# Supporting Information Atomically Precise Synthesis and Characterization of Heptauthrene with Triplet Ground State

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# **Contents:**

## Supplementary Methods:

- 1. Synthetic procedures (Supplementary Schemes S1-S3)
- 2. NMR and mass characterization (<sup>1</sup>H and <sup>13</sup>C-NMR, HR-APCI-MS, Supplementary Figures S1-S5)
  - 3. Sample preparation and AFM, STM, STS measurements
  - 4. Tight-binding calculations

## Supplementary Figures S6-S9:

- S6. Large-area STM image after annealing precursor  $\mathbf{2}$  on Au(111)
- S7. Temperature dependent Kondo resonance of 1/2 for Heptauthrene with extra H addition
  - S8. Spin quenched by the extra two H atoms adsorption
  - S9. Singlet and triplet states of heptauthrene by MFH calculation

## Supplementary References

## Supplementary methods

#### 1. Synthetic procedures

Unless otherwise noted, all starting chemical materials were purchased from TCI, Adamas, SCRC, and other chemical providers. All starting materials were received without further purification. The solution reactions were conducted under air- and moisture-free conditions by using a sealed Schlenk system under nitrogen atmosphere because some substances are air- or moisture-sensitive. The reaction progress was monitored by thin layer chromatography (TLC) which contains silica-coated glass plates and fluorescence marker  $F_{254}$ . Crude reaction products were purified by preparative silica gel chromatography (particle size: 45-75  $\mu$ m, Greagent). For structure characterization, proton and carbon nuclear magnetic resonance spectra (<sup>1</sup>H and <sup>13</sup>C-NMR, respectively) were carried out at 298 K on two BRUKER AVANCE III HD NMR instruments, operating at 400 MHz or 500 MHz for <sup>1</sup>H-NMR and 100 or 125 MHz for <sup>13</sup>C-NMR, respectively. The NMR measurements were carried out in the liquid-state using deuterated chloroform (CDCl<sub>3</sub>, 99.9 atom% D,  $\delta_{H-NMR}$ = 7.26 ppm /  $\delta_{\rm C-NMR}$  = 77.3 ppm) and dimethyl sulfoxide-D6 ((CD\_3)\_2SO, 99.9 atom% D,  $\delta_{\rm H-NMR} = 2.49$  ppm /  $\delta_{\rm C-NMR} = 40.5$  ppm), purchased from Cambridge Isotope Laboratories. The peak pattern in <sup>1</sup>H-NMR spectra is described by commonly used abbreviations: s = singlet, d = doublet, t = triplet and m = multiplet. High-resolution mass spectrometry (HRMS) was performed on a Q Exactive Focus high resolution instrument (Thermo Fisher, Massachusetts, USA) using atmospheric pressure chemical ionization (APCI).



Scheme S1. Summary of synthetic procedures toward formation of 1.



Scheme S2. Synthesis of compound 3.

1-bromo-8-methylnaphthalene (3): Commercially available 1,8-dibromonaphthalene (2) (2.0 g, 7.0 mmol, 1.0 eq.) was dissolved in 40 ml dry tetrahydrofuran (THF) and cooled to -78 °C. A solution of n-butyl lithium (n-BuLi) in hexane (2.5 M, 3.4 ml, 8.4 mmol, 1.2 eq.) was added dropwise under nitrogen atmosphere and the reaction was maintained at -78 °C for 30 minutes. Then iodomethane (6.8 g, 3.0 ml, 47.9 mmol, 6.8 eq.) was added under nitrogen atmosphere to the reaction mixture via syringe. The resulting mixture was allowed to warm up gradually to room temperature and stirred for another 3 hours. The reaction mixture was quenched with 40 ml water, extracted with EA (3 × 20 ml), and the combined organic layer was washed with brine and dried over magnetism sulfate (MgSO<sub>4</sub>). The solvent excess was removed by evaporation and the crude compound was purified by silica gel columns using hexane as eluent. **3** was obtained as yellow-green crystal (1.3 g, 80 %).

<sup>1</sup>**H** NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  7.83 (d, J = 7.4 Hz, 1H), 7.78 (d, J = 8.1 Hz, 1H), 7.71 (dd, J = 6.7, 2.9 Hz, 1H), 7.37 - 7.32 (m, 2H), 7.21 (t, J = 7.8 Hz, 1H), 3.13 (s, 3H). <sup>13</sup>**C** NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  136.56, 135.38, 133.40, 131.29, 130.98, 129.33, 128.08, 125.99, 125.62, 119.94, 26.21.



Scheme S3. Synthesis of compound 2 and byproduct 2'.

1,3-bis(8-methylnaphthalene-1-yl)benzene (2): compound 3 (0.5 g, 2.3 mmol, 1.0 eq.), commercially available 1,3-phenylenediboronic acid (0.4 g, 2.4 mmol, 1.0 eq.), tris(dibenzylideneacetone)dipalladium(0)  $(Pd_2(dba)_3)$  (0.4 g, 0.4 mmol, 0.2 eq.), bis(2-diphenylphosphinophenyl)ether (DPEPhos) (0.5 g, 0.9 mmol, 0.4 eq.) and potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) (4.1 g, 29.4 mmol, 12.8 eq.) were added into a Schlenk reactor. Under nitrogen atmosphere, 40 ml toluene, 16 ml ethanol (EtOH) and 8 ml water (H<sub>2</sub>O) were added via syringe and the mixture was heated to reflux for 24 hours. After cooled to room temperature, the reaction mixture was quenched with water and extracted with DCM, and the combined organic layer was washed with brine and dried over magnetism sulfate (MgSO<sub>4</sub>). The solvent excess was removed by evaporation and the crude compound was purified by two silica gel columns using hexane/EA 8 : 1 as eluent for the first one and hexane for the second. **2** as well as byproduct **2**' were obtained as white crystal (0.5 g, 61 %), as can be seen from NMR spectra. <sup>1</sup>**H NMR** (DMSO-*d*6, 500 MHz):  $\delta$  7.93 (dd, J = 8.2, 4.1 Hz, 2H), 7.84 (t, J = 9.0 Hz, 2H), 7.53 – 7.19 (m, 12H), 2.19 (s, 3H), 2.04 (s, 3H).

<sup>13</sup>**C NMR** (CDCl<sub>3</sub>, 100 MHz):  $\delta$  144.79, 144.21, 140.23, 140.16, 135.30, 135.13, 135.07, 134.99, 130.99, 130.96, 130.92, 130.20, 129.72, 129.64, 129.41, 128.90, 128.86, 128.42, 127.79, 127.43, 127.39, 126.82, 126.33, 125.46, 124.31, 124.21, 26.06, 25.19.

**HR-APCI-MS** (positive mode): calc. for  $[M+H]^+$ : 359.1794, found for  $[M+H]^+$ : 359.1792 (deviation: 0.72 ppm).



### 2. NMR and mass characterization

**Figure S1.** Liquid-state <sup>1</sup>H NMR spectrum of compound **3** measured in CDCl<sub>3</sub> at room temperature. Frequency: 500 MHz.



Figure S2. Liquid-state <sup>13</sup>C NMR spectrum of compound 3 measured in  $CDCl_3$  at room temperature. Frequency: 125 MHz.



**Figure S3.** Liquid-state <sup>1</sup>H NMR spectrum of compound **2** and byproduct **2'** measured in DMSO-*d*6 at room temperature. Frequency: 500 MHz.



**Figure S4.** Liquid-state <sup>13</sup>C NMR spectrum of compound **2** and byproduct **2'** measured in  $CDCl_3$  at room temperature. Frequency: 100 MHz.



Figure S5. Liquid-state HR-APCI-MS (positive mode) of compound 2.

#### 3. Sample preparation and AFM, STM, STS measurements

The STM/AFM experiments for the electronic and chemical structure characterization (Fig. 1, Fig. 2, Fig. 4a, Fig. 4b, Fig. S6, Fig. S7) were performed at 4.7 K with commercial Createc LT-STM/qPlus AFM. The Au(111) single-crystal was cleaned by cycles of argon ion sputtering and subsequently annealed to 800 K to get atomically flat terraces. Molecular precursors 2 were thermally deposited on the clean Au(111) surface, and subsequently annealed to 523 K to fabricate heptauthrene. The AFM measurements were performed with the qPlus sensor with the resonance frequency of 29.7 KHz and the oscillation amplitude of 50 pm. dI/dV measurements were performed with an internal lock-in amplifier at a frequency of 333 Hz. Lock-in modulation voltages for individual measurements were provided in the respective figure captions. All STM/STS and AFM measurements were acquired with CO-functionalized tungsten tip. To prepare the CO functionalized tungsten tip, NaCl were deposited on the sample. After dosing CO, we picked up CO molecule from the NaCl island. For the constant-height AFM images, the tip-sample distance is decreased a few hundred of pm from the STM set point V = 300 mV, I = 50 pA. For the Kondo resonance measurements (Fig. 3, Fig. 4c) were carried out using a commercial low-temperature Unisoku Joule-Thomson scanning probe microscope. dI/dV measurements were performed with lock-in amplifier at a frequency of 589 Hz. Lock-in modulation voltages for individual measurements were also provided in the corresponding figure captions. The spectra were also measured with CO tip.

#### 4. Tight-binding calculations

The tight binding (TB) calculations of the STM images were carried out in the C  $2p_z$ -orbital description by numerically solving the Mean-Field-Hubbard Hamiltonian with

nearest-neighbor hopping:

$$\hat{H}_{MFH} = \sum_{\langle i,j \rangle, \sigma} -t_{ij} c_{i,\sigma}^{\dagger} c_{j,\sigma} + U \sum_{i,\sigma} \langle n_{i,\sigma} \rangle n_{i,\overline{\sigma}} - U \sum_{i} \langle n_{i,\uparrow} \rangle \langle n_{i,\downarrow} \rangle$$

with  $t_{ij}$  is the nearest-neighbor hopping term depending on the bond length between C atoms (For simplicity, we choose  $t_{ij} = 2.7 \text{ eV}$ ), and  $c_{i,\sigma}^{\dagger}$  and  $c_{i,\sigma}$  denoting the spin selective  $(\sigma = \uparrow, \downarrow)$  creation and annihilation operators on the atomic site *i* and *j*, *U* the on-site Hubbard parameter (with U = 3.5 eV used here),  $n_{i,\sigma}$  the number operator and  $\langle n_{i\sigma} \rangle$  the mean occupation number at site *i*. Numerically solving the model Hamiltonian yields the energy Eigenvalues  $E_i$  and the corresponding Eigenstates  $\alpha_{i,j}$  (amplitude of state *i* on site *j*) from which the wave functions are computed assuming Slater type atomic orbitals:

$$\psi_i(\vec{r}) = \sum_j \alpha_{i,j} \cdot (z - z_j) \exp(-\zeta |\vec{r} - \vec{r_j}|)$$

with  $\zeta = 1.625 \ a.u.$  for the carbon  $2p_z$  orbital. The charge density map  $\rho(x, y)$  for a given energy range  $[\varepsilon_{min}, \varepsilon_{max}]$  and height  $z_0$  is then obtained by summing up the squared wave functions in this chosen energy range.

$$\rho(x,y) = \sum_{i,\varepsilon_i \in [\varepsilon_{\min},\varepsilon_{\max}]} \psi_i^2(x,y,z_0)$$

Constant charge density maps are taken as a first approximation to compare with experimental STM images. The value of the nearest-neighbor hopping parameter depends on the bond type between sites i and j, according to the Slater-Koster parametrization given by Y. Wang and C.H. Mak.<sup>1</sup> In our calculation, the hopping term is set as a constant value of 2.7 eV for simplicity, which corresponds to a bond distance of 1.42 Å, that is, a graphene lattice of 2.45 Å.

The on-site repulsion U is related to the superposition of electronic wave-functions in different atom sites.<sup>2</sup> In previous calculations, the values of U are usually in the range

of 3.0 - 3.5 eV for polycyclic aromatic hydrocarbons.<sup>3,4</sup> It has also been shown that the results of calculations performed using the mean-field Hubbard model are very close to those obtained by first-principles methods based on density functional theory for certain values of U/t. In particular, U/t = 1.3 can agree best with the results of the generalized-gradient-approximation density functions.<sup>5</sup> Therefore, in our calculation we followed the previous empirical parameter and took U = 3.5 eV and U/t = 1.3.

For that the gap deduced from TB calculation is smaller than that observed in experiments, it is mainly due to the mean filed approximation used in TB calculation, which is known to underestimate the electron-electron interactions, and thus gives a smaller energy gap. Similarly, Mean-field DFT calculations also greatly underestimate the energy gap. To quantitatively capture the energy gap, the high-level GW calculations and substrate screening effects need to be considered (where G and W denote Green's function and screened Coulomb potential, respectively). Increasing U will also slightly increase the energy gap in TB calculations. However, U is related to the on-site repulsion, that is, the energy gain for a double occupation on the same site. If U/t is above 2.3, the system will undergo a Mott-Hubbard transition.<sup>5</sup> From previous studies, the main reason for the underestimated energy gap is mainly from the Mean-field approximations.

# Supplementary Figures



Figure S6. Large-area STM image after annealing precursor 2 on Au(111). (a) Large scale STM image after annealing precursor 2 on Au(111) (V = 300 mV, I = 50 pA). The products of heptauthrene marked by white squares including with and without extra H addition at the radical sites. The byproducts with pentagon ring marked by white circles. (b) Zoom-in STM image (left) (V = 300 mV, I = 50 pA), AFM image (middle) (V = 300 mV, I = 50 pA),  $\Delta z = -0.05 \text{ nm}$ ) and the corresponding molecular model (right) of the byproduct with pentagon ring. Scale bars: (a) 5 nm, (b) 0.5 nm.



Figure S7. Temperature dependent Kondo resonance of 1/2 for Heptauthrene with extra H addition. (a) STM image of heptauthrene with extra H passivation (V = 300 mV, I = 50 pA). (b) Constant-height dI/dV map (V = 1 mV,  $V_{\text{rms}} = 2 \text{ mV}$ ). (c) dI/dV spectra measured at different temperatures at the position as marked in (a), dashed lines are the simulated curves using a Frota function.<sup>6</sup> (V = 30 mV, I = 200 pA,  $V_{\text{rms}} = 1 \text{ mV}$ ) (d) Full width at half maximum (FWHM) as a function of temperature. Upon simulating it with the empirical expression  $\Gamma = \sqrt{(\alpha k_B T)^2 + (k_B T_K)^2}$ , Kondo temperature of 50 K is derived.<sup>7</sup>



Figure S8. Spin quenched by the extra two H atoms adsorption. (a) STM image of heptauthrene with the two extra H atoms passivation (V = 300 mV, I = 50 pA). (b) Constant-height dI/dV map (V = 1 mV,  $V_{\text{rms}} = 2 \text{ mV}$ ). (c,d) AFM image (c) and the corresponding molecular model (d) of heptauthrene with two extra H atoms passivation. (e) Comparing the dI/dV spectra of heptauthrene with two/one/zero extra H atoms passivation, which are measured at the position as marked in inset figure. (V = 30 mV, I = 200 pA,  $V_{\text{rms}} = 1 \text{ mV}$ ). There is no Kondo peak that can be observed at the Fermi level in heptauthrene with two extra H atoms passivation, which can give an additional support to our conclusion.



Figure S9. Singlet and triplet states of heptauthrene by MFH calculation. (a,b) Calculated spin density distribution of singlet (a) and triplet (b) configurations by MFH model (U = 3.5 eV). Blue/red iso-surfaces denote spin up/spin down density. And the corresponding energies are marked at bottom. According to our calculations as well as the previous theoretical results,<sup>2</sup> the energy difference between the triplet and singlet state is ranging from 200 to 500 meV depending on the detailed methods. It is too large to observe the spin-flip process in inelastic electron tunneling spectroscopy considering the unstable heptauthrene molecule on Au(111).

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