Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Thermally responsive morphological change of layered coordination polymer induced by disordering/ordering of flexible alkyl chains

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1. Abbreviation

DSC: differential scanning calorimetry, DTA: differential thermal analysis, OAc: -OCOCH$_3$, PXRD: powder X-ray diffraction, SEM: scanning electron microscope, SCXRD: single crystal X-ray diffraction, TGA: thermogravimetric analysis, XRD: X-ray diffraction.

2. Materials and methods

Materials

All solvents, organic and inorganic reagents are commercially available and were used without further purification. Organic ligand (H$_2$**C16**) was prepared according to previously reported procedures.[1]

Single-crystal X-ray crystallographic analysis using MoKα radiation

Single crystal X-ray crystallographic analysis was performed using a Rigaku VariMax RAPID（1.2kW） diffractometer with confocal mirror optics MoKα radiation. Single crystals for diffraction measurement were mounted with epoxy resin on a glass fiber, the temperature of which was controlled using a nitrogen gas-flow. Crystal structures were solved with SHELXT[2] and L.S refinement was performed with SHELXL[3] within Olex2 GUI.[4] Hydrogen atoms were refined using the riding model.

Single-crystal X-ray crystallographic analysis using synchrotron

Single crystal X-ray diffraction data was collected at SPring-8, BL02B1 with wavelength 0.24792 Å. Data integration, scaling and multi-scan absorption corrections were carried out with CrysAlisPro[5]. For **HT**, all non-hydrogen atoms were refined anisotropically and hydrogen atoms were treated geometrically with HFIX 43, 23 and 133. **HT** required the following restraints and constraints: FLAT, DANG, ISOR, DELU. C$_{16}$-akyl chain of **HT** was treated as a rigid fragment, with PART-1. Initial orientation of the chain was assigned basing on two positive electron density peaks for atoms C15 and C16.

Powder X-ray diffraction (PXRD) measurements using CuKα radiation

PXRD analysis was carried out using a Rigaku SmartLab (9kW, CuKα) diffractometer equipped with a HyPix-3000 as a detector. Samples for diffraction measurement were placed on an oriented silicon plate or a glass plate. For the measurement under controlled temperature condition, an Anton Paar DHS 1100 sample stage was used. The sample was covered with a carbon dome and vacuumed during measurements.

Powder X-ray diffraction (PXRD) measurements using synchrotron

Synchrotron PXRD measurements carried out at SPring-8, BL02B2 beam line using a Large Debye Scherrer camera with an imaging plate as a detector. The samples (crystals of Zn**C16)** were installed in a glass capillary, the temperature of which was controlled using a nitrogen gas-flow high temperature device. An exposure time of X-ray for each profile was 5 min. The CeO2 (NIST SRM674a) standard powder was used for wavelength calibration. The wavelength was 0.78 Å.

Thermogravimetric analysis and differential thermal analysis (TGA/DTA)

TGA/DTA were performed using a Hitachi STA7200 under dried air. Samples (crystals of Zn**C16**) for the measurement were placed in standard aluminum pan and scanned at a heating rate of 1 °C/min in the temperature range of rt to 500 °C.

Differential scanning calorimetry (DSC) measurement

DSC measurements were performed using a Hitachi DSC7000X under N_2 atmosphere. Samples (crystals of Zn**C16**) for the measurement were placed in standard aluminum pan crimped with a cover and scanned at a heating/cooling rate of 1 °C/min in the temperature range of 130 to 170 °C.

Raman spectroscopy

Raman spectrum of the crystals of Zn**C16** were collected using a JACSO NRS-4100-30 spectrometer using laser of 532 nm for excitation. The sample was placed on a glass plate, the temperature of which was controlled using a Linkam 10083L sample stage.

Observation of crystal using optical microscope

Microscopic images of the crystals of Zn**C16** were collected using an Olympus BX51 attached with a Mettler HS82 sample stage.

Observation of crystal using scanning electron microscope (SEM)

SEM images of the crystals of Zn**C16** before/after one cycle of thermal phase transition were collected using a Hitachi SU6600. The samples were attached on a metal plate using conductive tape. Sample after one cycle of phase transition was prepared by heating and cooling the crystals of Zn**C16** in the 30–170 °C temperature range using DSC (heating/cooling rate: 1 °C/min).

3. Preparation of coordination polymer ZnC16

Procedure

5-(*n*-Hexadecyloxy)-isophthalic acid (H_2**C16**) (300.9 mg, 0.74 mmol, 1 eq) was dissolved in hot MeOH (37 mL) to give a colourless solution. To this solution was added a solution of $Zn(OAc)_2 \cdot 2H_2O$ (20 mM, 37 mL, 0.74 mmol, 1eq). After incubating the resulted colourless suspension at 60 °C for 7 days, colourless prismatic single crystals suitable for single crystal X-ray diffraction analysis were formed (During the incubation process, small amount of solid sample was collected and PXRD was measured to monitor the reaction, Fig. S1). To isolate coordination polymer (Zn**C16**), the single crystals were collected by centrifugation and washed by MeOH. After being kept under reduced pressure at room temperature, Zn**C16** (262.0 mg, 0.56 mml, 75%) were obtained as colourless single crystals (Fig. S5).

Elemental analysis: calcd for $C_{25}H_{38}O_4Zn$ (Zn**C16**): C, 61.34; H, 7.72. Found: C, 61.43; H, 7.78.

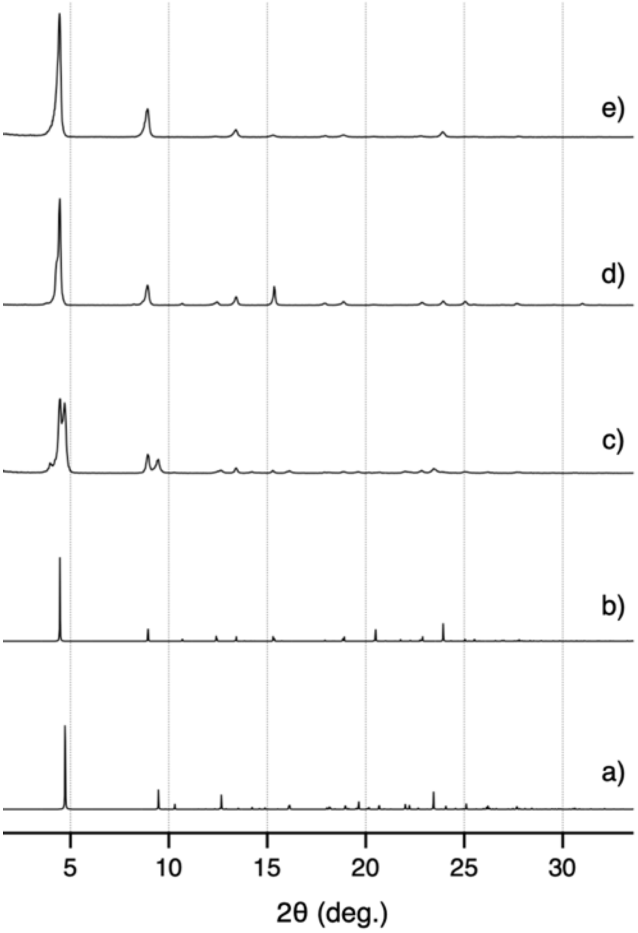


Fig. S1 PXRD profiles of a) Zn**C16** (**LT**) and b) Zn**C16**$(MeOH)_2$ calculated from respective single crystal structures at 20 °C. PXRD profiles (CuK*α*, $\lambda = 1.541$ Å, r.t.) of the a) solid samples formed after incubation of the mixture of H_2**C16** and $Zn(OAc)_2 \cdot 2H_2O$ in MeOH at 60 °C for c) 2 days and d) 7 days. e) PXRD profiles of Zn**C16** (**LT**) isolated as single crystals.

4. Experimental data

4-1. Single crystal structure of solvated coordination polymer ZnC16(MeOH)$_2$

Crystal data for ZnC16(MeOH)$_2$ at 293 K (20 °C)

Crystal data for $C_{26}H_{44}O_7Zn$: $Fw = 533.98$, crystal dimensions 0.2 × 0.1 × 0.03 mm, triclinic, space group P–1, $a = 8.0069(3)$, $b = 9.7526(4)$, $c = 18.8575(9)$ Å, $\alpha = 82.319(6)$, $\beta = 89.523(6)$, $\gamma = 68.639(5)$°, $V = 1357.78(11)$ Å^3, $Z = 2$, $\rho_{\mathrm{calcd}} = 1.306$ g·cm^{-3}, $\mu = 0.945$ mm^{-1}, $T = 293$ K, $\lambda(\mathrm{MoK}\alpha) = 0.71075$ Å, $2\theta_{\mathrm{max}} = 55.0$°, 6215/4588 reflection collected/unique ($R_{\mathrm{int}} = 0.0497$), $R_1 = 0.0488$ ($I > 2\sigma(I)$), $wR_2 = 0.1262$ (for all data), GOF = 1.022, largest diff. peak and hole 0.463/ –0.409 eÅ^{-3}. CCDC deposit number 2201471.

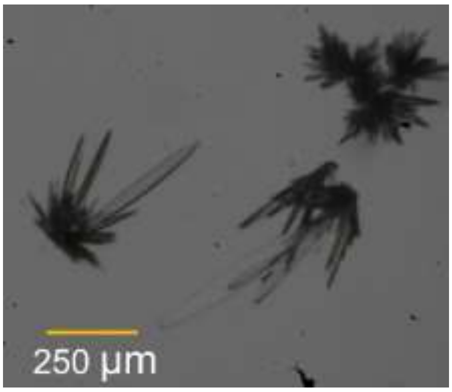


Fig. S2 Microscopic image of Zn**C16**(MeOH)$_2$.

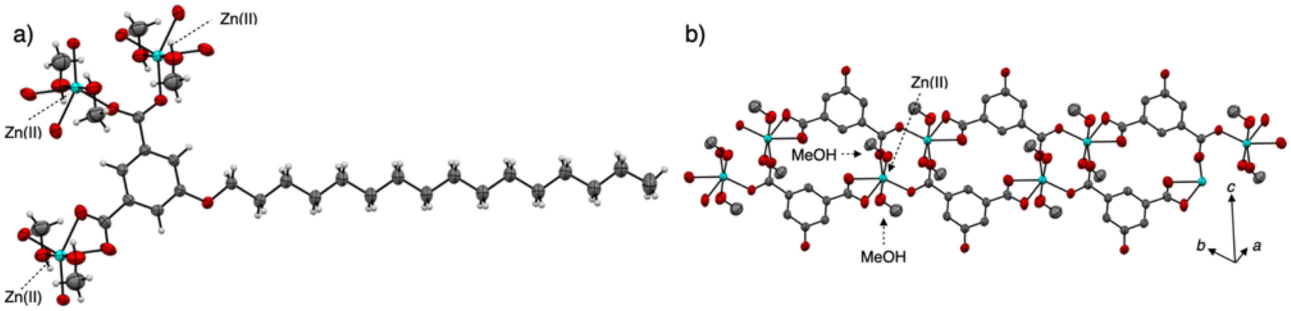


Fig. S3 Crystal structure of Zn**C16**(MeOH)$_2$. a) ORTEP view (50% probability level) of the single ligand. b) Structure of the 1D coordination polymer. Alkyl chains on Fig. S3b are omitted for clarity. (C: grey, H: white, O: red, Zn: pale blue)

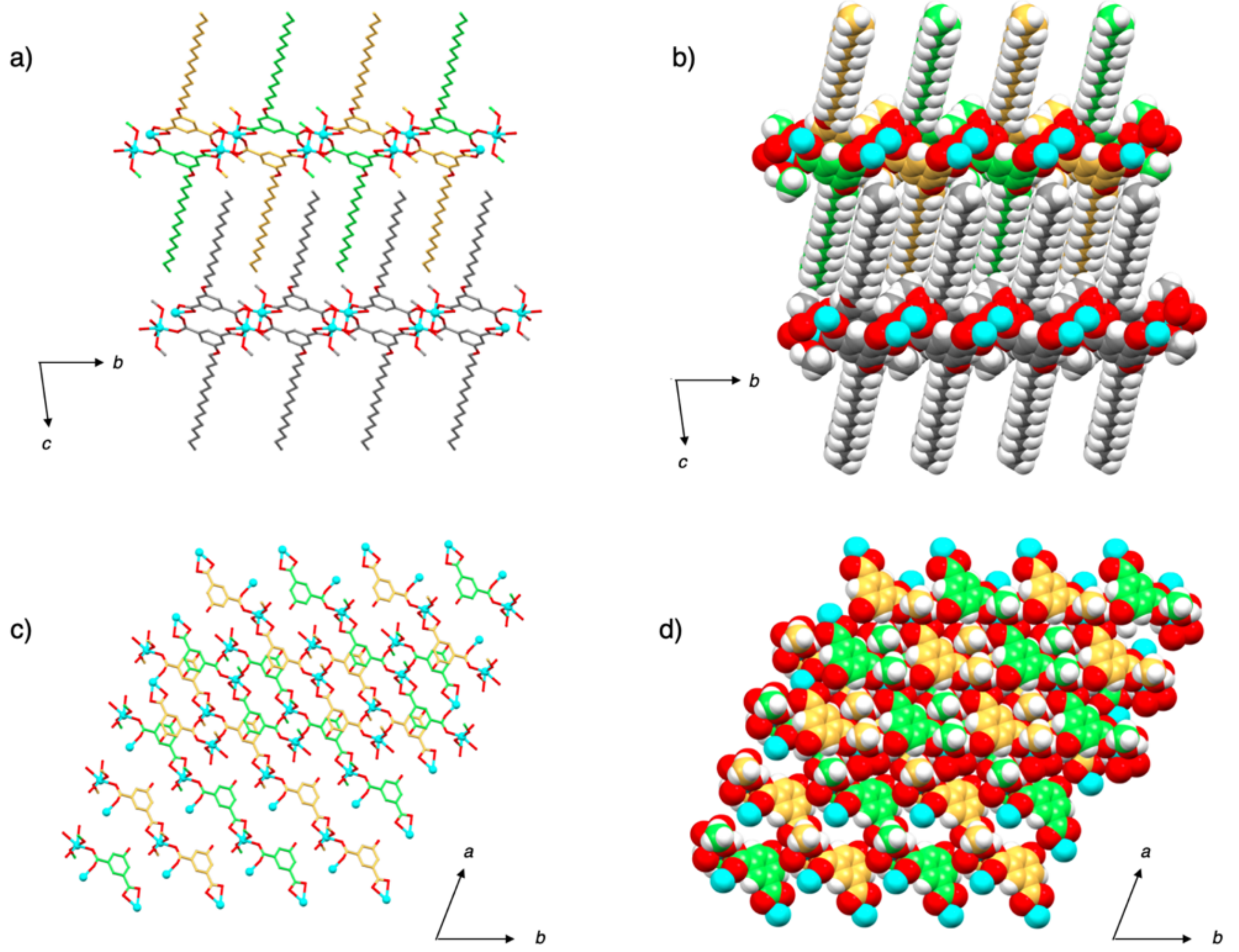


Fig. S4 Molecular packing of Zn**C16**(MeOH)$_2$. Views from *a*-axis with a) ball and stick model and b) space fill model. Views without showing alkyl chains from *c*-axis; c) ball and stick model and d) space fill model. C atoms are shown in different colours for clarity. Alkyl chains on Fig. S4c,d are omitted for clarity. (C: pale green, yellow or grey, H: white, O: red, Zn: pale blue)

4-2. Single crystal structure of coordination polymer ZnC16 (LT)

Crystal data for ZnC16 (LT) at 293 K (20 °C)

Crystal data for $C_{24}H_{36}O_5Zn$: $F_w = 469.90$, crystal dimensions 0.14 × 0.06 × 0.04 mm, triclinic, space group P–1, a = 7.0651(2), b = 9.0096(3), c = 20.2493(5) Å, α = 78.148(5), β = 89.073(6), γ = 69.912(5)°, V = 1182.65(7) Å^3, $Z = 2$, ρ_{calcd} = 1.320 gcm^{-3}, μ = 1.069 mm^{-1}, T = 293 K, λ(MoKα) = 0.71075 Å, $2\theta_{\max}$ = 55.0°, 5403/4989 reflection collected/unique (R_{int} = 0.0156), R_1 = 0.0266 ($I > 2\sigma(I)$), wR_2 = 0.0715 (for all data), GOF = 1.130, largest diff. peak and hole 0.502/–0.214 eÅ^{-3}. CCDC deposit number 2194401.

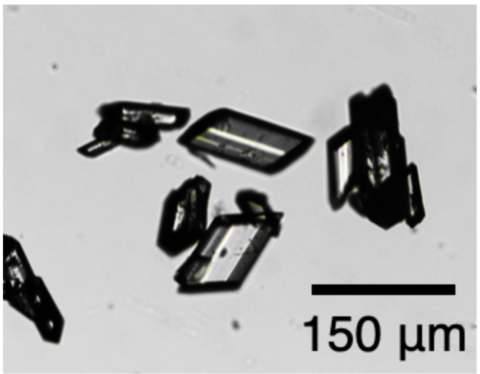


Fig. S5 Microscopic image of Zn**C16** (**LT**) isolated as single crystals.

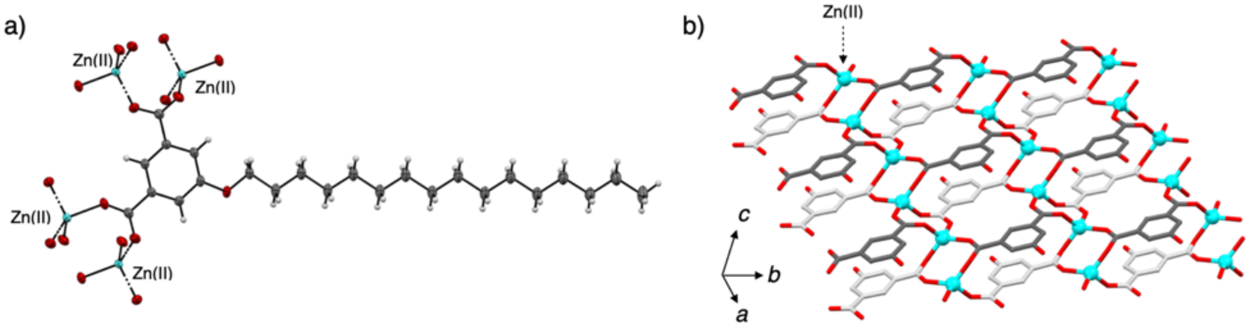


Fig. S6 Crystal structure of Zn**C16** (**LT**). a) ORTEP view (50% probability level) of the single ligand. b) Structure of the 2D coordination polymer network. Alkyl chains on Fig. S6b are omitted for clarity. (C: grey and pale grey, H: white, O: red, Zn: pale blue)

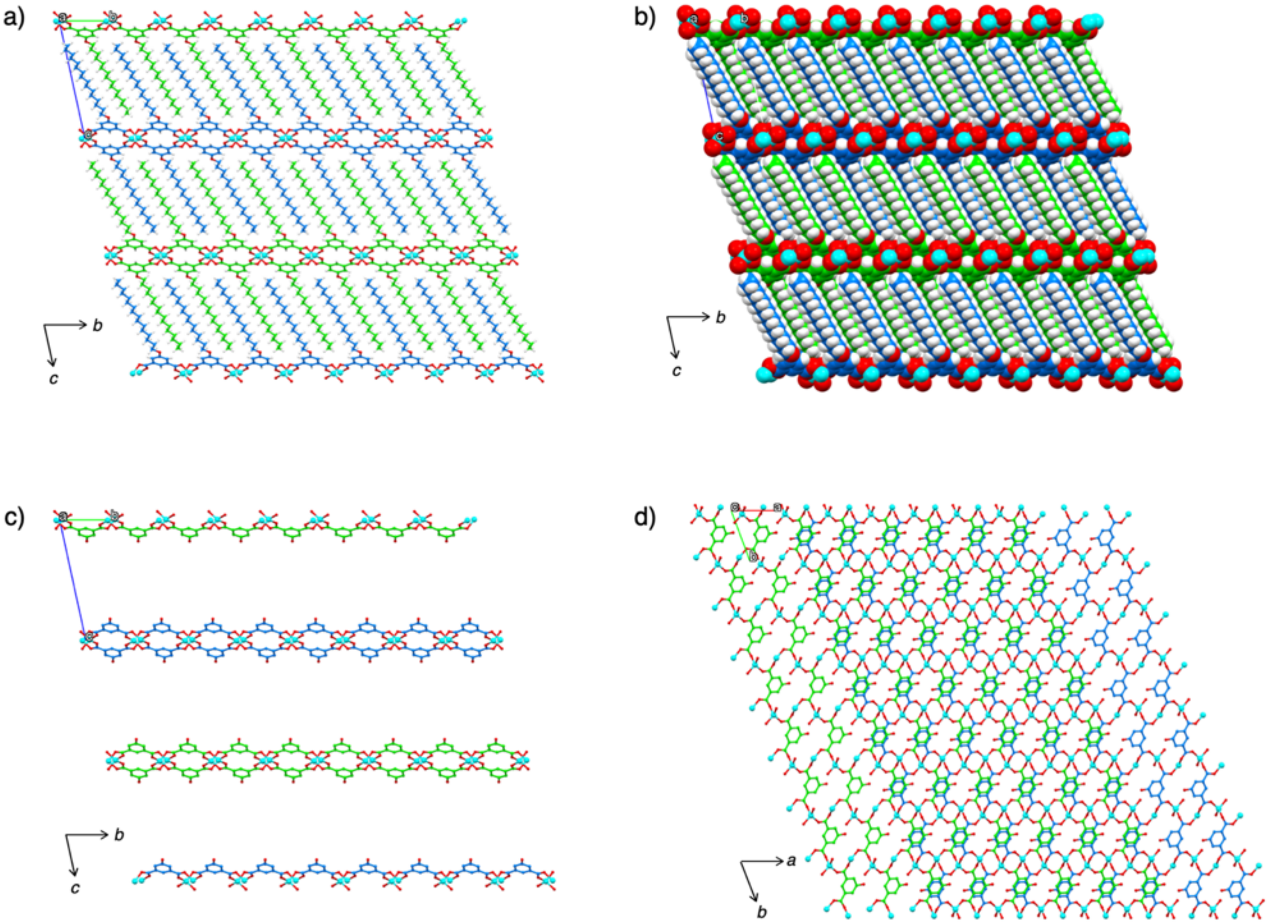


Fig. S7 Molecular packing of Zn**C16** (**LT**). Views from *a*-axis with a) ball and stick model and b) space filling model. Views without showing alkyl chains c) from *a*-axis and d) from *c*-axis. C atoms of the adjacent layer are shown in different colours. Alkyl chains on Fig. S7c,d are omitted for clarity. (C: pale green or blue, H: white, O: red, Zn: pale blue)

4-3. TGA/DTA thermograms of coordination polymer ZnC16

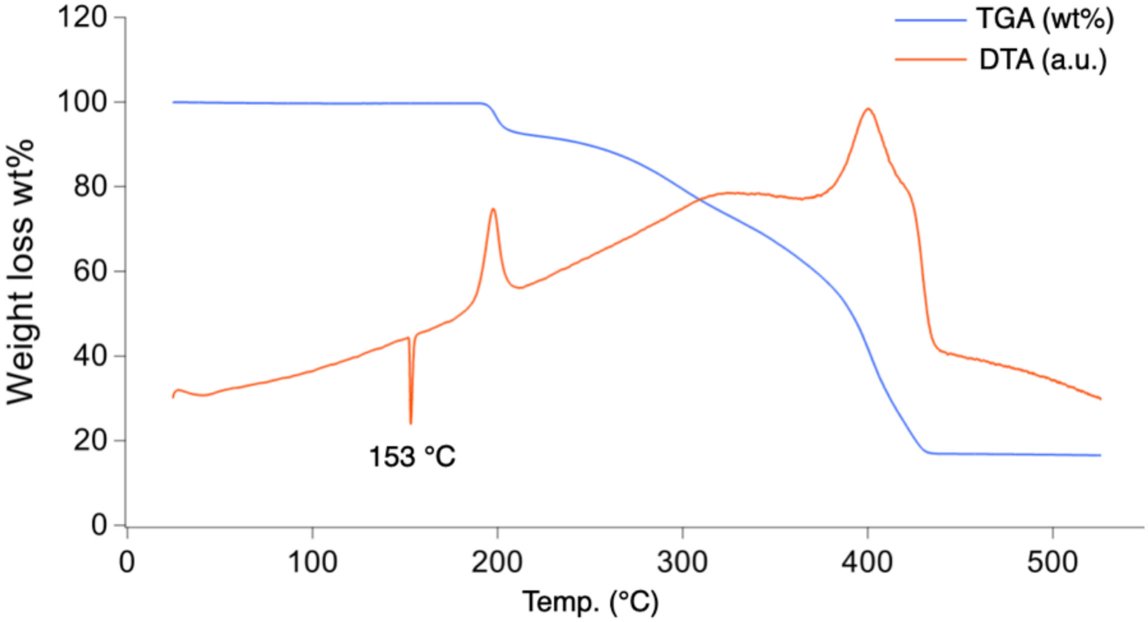


Fig. S8 TGA/DTA thermograms of Zn**C16** measured under dried air (scan rate 1 °C/min).

4-4. Variable temperature PXRD of coordination polymer ZnC16

4-4-1. PXRD of ZnC16 under the temperature window of 27–187 °C

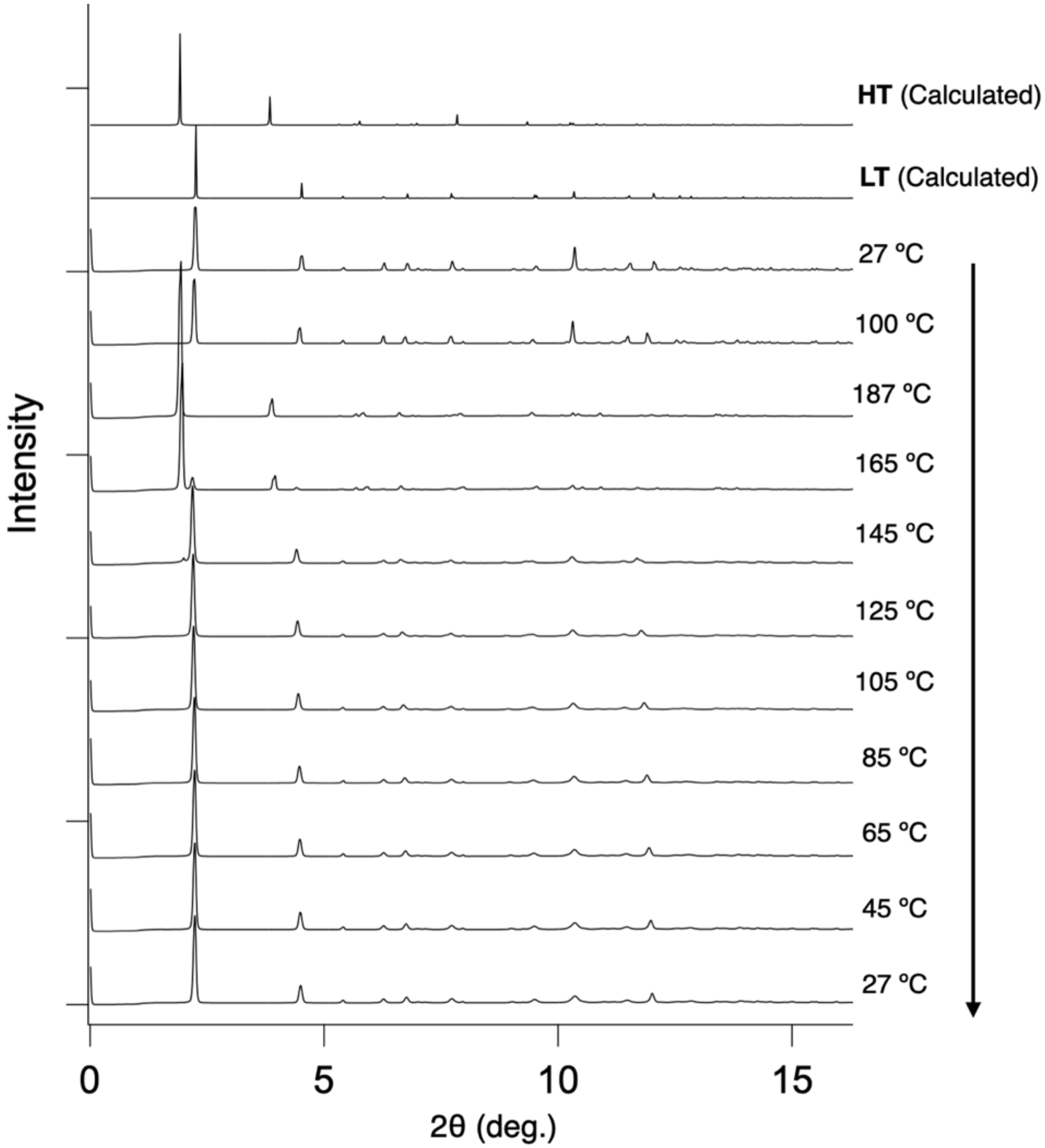


Fig. S9 PXRD profiles (λ = 0.78 Å, synchrotron) of Zn**C16** measured sequentially at 27 °C to 187 °C and back to 27 °C. The theoretical diffraction patterns of **HT** and **LT** are simulated from their single crystal structures at 20 °C and 177 °C respectively. The black arrow shows the order of the measurements.

4-4-2. PXRD of ZnC16 under repetitive heating/cooling scan in the temperature window of 130–170 °C

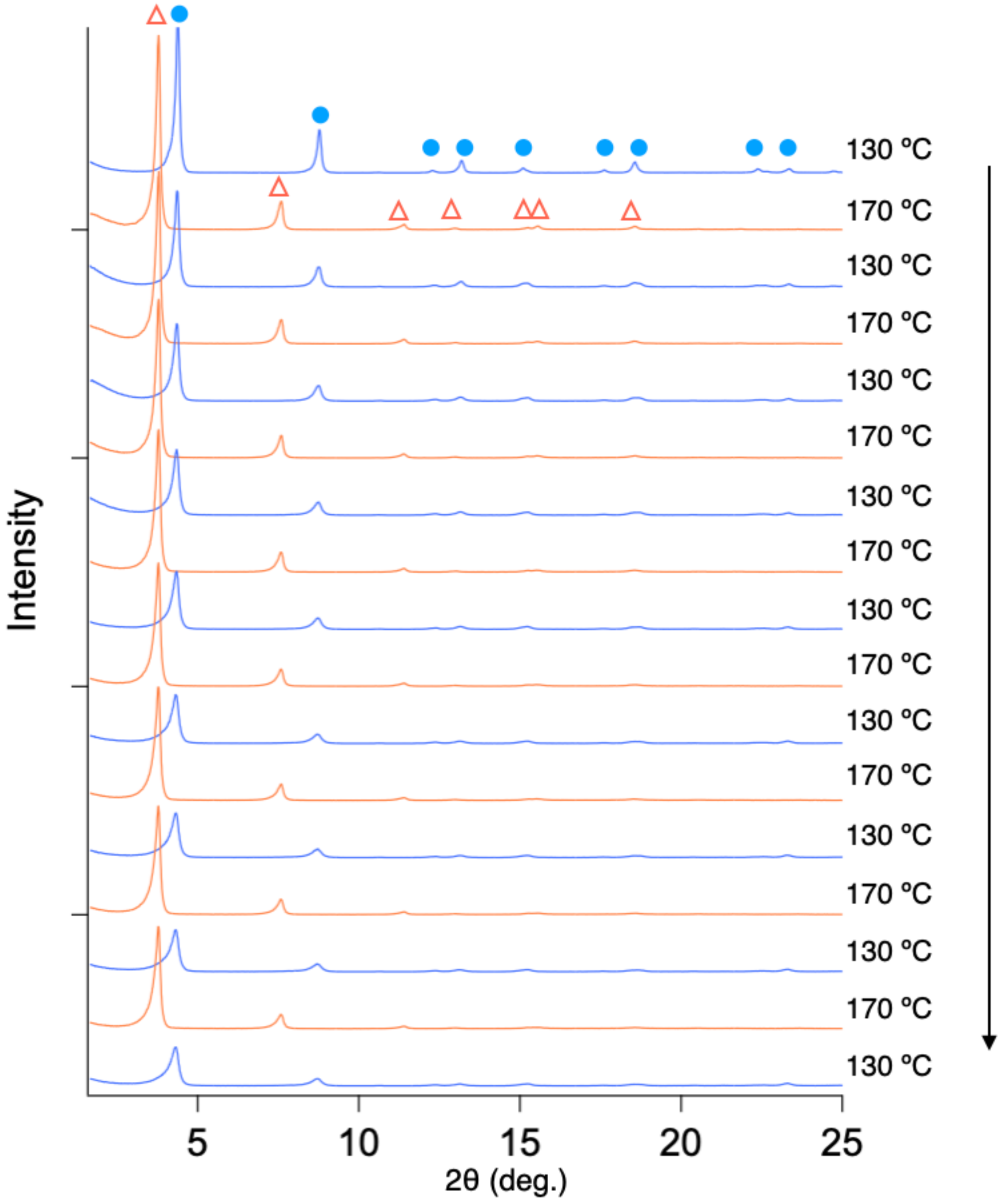


Fig. S10 PXRD profiles (λ = 1.54 Å, CuKα) of Zn**C16** measured during repetitive temperature increasing/decreasing cycles within the 130–170 °C window. The peaks marked by blue circles and red triangles are assignable to the diffraction of **LT** and **HT** respectively. The black arrow shows the order of the measurements.

4-5. Single crystal structure of coordination polymer ZnC16 (HT)

Crystal data for ZnC16 (HT) at 460 K (177 °C)

Crystal data for $C_{24}H_{36}O_5Zn$: $F_w = 469.90$, crystal dimensions 0.1 × 0.1 × 0.1 mm, monoclinic, space group *C2/m*, $a = 7.3454(16)$, $b = 16.8251(13)$, $c = 23.326(14)$ Å, $\beta = 91.95(4)$°, $V = 2881.1(19)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.083$ g·cm^{-3}, $\mu = 0.063$ mm^{-1}, $T = 450$ K, $\lambda(\mathrm{MoK}\alpha) = 0.24792$ Å, $2\theta_{\max} = 14.16000$°, 3027/913 reflection collected/unique ($R_{\mathrm{int}} = 0.0977$), $R_1 = 0.1156$ ($I > 2\sigma(I)$), $wR_2 = 0.4144$ (for all data), GOF = 1.035, largest diff. peak and hole 0.454/-0.230 eÅ^{-3}. CCDC deposit number 2194402.

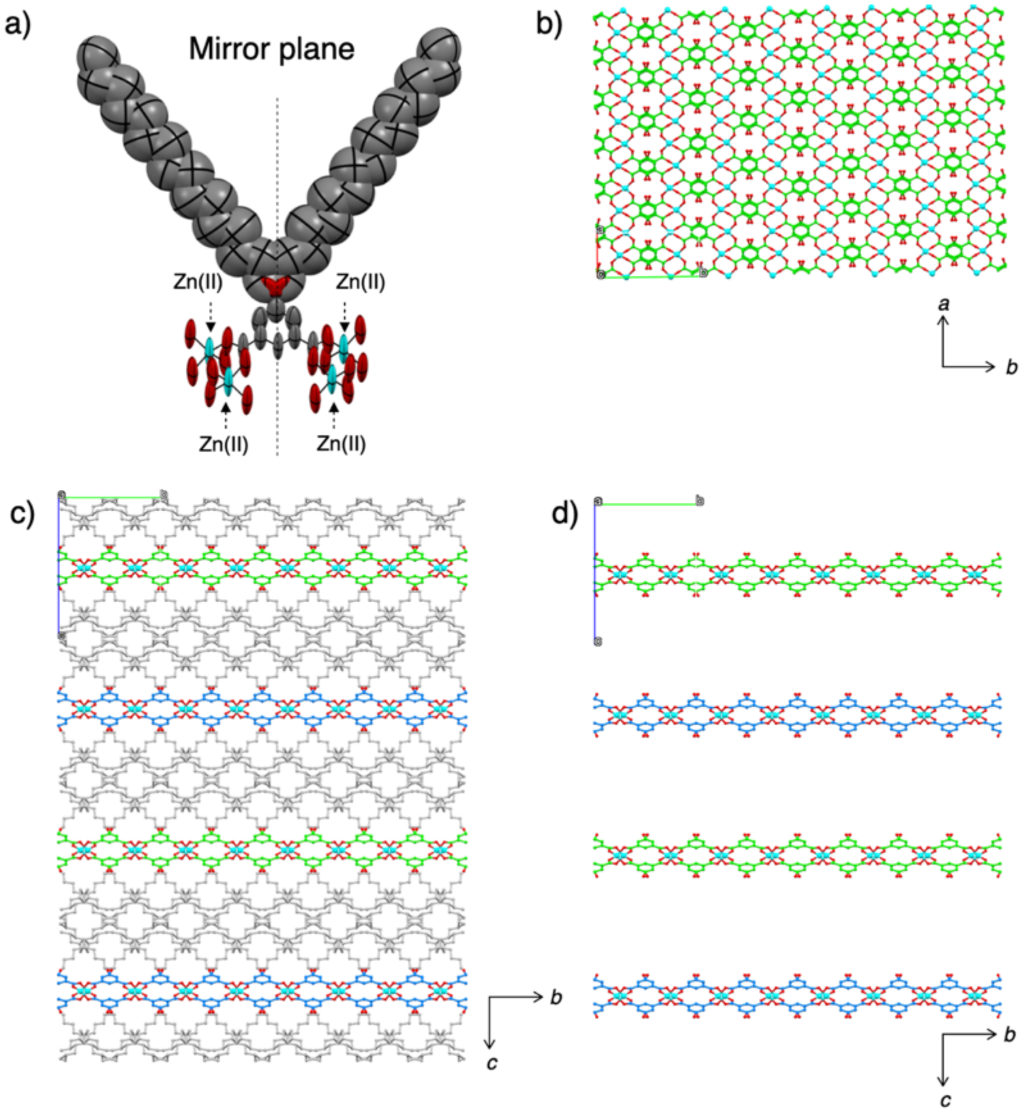
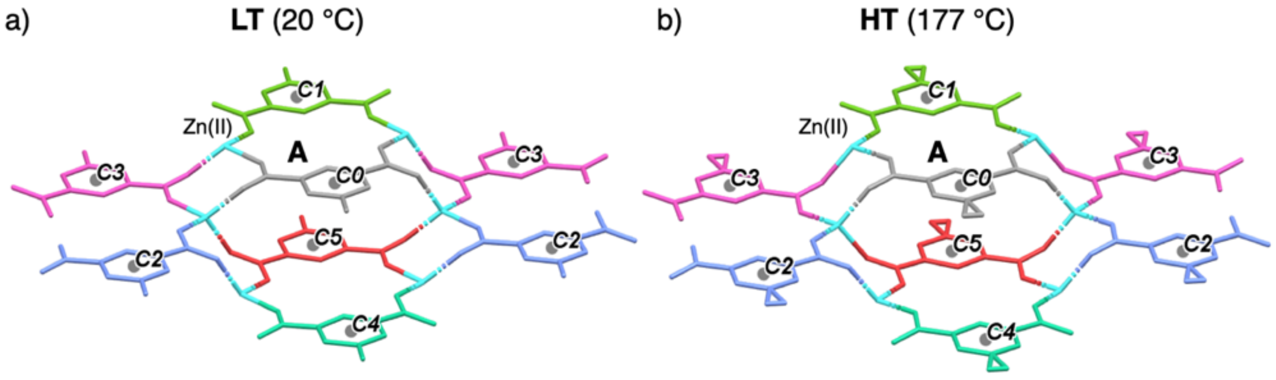


Fig. S11 Crystal structure of Zn**C16** (**HT**) at 177 °C. a) ORTEP view (50% probability level) of single ligand. Structure of 2D coordination polymer network. Views from b) *c*-axis and c,d) from *a*-axis with ball and stick model. C atoms of the aromatic rings of the adjacent layer are shown in different colours. Atoms of *n*-hexadecyloxy chains of each **C16**$^{2-}$ on Fig. S11a,c are disordered over two sites with 50% occupancy. Alkyl chains on Fig. S11b,d are omitted for clarity. (C of the aromatic rings: pale green or blue, C of the alkyl chains: pale gray, O: red, Zn: pale blue)

Table S1. Comparison of the key cell parameters of the single crystal structures of **LT** and **HT**.

	LT (293 K)	**HT (450 K)**
Empirical formula	$C_{24}H_{36}O_5Zn$	$C_{24}H_{36}O_5Zn$
Crystal system	Triclinic	Monoclinic
Space Group	*P*–1	*C*2/m
a (Å)	7.0651(2)	7.3454(16)
b (Å)	9.0096(3)	16.8251(13)
c (Å)	20.2493(5)	23.326(14)
α (°)	78.148(5)	90
β (°)	89.073(6)	91.95(4)
γ (°)	69.912(5)	90
V (Å^3)	1182.65(7)	2881.1(19)
Z	2	4



c)

Distance	**LT** (Å)	**HT** (Å)	|Δ| (Å)
C0–C1	8.246	8.195	0.051
C0–C2	9.347	9.179	0.168
C0–C3	10.223	9.949	0.273
C0–C4	7.065	7.345	0.280
C0–C5	4.158	3.985	0.173

Fig. S12 Comparison of the coordination polymer network of **LT** and **HT**. Partial crystal structures of coordination polymer network of a) **LT** (20 °C) and b) **HT** (177 °C). Alkyl chains are omitted for clarity. Ligands locating around the inequivalent relative position to the central one (marked by **A**, coloured by grey) are shown in different colours. *C0*–C*5* represent centroids of each aromatic rings. c) List of the distances among the centroids of aromatic rings in **LT** and **HT**, and their absolute differential values between **LT** and **HT**.

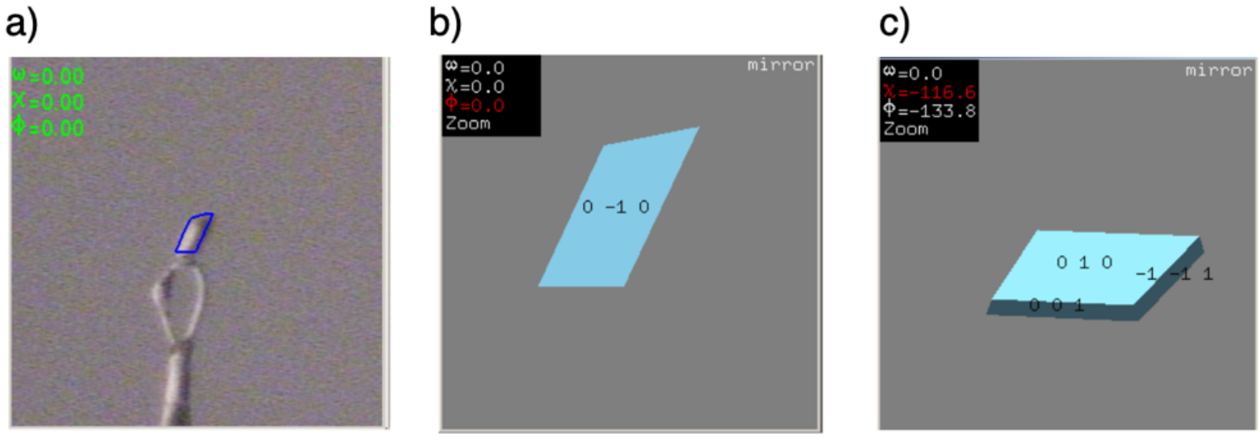


Fig. S13 a) Photograph of a single crystal of **LT**. b-c) Face-indexing graphics of **LT**.

4-6. Visual observation of coordination polymer ZnC16

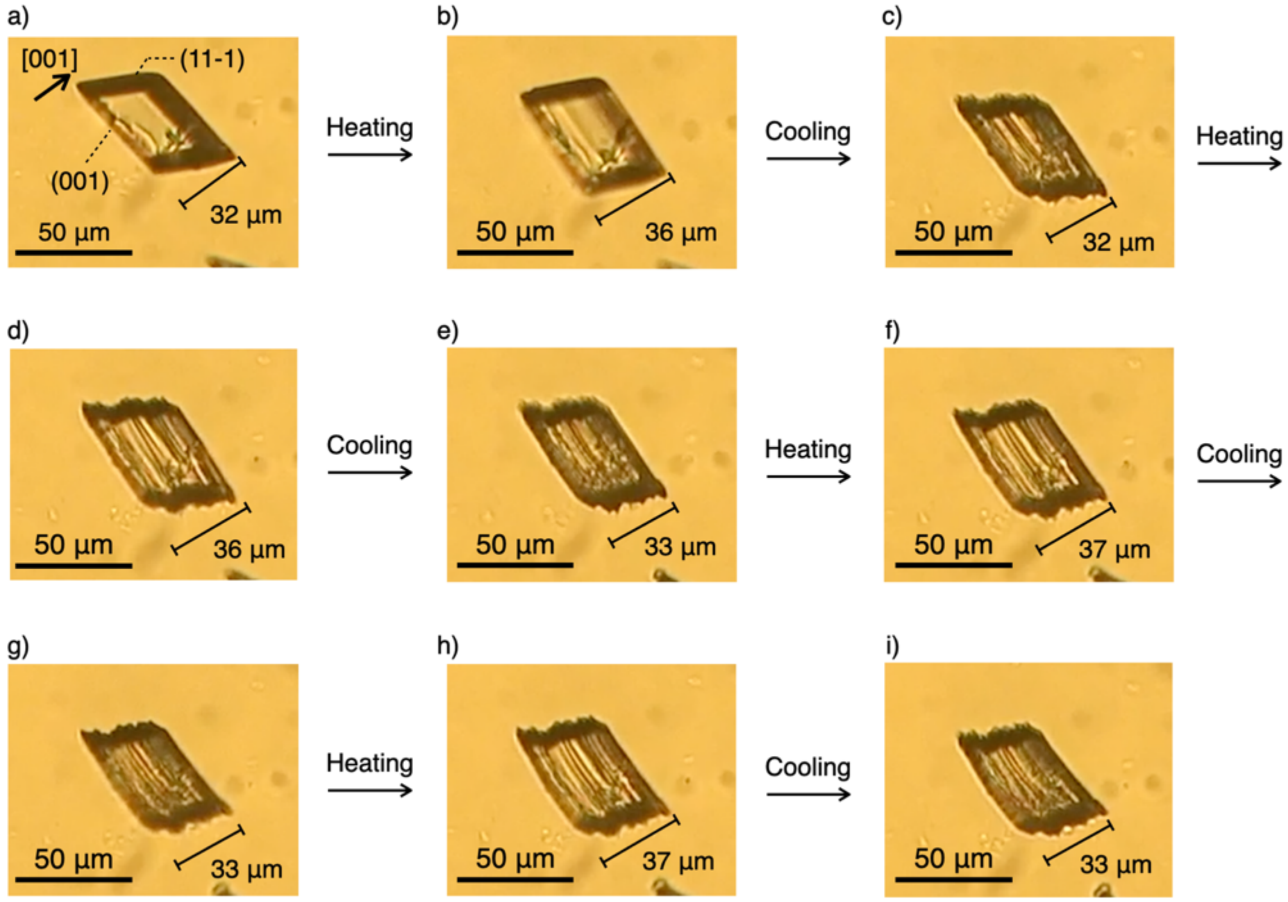


Fig. S14 Photographs showing shape deformation of crystals of Zn**C16** upon repetitive temperature increasing/decreasing cycles within the 140–160 °C window at ca. 20 °C/min (Movie S1). Captions a–i show the sequence of transition. Change in crystal thickness along [001] direction upon temperature cycles is shown in Fig S14, which were estimated by measuring the distances between the opposite (001) axis of the parallelogram shape using microscopic images.

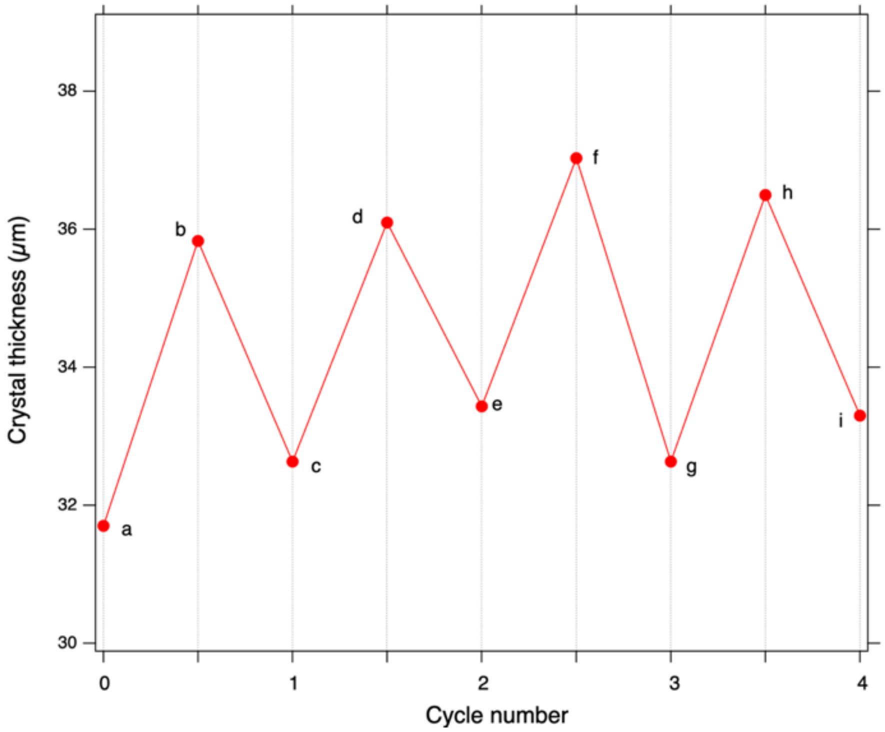


Fig. S15 Change in crystal thickness along [001] direction upon repetitive temperature increasing/decreasing cycles within the 140–160 °C window 20 °C/min. Captions a–i locating next to the circle show the pictures of corresponding crystals in Fig. S13.

4-7. DSC thermograms of coordination polymer ZnC16

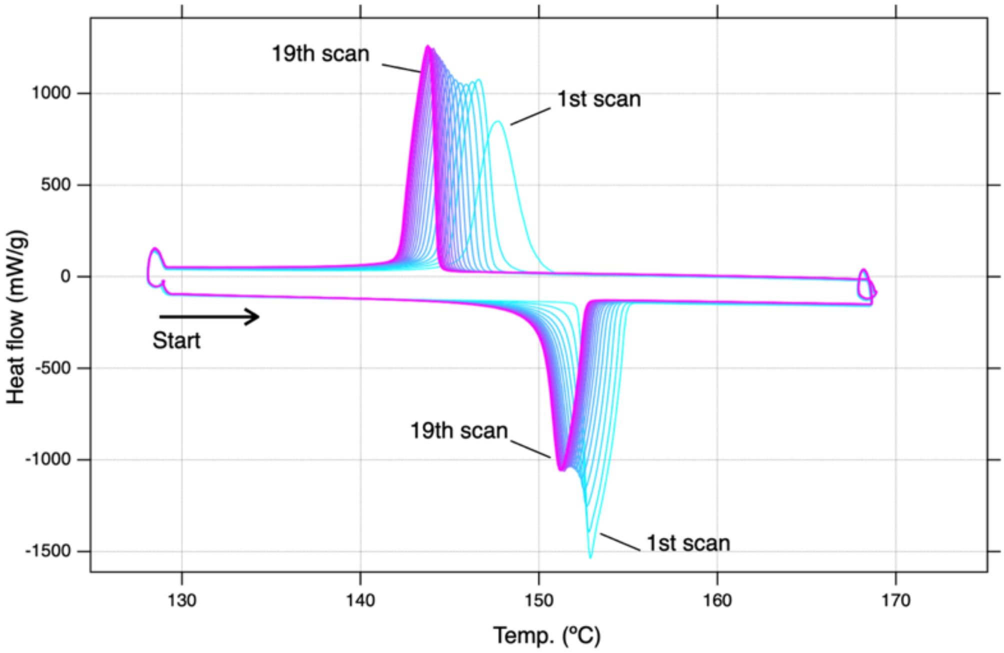
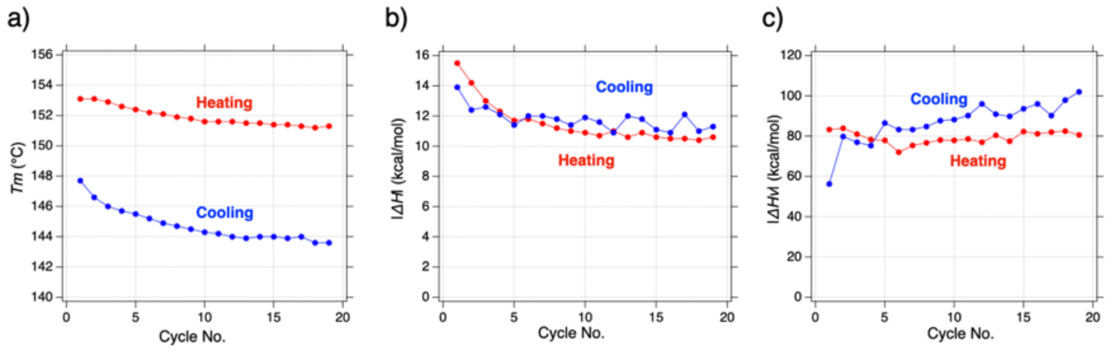


Fig. S16 DSC thermogram of Zn**C16** measured under repetitive temperature increasing/decreasing cycles within the 130–170 °C window. (scan rate 1 °C/min). Thermograms are coloured by cyan (1st scan) to magenta (19th scan) sequentially.



$$C_p(T) = \frac{K(T)\,\Delta Hv\,\Delta H}{(K(T)+1)^2\,RT^2} \qquad \cdots (1)$$

$$K(T) = \exp\left(\frac{-\Delta Hv}{RT}\left(1-\frac{T}{T_m}\right)\right) \qquad \cdots (2)$$

$C_p(T)$: Molar heat capacity

$K(T)$: Equilibrium constant between **LT** and **HT**

Fig. S17 Changes in a) phase transition temperatures (Tm), b) absolute values of transition enthalpy ($|\Delta H|$), and c) absolute values of van't Hoff enthalpy ($|\Delta Hv|$) estimated from the curve fitting of the DSC thermograms using eq (1) and eq (2) (Fig. S16). The error values of the curve fitting for Tm, $|\Delta H|$, and $|\Delta Hv|$ are less than 0.06 °C, 0.5 kcal/mol, and 6.0 kcal/mol respectively.

5. References

1. P. Reb, K. Margarit-Puri, M. Klapper and K. Müllen, *Macrocolecules*, 2000, **33**, 7718–7723.
2. G. M. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3─8.
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4. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339─341.
5. CrysAlisPro, version 1.171.42.56a. Rigaku Corporation, Oxford, UK, 2022.