Supplementary Information

Polymorphism or Pseudopolymorphism of a Macrocyclic Compound: Helical Structure, Layered Structure, and Pseudorotaxane Constructed by Weak Intermolecular Interactions

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1. General Information

Melting points were determined by using ATM-01 (AS ONE). ^{1}H and ^{13}C NMR spectrum was performed on a Bruker AV400 spectrometer (^{1}H operating frequency of 400 MHz) at 298 K in chloroform-d_3. Low mass spectrum was obtained on a JEOL MStation JMS-700 spectrometer, and high mass spectrum was obtained on a JEOL AccuTOF JMS-T100LC spectrometer. X-ray data were collected on a Bruker SMART ApexII and a Bruker SMART 1000 CCD detector. Crystal structures were solved by direct methods SHELXS-97 (Sheldrick, 1996) and refined by full-matrix least-squares SHELXL-97 (Sheldrick, 1997). All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included as their calculated positions. Column chromatography was performed by using a Wakogel C200, and thin-layer chromatography was carried out on 2.00 mm Merck precoated silica gel glass plates. Gel Permeation Chromatography (GPC) was performed using recycling preparative HPLC (LC-9204, Japan Analytical Industry Co., Ltd.) and a JAIGEL H series column (Japan Analytical Industry Co., Ltd.). Solid-state CD spectra were measured using a KBr tablet. A mixture of 0.1 mg of the crystal and 100 mg of KBr were well-ground and formed into the tablet with a radius of 5 mm. Differential scanning calorimetry (DSC) was measured at a heating rate of 10 K/min. Samples weighing 1–3 mg were heated in open aluminum pans at a rate of 10 K/min under a nitrogen gas flow of 4 mL/min.

2. Preparation of cyclic aromatic hydrocarbon 1. To a solution of tetrachlorotitanium (2.19 mL, 20 mmol) in 1,4-dioxane (150 mL), the zinc powder (2.61 g, 40 mmol) was added slowly with stirring at –10 °C under argon atmosphere, and then the mixture was heated at reflux for 2 h. To the suspension, a solution of 1-acetyl-4-(4'-acetylphenyl)benzene (0.482 g, 2 mmol) in 1,4-dioxane (50 mL) was added, and then the mixture was heated at reflux for 18 h. A quenching solution of 10% K_2CO_3 in water was carefully introduced and the mixture was extracted with diethyl ether. The organic layer was washed with brine and dried over Na_2SO_4, and evaporated to give a crude product, which was purified by silica gel column chromatography (eluent: $CHCl_3$:hexane=1:3) and preparative gel permeation chromatography with chloroform as the mobile phase to give the macrocycle **1** in 11% yield: mp >300 °C (decomposed); FT-IR (ATR, cm–1): 3019, 1652, 1540, 1507, 820.; ^{1}H NMR (400 MHz, $CDCl_3$, 27 °C): δ 7.30 (d, J = 8.4 Hz, 12H), 6.93 (d, J = 8.4 Hz, 12H) and 2.17 ppm (s, 18H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 143.62, 137.15, 133.15 (*C*), 129.34 (*C*H), 125.42 (*C*H) and 21.10 (*C*H_3) ppm.; FAB-MS *m/z* 618.7; ESI-HRMS *m/z* found 619.33593, calc. for $C_{48}H_{42}$ *m/z* 619.33526.

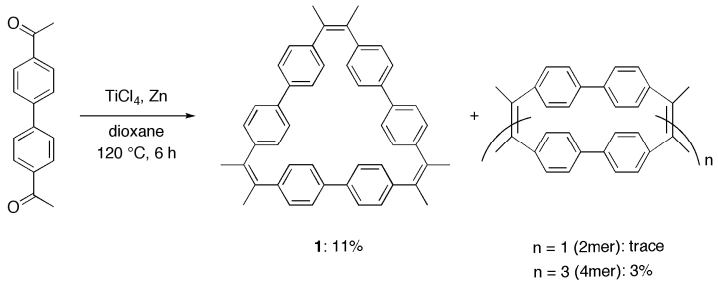


Fig. S1 Synthesis of macrocyclic hydrocarbons.

3. ^{1}H NMR and ^{13}C NMR Spectrum Data

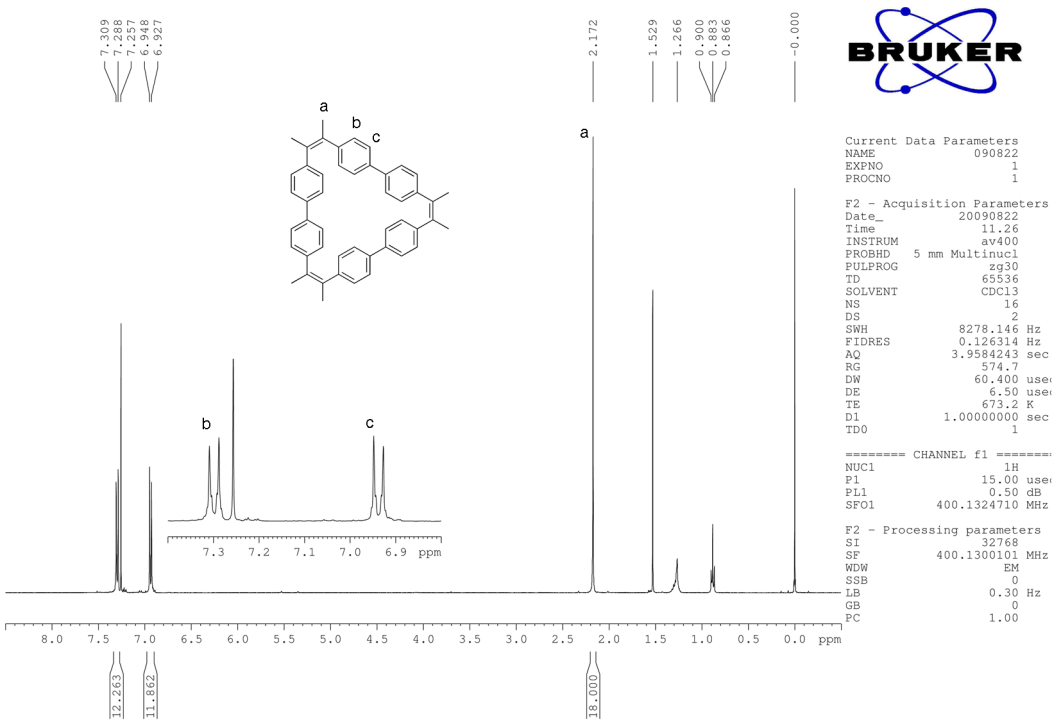


Fig. S2 ^{1}H NMR of **1**

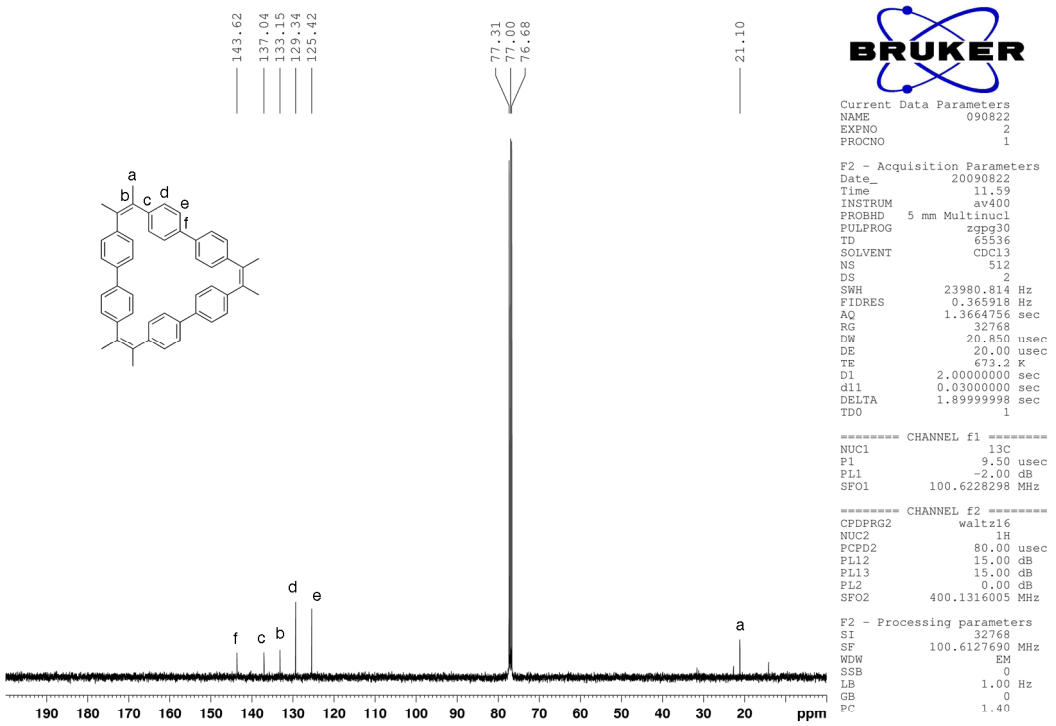


Fig. S3 ^{13}C NMR of **1**

4. X-ray Crystallographic Analyses Data.

Crystal data for 1a. $C_{48}H_{42}$; M = 618.82 g mol^{-1}, colorless plate measuring 0.40 × 0.20 × 0.20 mm, hexagonal, $P6_1$, $a = b$ = 15.071(17), c = 28.95(4) Å, V = 5695(12) Å^3, Z = 6, D_c = 1.083 Mg m^{-3}, T = 100 K, μ (MoKα) = 0.061 mm^{-1}, $2\theta_{max}$ = 41.34°, 16750 reflections, 1989 unique reflections (R_{int} = 0.0940) which were used in all calculations. R_1 = 0.1078, wR_2 = 0.1858 (all data) R_1 = 0.0615, wR_2 = 0.1447 ($I > 2\sigma(I)$) for 440 parameters. CCDC reference number 748361.

Chirality and space group of the crystal were not determined because Friedel pairs were merged before the final refinement.

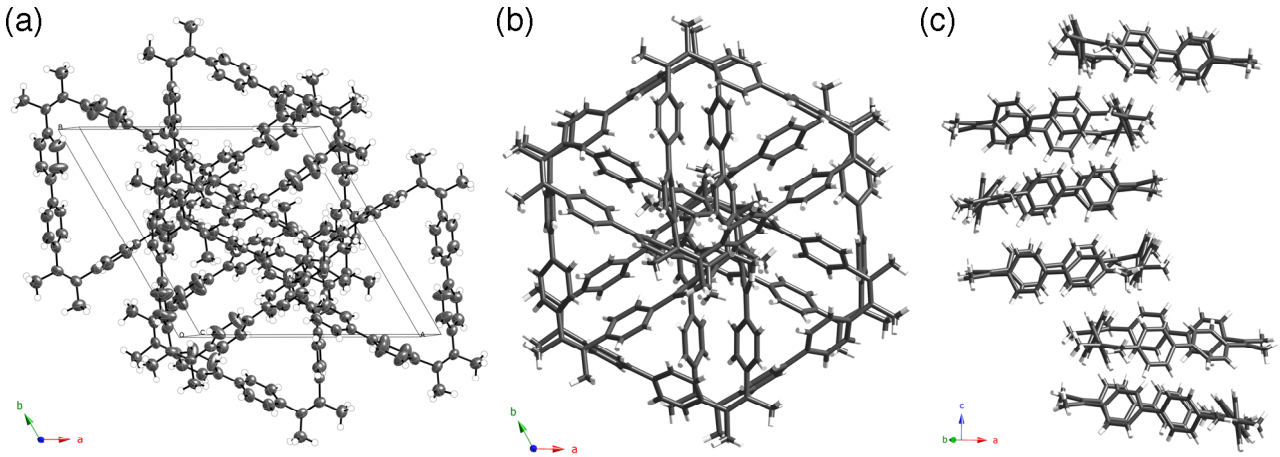


Fig. S4 (a) Thermal ellipsoids model of unit cell of **1a**. Ellipsoids of all non-hydrogen atoms are drawn at the 50% probability. (b) Top view of helical structure of **1a**. (c) Side view of helical structure of **1a**.

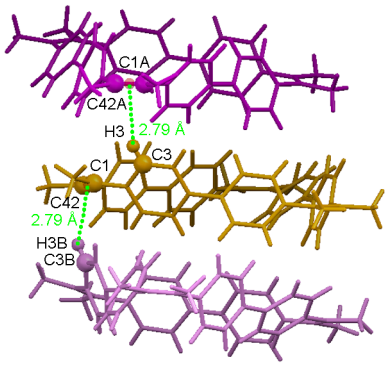


Fig. S5 C–H···π (olefin) interactions between adjacent molecules in the crystal **1a**. Symmetry codes: A = -1+x, -1+y, z; B = y, 1-x, -/6+z.

Table S1 Details of the selected interactions of the crystal **1a**.

D–H···A	D–H	H···A	D···A	D–H···A	symop-for-A
C3 H3 Cg1[a]	0.95	2.79	3.632(12)	148	y, -x+y, -1/6+z
C43 H43A Cg2[b]	0.99	2.93	3.742(15)	141	-x+1, y, z

[a]Cg1: the center of the olefine (C1=C42)
[b]Cg2: the center of the phenyl ring (C16–C21)

Crystal data for 1b. $C_{48}H_{42}$; M = 618.82 g mol^{-1}, colorless plate measuring 0.40 × 0.20 × 0.20 mm, monoclinic, $P2_1/c$, a = 11.951(1), b = 24.458(3), c = 13.2828(1) Å, β = 113.400(1) °, V = 3562.9(7) Å^3, Z = 4, D_c = 1.154 Mg m^{-3}, T = 150 K, μ (MoKα) = 0.065 mm^{-1}, $2\theta_{max}$ = 27.02°, 16772 reflections, 7073 unique reflections (R_{int} = 0.406) which were used in all calculations. R_1 = 0.1139, wR_2 = 0.1742 (all data) R_1 = 0.0547, wR_2 = 0.1388 ($I > 2\sigma(I)$) for 439 parameters. CCDC reference number 748362.

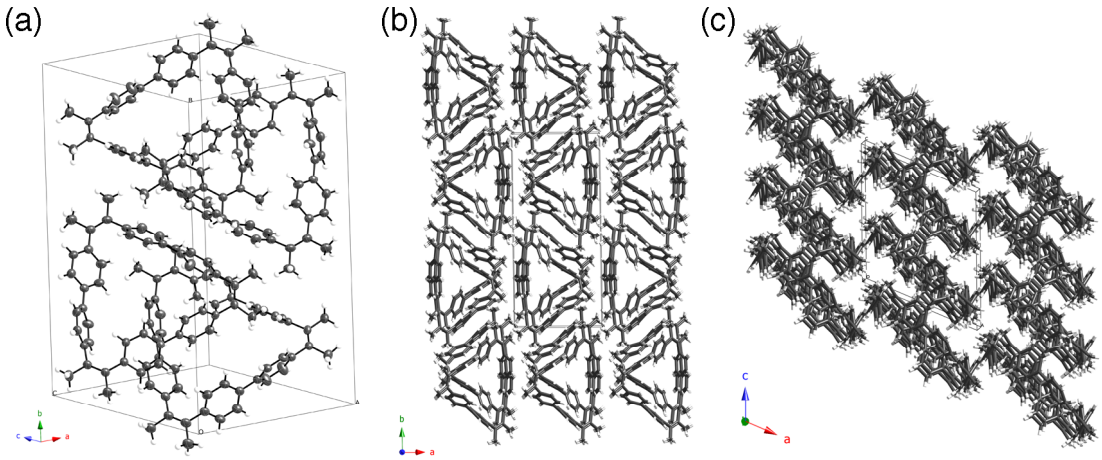


Fig. S6 (a) Thermal ellipsoids model of unit cell of **1b**. Ellipsoids of all non-hydrogen atoms are drawn at the 50% probability. **(**b) Top view of layer structure of **1b**. (c) Side view of layer structure of **1b**.

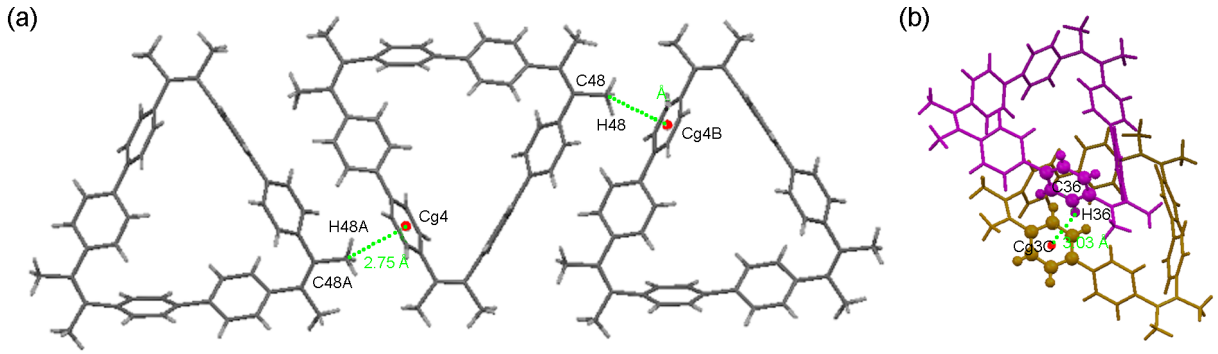


Fig. S7 (a) Weak C–H···π interactions between adjacent molecules of **1b**. (b) Tilted T-shaped aromatic–aromatic interactions between adjacent molecules in the crystal **1b**. Symmetry codes: A = 1-x, 1/2+y, 1/2-z; B = 1-x, -1/2+y, 1/2-z; C = x, 1/2-y, -1/2+z.

Table S2 Details of the selected interactions of the crystal **1b**.

D–H···A	D–H	H···A	D···A	D–H···A	symop-for-A
C20 H20 Cg2[a]	0.95	2.52	3.286(2)	137	x, y, z
C36 H36 Cg3[b]	0.95	3.03	3.834(4)	143	x, 1/2-y, -1/2+z
C48 H48 Cg4[c]	0.98	2.75	3.395(1)	124	1-x, -1/2+y, 1/2-z

[a]Cg2: the center of the phenyl ring (C9–C14)
[b]Cg3: the center of the phenyl ring (C19–C24)
[c]Cg4: the center of the phenyl ring (C25–C30)

Crystal data for 1c. $C_{48}H_{42}{\cdot}C_6H_{12}$; M = 704.99 g mol^{-1}, colorless plate measuring 0.30 × 0.20 × 0.20 mm, triclinic, P-1, a = 14.762(9), b = 15.100(9), c = 22.11(1) Å, α = 77.18(1), β = 74.95(1), γ = 62.186(9) °, V = 4181(4) Å^3, Z = 4, D_c = 1.120 Mg m^{-3}, T = 150 K, μ (MoKα) = 0.063 mm^{-1}, $2\theta_{max}$ = 27.69°, 25347 reflections, 18414 unique reflections (R_{int} = 0.0912) which were used in all calculations. R_1 = 0.2878, wR_2 = 0.2262 (all data) R_1 = 0.0849, wR_2 = 0.1836 ($I > 2\sigma(I)$) for 989 parameters. CCDC reference number 748363.

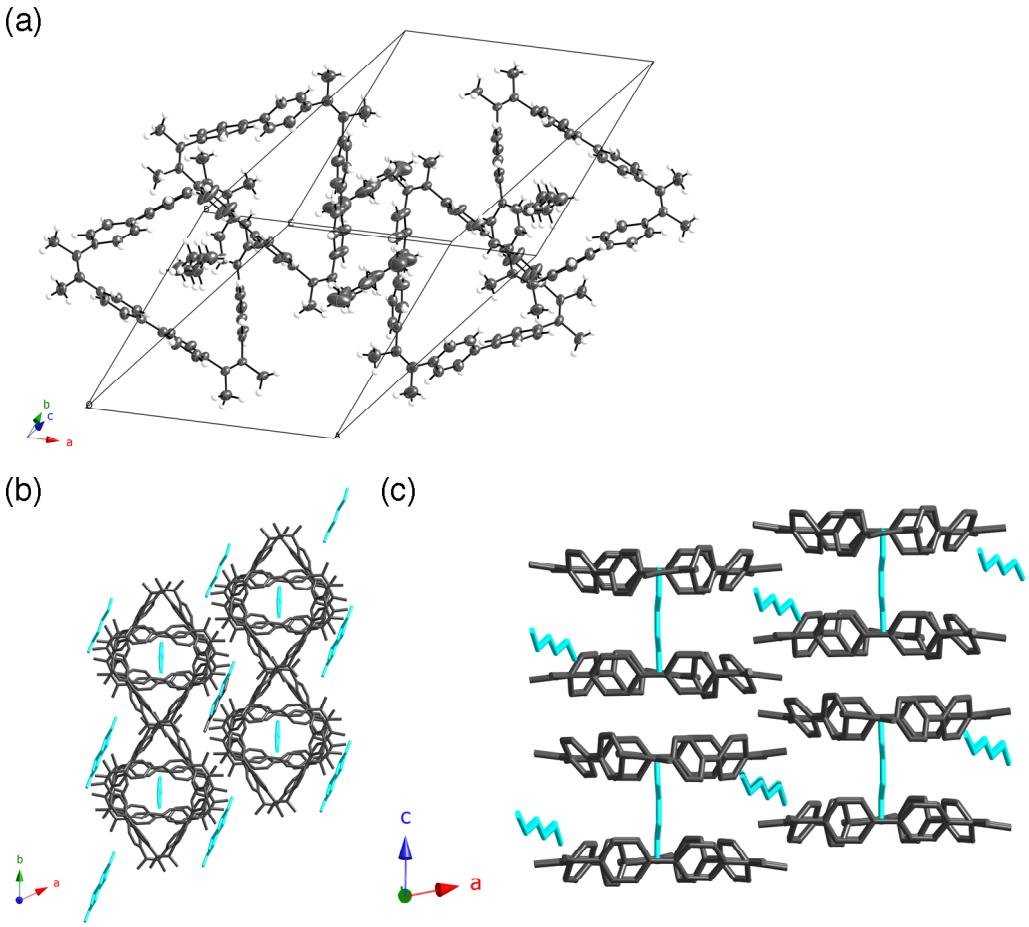


Fig. S8 (a) Thermal ellipsoids model of unit cell of **1c**. Ellipsoids of all non-hydrogen atoms are drawn at the 50% probability. **(**b) Top view of **1c**. (c) Side view of **1c**. The hydrogen atoms are omitted for clarity, and *n*-hexane is shown in turquoise blue.

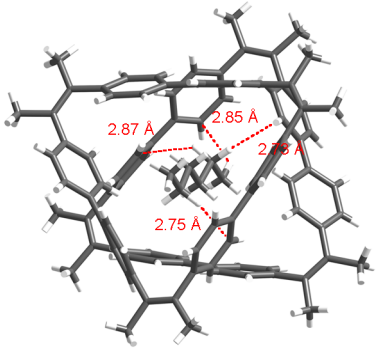


Fig. S9 van der Waals contacts between the hexane and the cyclic trimers.

Crystal data for 1d. $C_{48}H_{42}{\cdot}C_4H_8O_2$; M = 706.92 g mol^{-1}, colorless plate measuring 0.20 × 0.20 × 0.20 mm, triclinic, P-1, a = 11.385(3), b = 14.405(4), c = 14.984(4) Å, α = 115.121(4), β= 95.522(4), γ= 109.930(4) °, V = 2006.0(9) Å^3, Z = 2, D_c = 1.170 Mg m^{-3}, T = 120 K, μ (MoKα) = 0.069 mm^{-1}, $2\theta_{max}$ = 27.56 °, 11995 reflections, 8724 unique reflections (R_{int} = 0.0279) which were used in all calculations. R_1 = 0.1252, wR_2 = 0.2665 (all data) R_1 = 0.0831, wR_2 = 0.2373 ($I > 2\sigma(I)$) for 495 parameters. CCDC reference number 748364.

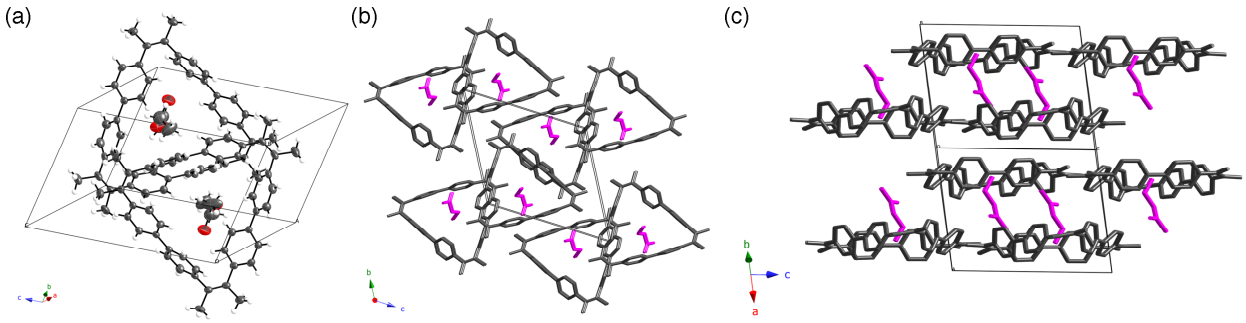


Fig. S10 (a) Thermal ellipsoids model of unit cell of **1d**. Ellipsoids of all non-hydrogen atoms are drawn at the 50% probability. **(**b) Top view of **1d**. (c) Side view of **1d**. The hydrogen atoms are omitted for clarity, and ethyl acetate is shown in magenta.

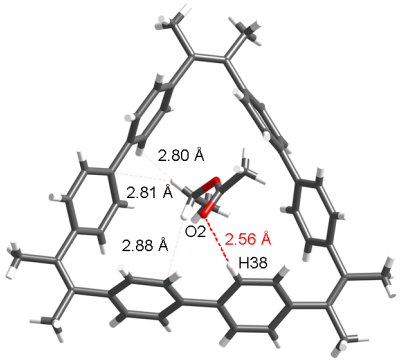
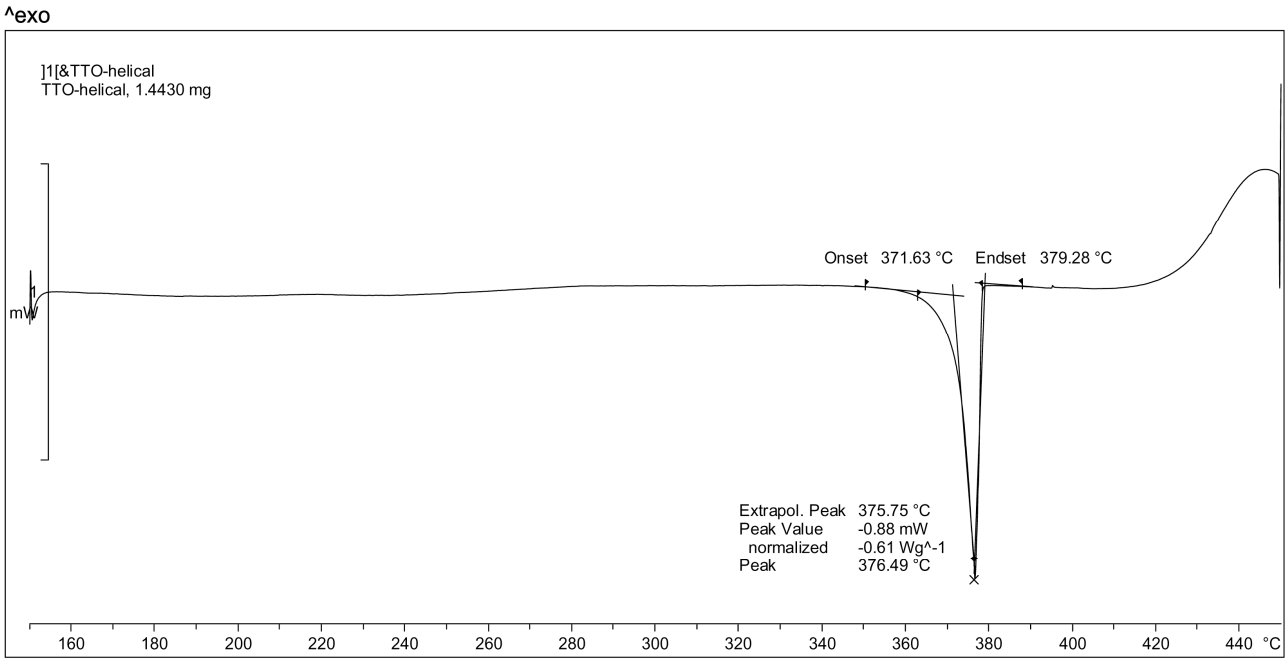


Fig. S11 Hydrogen-bonds (C–H···O) and weak interactions between the guest molecule (ethyl acetate) and the host molecule **1**.

Table S3 Details of the selected interactions of the crystal **1d**.

D–H···A	D–H	H···A	D···A	D–H···A	symop-for-A
C38 H38 O2	0.95	2.56	3.493(5)	169	x, y, z

5. DSC Spectra for crystal 1a.



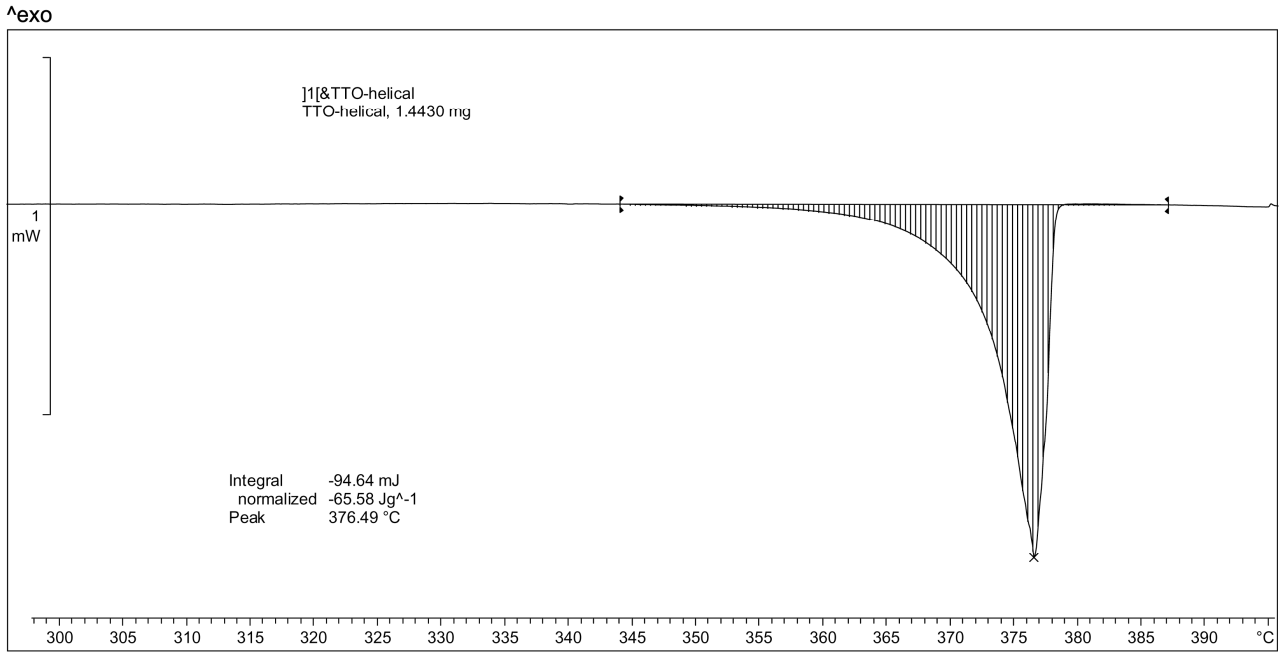


Fig. S12 DSC heating curves of **1a**; scanning rate 10 °C/min.

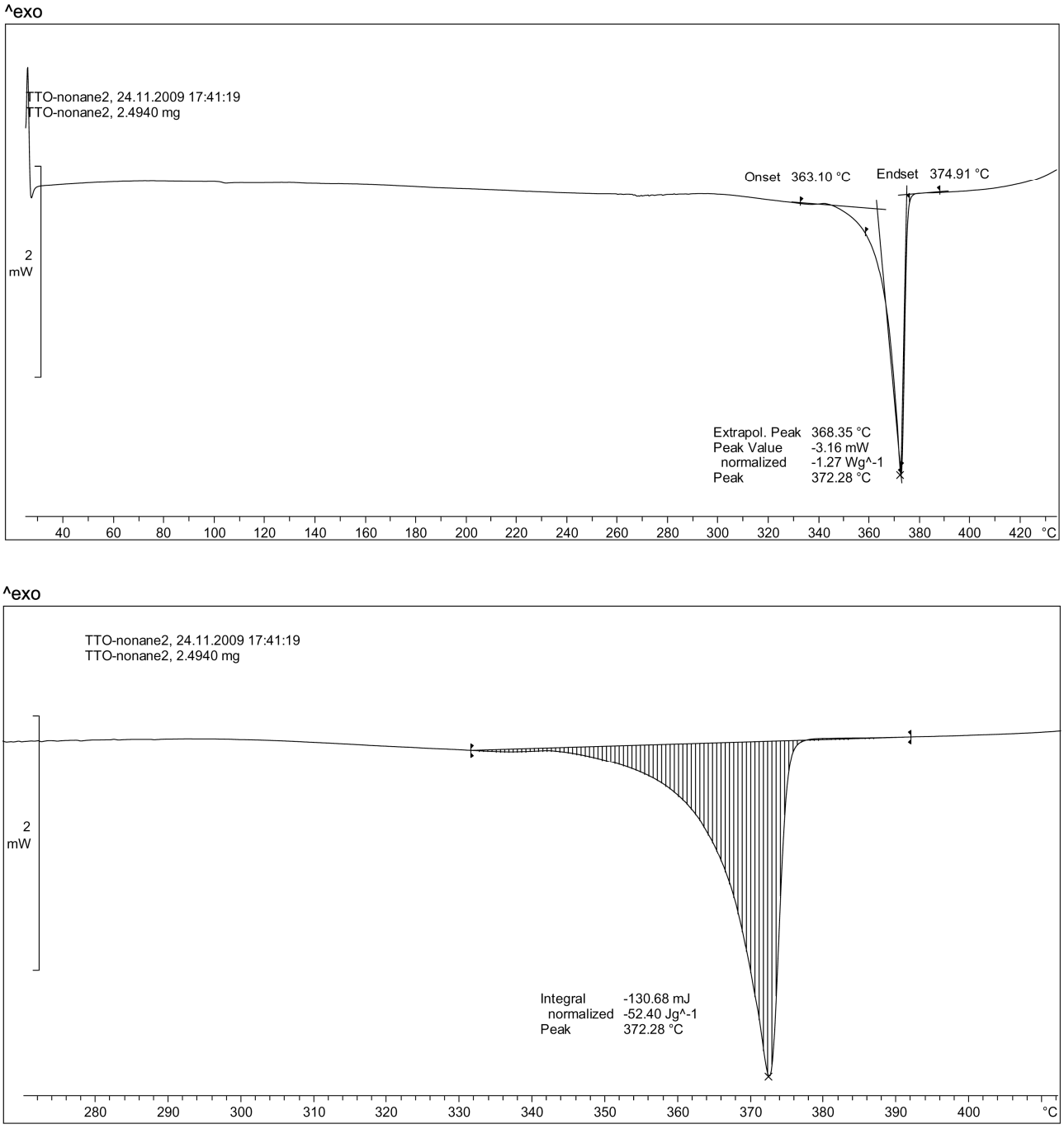


Fig. S13 DSC heating curves of **1b**; scanning rate 10 °C/min.

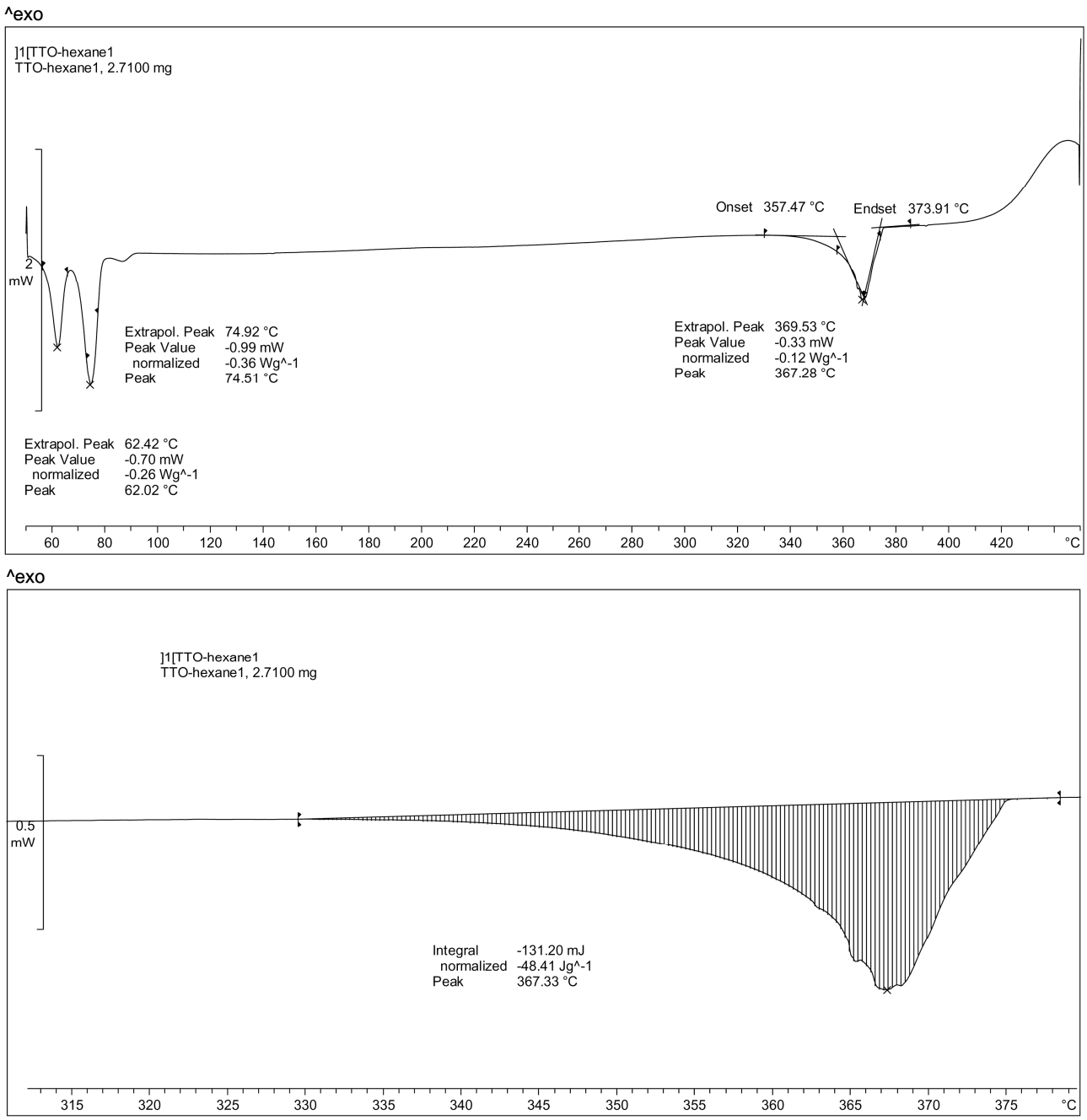


Fig. S14 DSC heating curves of **1c**; scanning rate 10 °C/min.

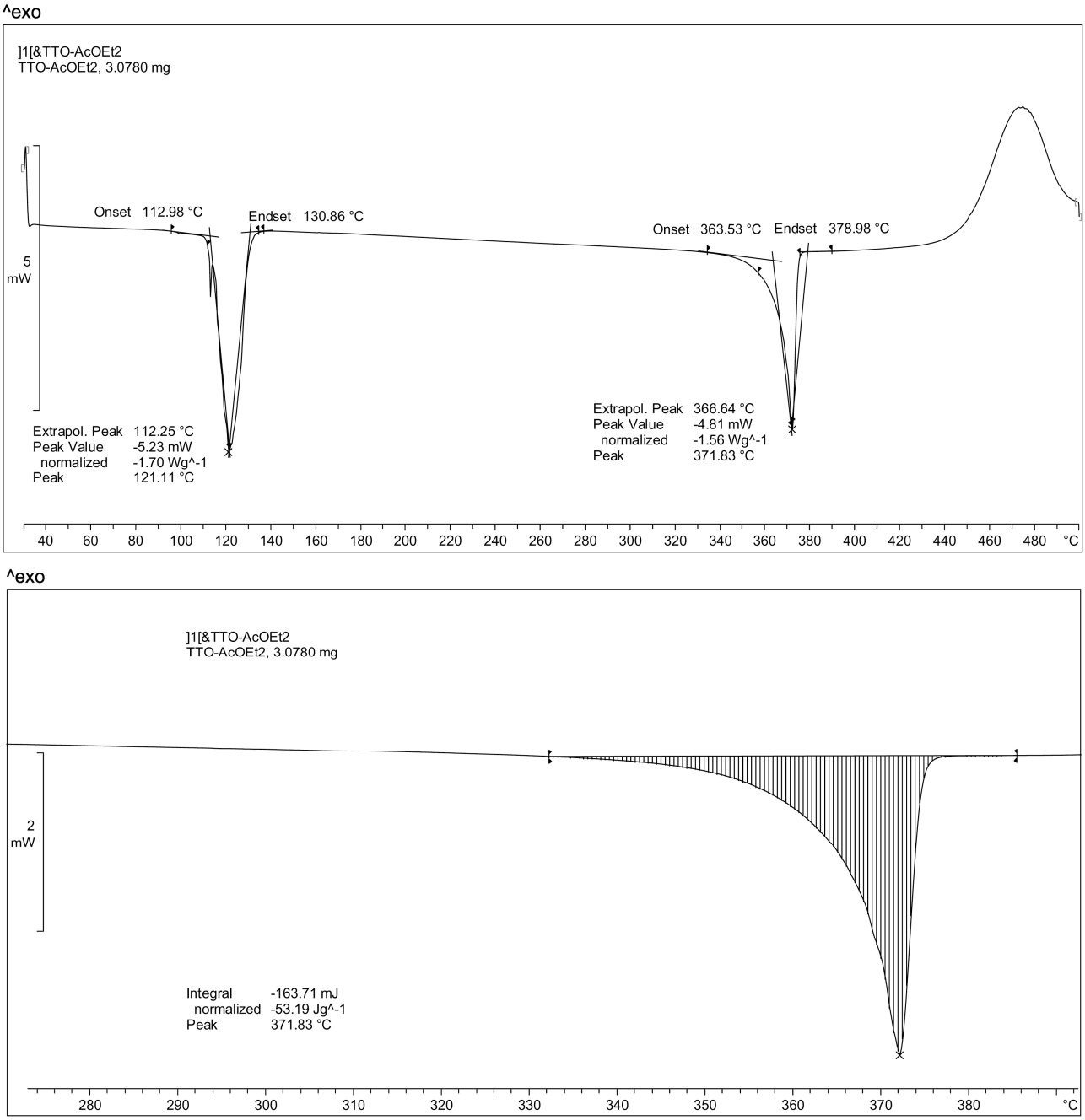


Fig. S15 DSC heating curves of **1d**; scanning rate 10 °C/min.