#### **Supplementary Information**

## Thermal and optical properties of multiblock macrocycles with hysteretic polymorphic transition

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## 1. ORTEP drawings of 1





c)



**Fig. S1** a–c) ORTEP drawings of **1** (50% thermal ellipsoids) from three different angles. The X-ray diffraction data were collected at 100 K. The TEG chain contains disordered parts.

#### 2. Differential scanning calorimetry of 1



**Fig. S2** a) A differential scanning calorimetry profile of the as-grown crystals of 1 prepared by vapor diffusion between THF and *n*-hexane. b) A magnified view of the differential scanning calorimetry profile in the heating process shown in Fig. 2a. Rate:  $5.0 \,^{\circ}\text{C min}^{-1}$ .

3. Polarized optical micrographs and powder X-ray diffraction of 1



**Fig. S3** Polarized optical micrographs of **1** at a) 140 °C and b) 200 °C in the temperature elevation process from the as-grown crystals prepared by vapor diffusion between THF and *n*-hexane (scale bars: 50  $\mu$ m). Powder X-ray diffraction patterns of **1** at c) 150 °C and d) 200 °C.

# 4. Differential scanning calorimetry, polarized optical micrographs and powder X-ray diffraction of 2



**Fig. S4** a) Differential scanning calorimetric profile of **2** in the temperature elevation followed by reduction processes (rate:  $5.0 \,^{\circ}\text{C} \,^{\min^{-1}}$ ), Cr and N represent crystal and nematic phase, respectively. Polarized optical micrographs of **2** at b) 30  $^{\circ}\text{C}$  and c) 250  $^{\circ}\text{C}$  in the temperature elevation process after cooling from 250  $^{\circ}\text{C}$  (scale bars: 100  $\mu$ m). d) Powder X-ray diffraction patterns of **2** at 50  $^{\circ}\text{C}$  after cooling from 250  $^{\circ}\text{C}$  and at 240  $^{\circ}\text{C}$  upon heating.



#### 5. UV-vis absorption, fluorescence and infrared spectra of 2

**Fig. S5** a) UV-vis absorption and b) fluorescence spectra of **2** at 25 °C (Cr state). Excitation at 370 nm. c) Variable-temperature infrared (IR) spectra of **2** upon heating (40, 60, 80, 100 and 120 °C).



### 6. High-resolution electrospray ionization time-of-flight mass spectra of 1 and 2



**Fig. S6** High-resolution electrospray ionization time-of-flight mass spectra of a) **1** and b) **2**. Solvent: MeCN.

7. Powder X-ray diffraction of 1



**Fig. S7** Powder X-ray diffraction patterns of a) as-grown crystals (25 °C), b) Cr1 (80 °C), and c) Cr2 (120 °C) of **1**.