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Supplementary Materials

STM/TERS observation of (*M*)-type diphenyl [7]thiaheterohelicene on Ag(111)

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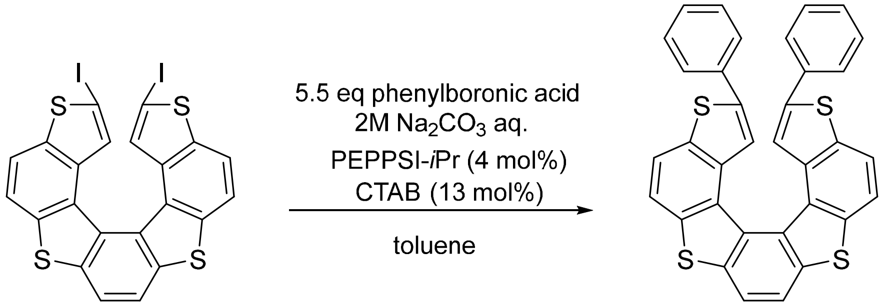
Synthesis and Optical resolution of Ph-[7]TH



Scheme S1. Synthesis of Ph-[7]TH from 2,13-diiodo[7]thiaheterohelicene.

To a stirred solution of a mixture of 2,13-diiodo[7]thiaheterohelicene[1] (25 mg, 0.038 mmol) and phenylboronic acid (26 mg, 0.21 mmol) in toluene (2.5 mL) were added PEPPSI-*i*Pr (1.0 mg, 0.0015 mmol, 4 mol%), hexadecyltrimethylammonium bromide (CTAB) (1.8 mg, 0.0049 mmol, 13 mol%) and 2 M aqueous Na_2CO_3 (2.5 mL), and the mixture was stirred for 2 h at reflux temperature. After addition of water, the organic layer was separated. The aqueous layer was extracted with ethyl acetate. The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated. The crude product was chromatographed on silica gel column using hexane-chloroform (5:1) as an eluent to give 2,13-diphenyl[7]thiaheterohelicene (14 mg, 64%) as a yellow solid.

Resolution of the enantiomers of Ph-[7]TH was performed on chiral analytical HPLC. The enantiomers were resolved from 5 mg of racemic mixture dissolved in 20 mL of chloroform/*n*-hexane (1:1). This solution was injected in 300 μL aliquots onto a CHIRALPAK® IG column (4.6 mm I.D. × 250 mm, 5 μm), with chloroform/*n*-hexane (1:1) eluent flowing at 1.0 mL/min at 40°C.

Figure S2(a) shows CD spectra of (*M*)- and (P)-Ph-[7]TH in chloroform. CD spectra were recorded on a J-820AC spectropolarimeter (JASCO Co.). We calculated CD spectrum of (*M*)-Ph-[7]TH by the DFT-based calculation using the B3LYP functional and the aug-cc-pVDZ basis set with Gaussian16 program package as shown in Figure S2(b). The spectrum was consistent with the experiments.

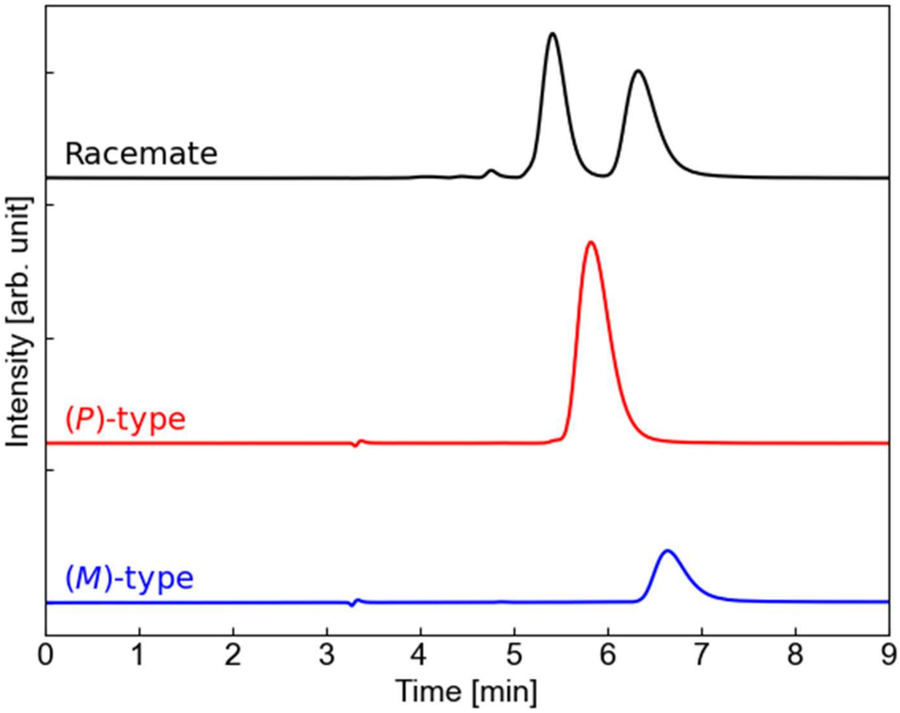


Figure S1. HPLC chromatograms of Ph-[7]TH: racemates (black) and (*P*)- (red), and (*M*)-enantiomers (blue).

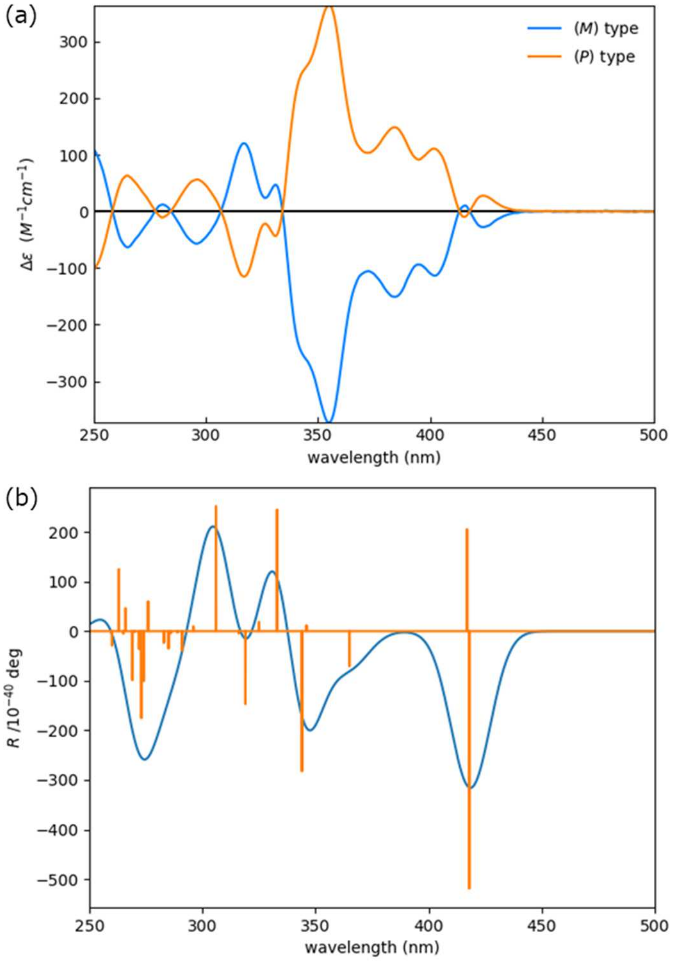


Figure S2: (a) CD spectrum of (*M*)- and (*P*)-Ph-[7]TH in chloroform. (b)DFT-based calculated CD spectrum of (*M*)-Ph-[7]TH. The orange sticks indicate the position and rotation strength of calculated states. The blue spectrum was obtained by broadening of gaussian distribution of the rotation strength.

TERS measurement position

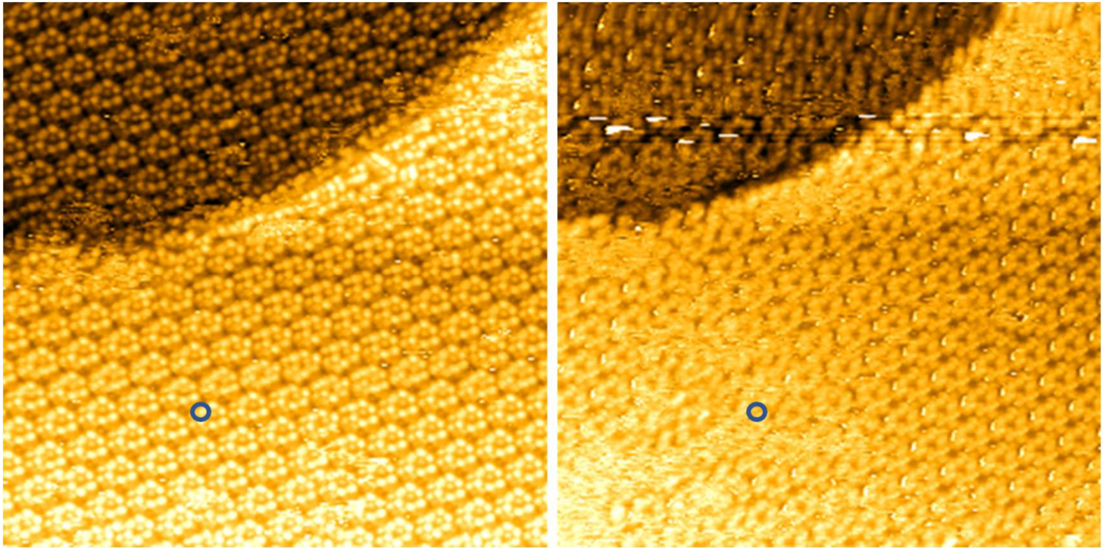


Figure S3: STM images of (*M*)-Ph-[7]TH on Ag(111) before (left) and after (right) the TERS measurements of Fig. 3 (50×50 nm^2 , -3. 0 V, 20 pA). TERS spectra were obtained at blue circles.

Raman active vibration mode

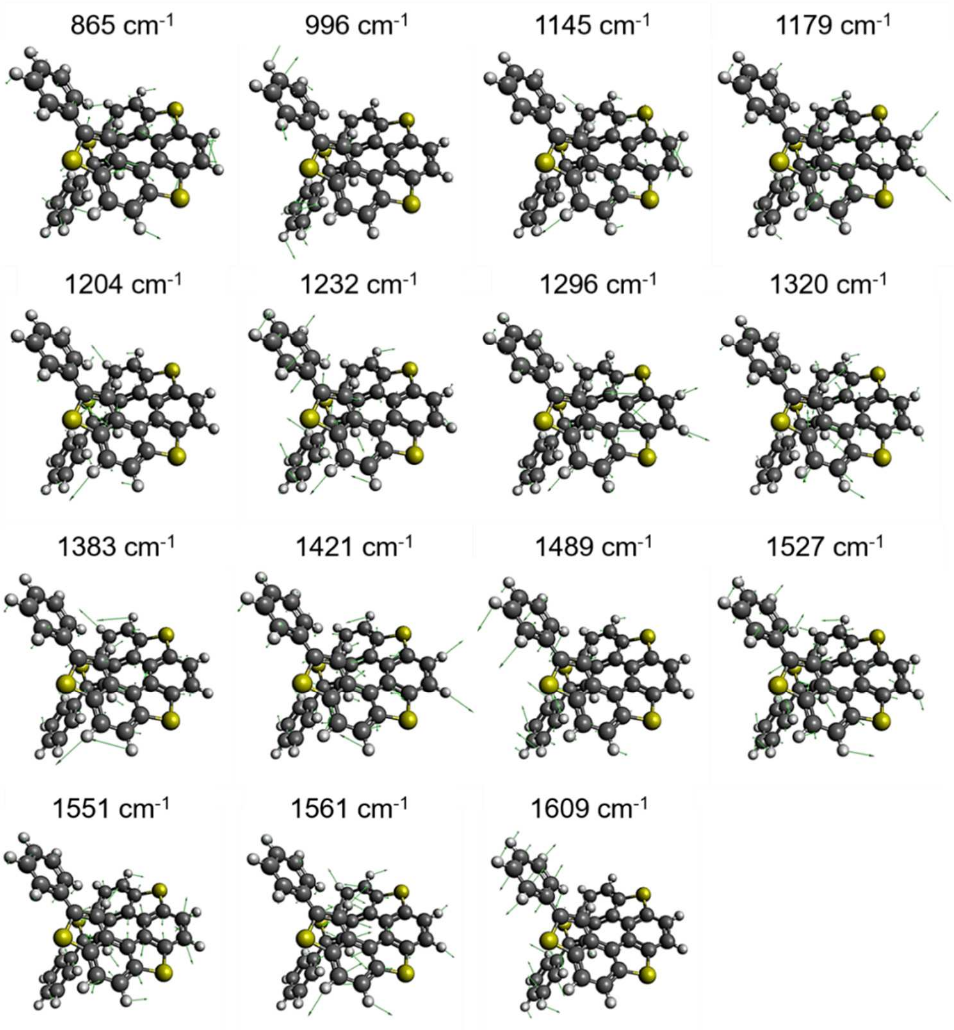


Figure S4: Raman active vibration modes of (*M*)-Ph-[7]TH. The green arrows indicate displacement of each vibration modes.

Sample bias voltage dependence of (*M*)-Ph-[7]TH on Ag(111)

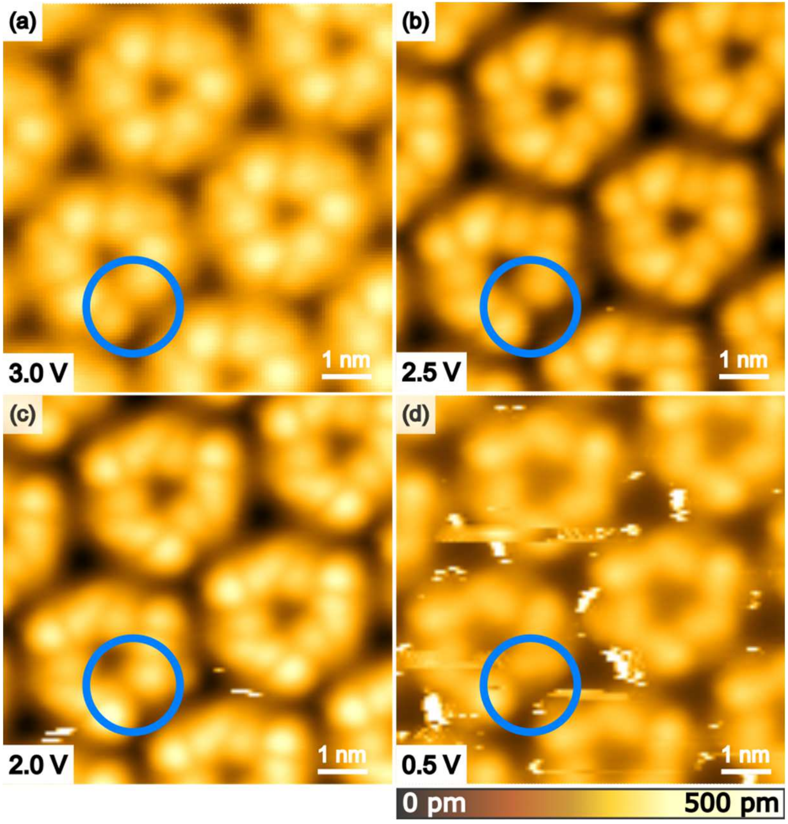


Figure S5: STM images of (*M*)-Ph-[7]TH in the large scale at (a)+3.0 V, (b)+2.5 V, (c)+2.0 V, (d)+0.5 V. All STM images were acquired at 50 pA. Defects indicated by blue circles ensure that these images were obtained at the same area.

Molecular orbitals

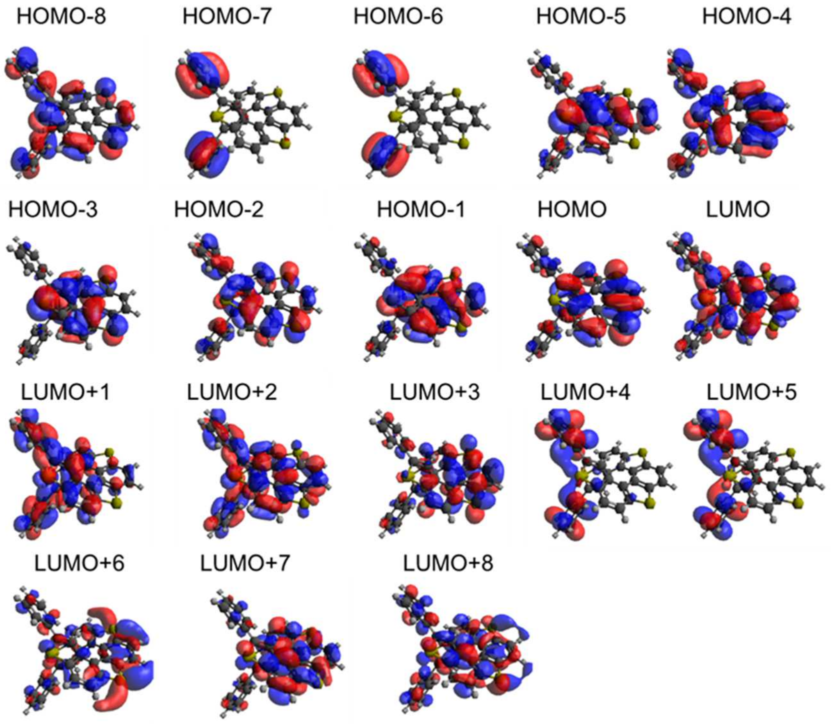


Figure S6: Molecular orbitals of (*M*)-Ph-[7]TH by the DFT-based calculation. Molecular orbitals spread entire (*M*)-Ph-[7]TH except for those for LUMO+5, LUMO+4, HOMO-6, and HOMO-7.

STM image superimposed with model

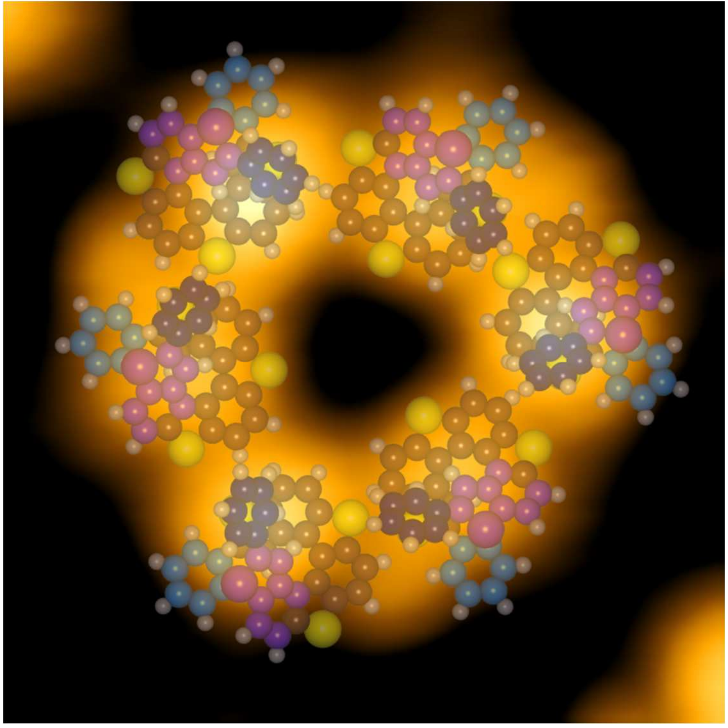


Figure S7: STM images of (*M*)-Ph-[7]TH on the Ag(111) substrate at +3.0 V, 50 pA (3.6×3.6 nm^2) which is the same as Fig.4(a). The model shown in Fig.6(a) is superimposed.

Reference

1. A. Bossi, S. Maiorana, C. Graiff, A. Tiripicchio and E. Licandro, *Eur. J. Org. Chem.*, 2007, **2007**, 4499-4509.