) \}^{1/2}. \ {}^{c}WR = \{ \sum w[(F_{o}^{2} - F_{c}^{2})^{2} / (n-p) \}^{1/2}. \ {}^{c}WR = \{ \sum w[(F_{o}^{2} - F_{c}^{2})^{2} / (n-p) \}^{1/2}. \ {}^{c}WR = \{ \sum w[(F_{o}^{2} - F_{c}^{2}$ 

where n is the number of reflections and p is total number of parameters refined.

	1		
Zn(1)-O(3)	2.0436(16)	Zn(1)-O(4A)	2.0582(17)
Zn(1)-O(2)	2.111(2)	Zn(1)-N(2B)	2.1460(16)
Zn(1)-N(1)	2.1717(17)	Zn(1)-O(1)	2.412(3)
O(3)-Zn(1)-O(4A)	127.26(8)	O(3)-Zn(1)-O(2)	91.74(8)
O(4A)-Zn(1)-O(2)	140.44(7)	O(3)-Zn(1)-N(2B)	93.80(6)
O(4A)-Zn(1)-N(2B)	89.27(6)	O(2)-Zn(1)-N(2B)	95.01(7)
O(3)-Zn(1)-N(1)	89.59(7)	O(4A)-Zn(1)-N(1)	85.30(7)
O(2)-Zn(1)-N(1)	89.11(7)	N(2B)-Zn(1)-N(1)	174.57(6)
O(3)-Zn(1)-O(1)	147.71(7)	O(4A)-Zn(1)-O(1)	84.86(8)
O(2)-Zn(1)-O(1)	55.97(7)	N(2B)-Zn(1)-O(1)	89.34(7)
N(1)-Zn(1)-O(1)	90.06(7)		

 Table S2. Selected bond lengths (Å) and angles (°) for 1, 1a and regenerated 1.

1a

Zn(1)-O(3)	2.038(2)	Zn(1)-O(4A)	2.065(2)
Zn(1)-N(1)	2.135(2)	Zn(1)-N(2B)	2.168(2)
Zn(1)-O(2)	2.210(3)	Zn(1)-O(1)	2.251(3)
O(3)-Zn(1)-O(4A)	124.88(11)	O(3)-Zn(1)-N(1)	93.86(9)
O(4A)-Zn(1)-N(1)	91.56(9)	O(3)-Zn(1)-N(2B)	90.16(10)
O(4A)-Zn(1)-N(2B)	85.45(10)	N(1)-Zn(1)-N(2B)	175.90(9)
O(3)-Zn(1)-O(2)	89.91(10)	O(4A)-Zn(1)-O(2)	144.59(11)
N(1)-Zn(1)-O(2)	92.51(9)	N(2B)-Zn(1)-O(2)	88.33(10)
O(3)-Zn(1)-O(1)	147.81(10)	O(4A)-Zn(1)-O(1)	86.93(10)
N(1)-Zn(1)-O(1)	89.61(9)	N(2B)-Zn(1)-O(1)	87.43(10)
O(2)-Zn(1)-O(1)	57.95(9)		

## regenerated 1

Zn(1)-O(4A)	2.055(3)	Zn(1)-O(3)	2.063(2)
Zn(1)-O(2)	2.130(3)	Zn(1)-N(2B)	2.133(2)
Zn(1)-N(1)	2.158(3)	Zn(1)-O(1)	2.391(3)
O(4A)-Zn(1)-O(3)	126.29(11)	O(4A)-Zn(1)-O(2)	91.06(11)
O(3)-Zn(1)-O(2)	142.11(11)	O(4A)-Zn(1)-N(2B)	94.03(10)
O(3)-Zn(1)-N(2B)	89.33(9)	O(2)-Zn(1)-N(2B)	94.71(10)
O(4A)-Zn(1)-N(1)	89.63(10)	O(3)-Zn(1)-N(1)	85.28(10)
O(2)-Zn(1)-N(1)	89.21(10)	N(2B)-Zn(1)-N(1)	174.58(10)
O(4A)-Zn(1)-O(1)	147.84(10)	O(3)-Zn(1)-O(1)	85.63(11)
O(2)-Zn(1)-O(1)	56.79(10)	N(2B)-Zn(1)-O(1)	89.66(10)
N(1)-Zn(1)-O(1)	89.36(11)		

Symmetry codes: (1) A: -x + 1, -y + 1, -z + 2; B: x - 1, y - 1, z + 1. (1a) A: -x + 3, -y + 2, -z; B: x + 1, y + 1, z - 1. (regenerated 1) A: -x + 1, -y + 1, -z; B: x + 1, y + 1, z - 1.





**Fig. S1** Interrelated structural figures for **1**. (a) The 2D (4,4) layer of  $[Zn(1,4-pda)]_n$  in **1**. (b) The single 3D  $[Zn(1,4-pda)(4,4'-dpsb)]_n$  framework in **1**. (c) View of the relative separation of two interlocked frameworks in **1**.



## S9



Fig. S2 PXRD patterns for 1 (a), 1a (b, c) and regenerated 1 (d).



**Fig. S3** The TGA curves for **1** and **1a**. Both **1** and **1a** are stable up to about 310°C upon at which temperature decomposition are observed. The final residues were assumed to be ZnO (*ca.* 13.75%), which is consistent with the experimental weights of residues (14.06% for **1** and 13.61% for **1a**).



Fig. S4 Illustration of the spatial structures of each distorted cubic unit in 1 (left) and 1a (right).



**Fig. S5** Interrelated structural figures for **1a**. (a) The 2D (4,4) layer of  $[Zn(1,4-pda)]_n$  in **1a**. (b) The single 3D  $[Zn(1,4-pda)(tppcb)_{0.5}]_n$  framework in **1a**. (c) View of the twofold interpenetrating architecture of **1a**. (d) View of the relative separation of two interlocked frameworks in **1a**.





**Fig. S6** The <sup>1</sup>H NMR spectra of crystals **1** (a), **1a** (b) and regenerated **1** (c) in  $d_6$ -DMSO. For <sup>1</sup>H NMR analyses of **1**, **1a** and regenerated **1**, all of the single crystals (10 mg) were digested by 12 M HCl aqueous solution and dried in an oven at 100°C. The solid was then dissolved in about 0.6 mL  $d_6$ -DMSO.



**Fig. S7** Interrelated structural figures for regenerated **1**. (a) View of the single 3D framework of regenerated **1**. (b) View of the twofold interpenetrating architecture of regenerated **1**.



Fig. S8 The UV-vis absorption spectra of 1, 1a and regenerated 1. For UV-vis absorption analyses of 1, 1a and regenerated 1, all of the samples (7.4 mg) were dissolved in 250 mL of absolute ethanol solution with hydrogen chloride (100  $\mu$ M).





**Fig. S9** Solid-state emission spectra of a sample of the photoreactive coordination network for each photocyclization-cycloreversion cycle.



8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 fl (ppm)

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**Fig. S10** (a) <sup>1</sup>H NMR spectra of the crystals of **1** irradiated by 365 nm UV light within different irradiation time intervals. (b) <sup>1</sup>H NMR spectra of the crystals of **1a** irradiated by 254 nm UV light within different irradiation time intervals. To make these sample be soluble in DMSO- $d_6$ , all of these coordination polymers were digested by concentrated HCl and dried in oven. (c) Time versus reaction ratio plot for **1** to **1a**. (d) Time versus reaction ratio plot for **1a** to **1**.

Upon UV irradiation of single crystals of **1** with 365 nm UV light for 5 min, about 45.9% of the 4,4'-dpsb ligands were converted to tppcb ligands. After 25 min, the conversion ratio of the photocyclization reaction was found to be 95.2%. With the irradiation of 254 nm UV light for 5 min, about 50.6% of the tppcb ligands in **1a** were transformed to 4,4'-dpsb ligands, and the conversion ratio can reach 97.1% after 25 min. The complete conversion of both cyclization and cycloreversion reactions can be achieved after 30 min.



Fig. S11 Scanning electron microscopy (SEM) image of dispersive tiny particles of 1.



**Fig. S12** (a) <sup>1</sup>H NMR spectrum of dispersive tiny particles of **1a** in  $d_6$ -DMSO. The sample was obtained by the irradiation of dispersive tiny particles of **1** with 365 nm light for 15 s. (b) <sup>1</sup>H NMR spectrum of dispersive tiny particles of regenerated **1**. The sample was obtained by the irradiation of dispersive tiny particles of **1a** with 254 nm light for 15 s.



**Fig. S13** The <sup>1</sup>H NMR spectrum of the 4,4'-dpsb ligand in  $d_6$ -DMSO.



Fig. S14 HRMS spectrum of the 4,4'-dpsb ligand.