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Preparation of Tetrabenzo[4.4.2]undecastarphene by On-Surface Synthesis

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Abstract: A large dissymmetric starphene molecule, the tetrabenzo[*a,c,u,w*]naphtho[2,3-*f*]nonaphene, can be obtained by first preparing a soluble precursor which is then sublimated on a Au(111) surface in ultra-high vacuum. In a second step, controlled annealings from 200°C to 275°C initiate two successive cyclodehydrogenation steps with the formation of 3 new carbon-carbon bonds. A second conformer is also stable enough during the annealing step to give another compound in similar yield, the benzodibenzo[7,8,9,10]naphthaceno[2,1-*h*]phenanthro[9,10-*p*]hexaphene. The formation of this more hindered species stresses the importance of strong molecule-surface interactions during the cyclodehydrogenations steps of these large polyaromatic hydrocarbons.

Introduction

Starphene^[1], molecules comprising three acene branches, have been recently proposed as single molecular gates in the Quantum Hamiltonian Computing approach. It has in particular been shown that [2,2,2]-heptastarphene could be implemented as a NOR logic gate^[2] whereas the asymmetric [3,3,2]-nonastarphene was a NAND gate.^[3]

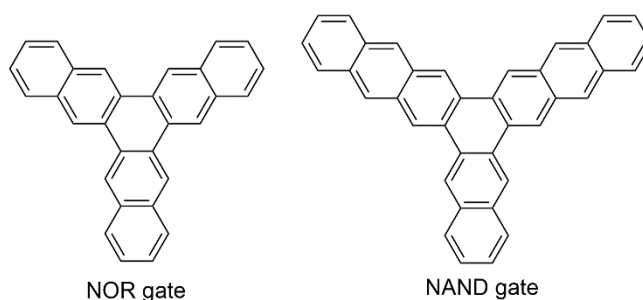
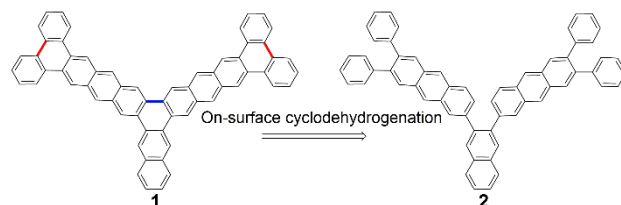


Figure 1. Polyaromatic logic gates for single molecule computing.

To go beyond and be able testing more powerful logic gates such as a half-adder,^[4–7] it is necessary to increase the complexity and the asymmetry of these conjugated three branches molecules. However, the synthesis of large unsubstituted starphenes in solution is a difficult task due to their insolubility, and the largest starphene to-date, the [3,3,3]-decastarphene,^[8,9] has been reported by Clar and Müllen more than fifty years ago.^[10] Indeed, it is possible to increase the solubility of large polyaromatic hydrocarbon molecules by preventing complete planarity, and therefore the intermolecular π -stacking forces. This can be done by designing sterically congested structures like cloverphenes^[11] or by adding bulky substituents^[12], but this strategy also modifies electronic properties of the molecular gate. Alternatively, we have recently shown that it was possible to yield unsubstituted and planar [5,5,5]-hexadecastarphene by decarbonylation in the solid state or on a surface of a soluble precursor.^[13] Another potential route is on-surface synthesis which allows the preparation of insoluble molecules by coupling smaller functionalized precursors on surfaces in ultra-high vacuum.^[14,15] It allowed Fasel *et al.*^[16] to synthesize the symmetric [4,4,4]-tridecastarphene from *ortho*-dibromotetracene on a Ag(111) surface and Grill, Hecht *et al.*^[17] to get decastarphene by coupling of *ortho*-dibromoanthracene on a Au(111) surface. However, the preparation of an asymmetric

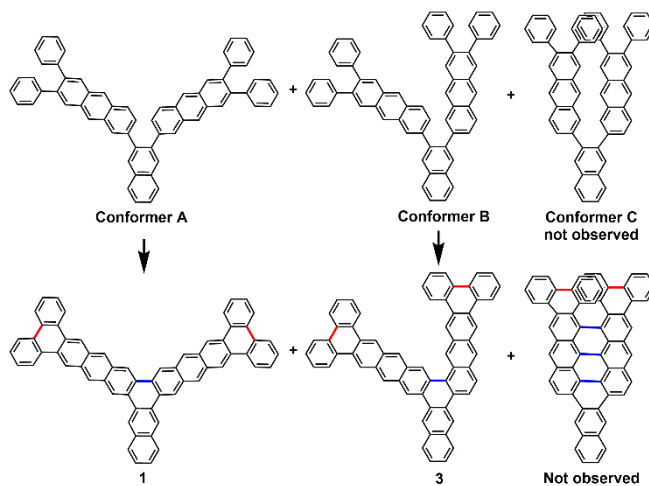
starphene by on-surface Ullmann reaction would require a statistical asymmetric coupling of two different 2,3-dihaloacenes, which is not a satisfactory approach indeed.

In this work, our objective was to test the feasibility of preparation of a large asymmetric starphene by first synthesizing soluble precursors (*ie* which can be purified, characterized and sublimated) by multistep in-solution synthesis, and in a second step complete the reaction scheme by several surface activated cyclodehydrogenations. To understand the potential and the limits of this strategy, we have designed a Y shape molecular gate comprising one naphthalene branch, and two symmetric dibenzo[*a,c*]naphthacene as a potential molecular gate. This extension corresponds to the addition of a phenanthrene group to the ends of the anthracene moieties of the [3,3,2]-nonastarphene NAND gate (Fig. 1),^[3] *ie* a total of six supplementary benzene rings.



Scheme 1. Retrosynthetic strategy for the on-surface preparation of the molecular gate **1** from the molecule **2** in its conformation A.

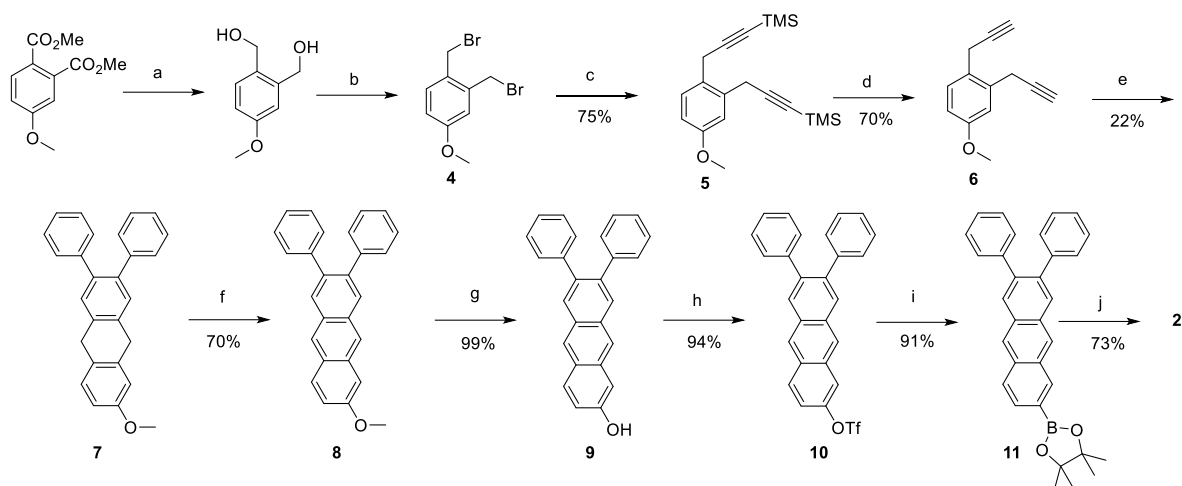
Indeed, this large planar polyaromatic hydrocarbon **1**, tetrabenzo[*a,c,u,w*]naphtho[2,3-]nonaphene, is expected to be fully insoluble, thanks to strong π - π intermolecular interactions, so that its synthesis and purification in solution would not be possible. Furthermore, the sublimation of this type of large polyaromatics with strong intermolecular π -stacking in the solid state, a necessary step to transfer the molecular gate on ultra clean surfaces in ultra-high vacuum (UHV), is known to be problematic. Increasing the sublimation temperature often leads to fragmentation of the molecules. In these conditions, on-surface synthesis appears as a potential answer to this problem. We therefore decided to synthesize the precursor **2**, in which six single bonds together with internal steric crowding should ensure some solubility and after standard purification and characterization steps to transfer this non-planar molecule by sublimation on Au(111) surfaces. One potential expected difficulty was that the on-surface cyclodehydrogenation could yield by-products depending on the conformation of the molecules on the surface (Scheme 2). Indeed, rotations around the bonds linking the naphthalene moieties to the anthracene branches from the conformer A give also the conformers B and C on the surface, so that it should be possible to obtain also two other compounds. Indeed, one of the objectives of this work was to understand how the balance between intramolecular molecular hindering and molecule-surface adsorption energies controls the distribution between these different isomers.



Scheme 2 The three possible products by on-surface-cyclodehydrogenation of **2** in the conformation A (gives **1**), B (gives **3**), and C (not observed).

Results and Discussion

Synthesis. The synthesis of **2** is described in scheme 3. Our disconnection approach involves breaking down of **2** into a naphthalene moiety and two 2,3-diphenylanthracene units. The preparation starts from 1,2-bis(bromomethyl)-4-methoxybenzene **4** which can be obtained from dimethyl 4-methoxy-1,2-benzenedicarboxylate by reduction of the two ester functions followed by bromination of the two alcohol groups by PBr_3 in dichloromethane.^{[18],[19]}



Scheme 3. Synthesis of the precursor **2**: (a) LiAlH_4 , THF, 0°C (b) PBr_3 , DCM, 0°C (c) TMSA (4 equiv.), EtMgBr (4 equiv.), CuCl (0.5 equiv.), THF, reflux, 3h, 75%; (d) TBAF (2.2 equiv.), THF, rt, 6h, 70%; (e) diphenylacetylene (10 equiv.), $(\text{Ph}_3\text{P})_2\text{Ni}(\text{CO})_2$ (0.1 mol%), toluene, 135°C , 3h, 22%; (f) DDQ (1.5 equiv.), toluene, 120°C , 3h, 70%; (g) BBr_3 (3 equiv.), DCM, 0°C to rt, 8h, 99%; (h) Et_3N (3 equiv.), triflic anhydride (1.3 equiv.), DCM, 0°C to rt, 2h, 94%; (i) B_2Pin_2 (1.5 equiv.), $\text{PdCl}_2(\text{dppf})$ (4 mol%), dppf (4 mol%), KOAc (3 equiv.), dioxane, 80°C , 24h, 91%. (j) 2,3-dibromonaphthalene, **11** (1.05 equiv.), XPhosPdG2 (10%), K_3PO_4 (1.40 equiv.), THF, RT, 24h, 73%.

Metallation of **4** by ethylmagnesium bromide followed by copper coupling with trimethylsilyl acetylene gave **5**. Deprotection by tetrabutylammonium fluoride in THF yielded **6**. This latter was involved in [2+2+2] cyclotrimerization with diphenyl ethylene catalysed by nickel^[20,21] to get the 6-methoxy-2,3-diphenyl-9,10-dihydroanthracene **7** which was then aromatized by DDQ leading to **8**. Cleavage of the methoxy groups by boron tribromide in DCM was followed by triflation of the so-obtained alcohol groups by triflic anhydride to give **10**. Then, 2-(6,7-diphenylanthracen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane compound **11** was obtained from **10** by palladium catalytic coupling with bis(pinacolato)diboron. The final step is a double Suzuki coupling with 2,3-dibromonaphthalene yielding the target molecule **2**. This compound is a well-soluble crystalline compound which can be sublimated at 340°C under ultra-high vacuum (UHV) conditions.

On-surface cyclodehydrogenation. After thermal sublimation of precursor **2** on the Au(111) surface kept at room temperature, the adsorbed molecules have been imaged by scanning tunnelling microscopy (STM) at low temperature ($T = 5\text{ K}$) (Figure 2a). In the STM images we observe only non-planarized precursor molecules **2**, thus excluding that intramolecular reactions already happened in the crucible. The precursors form small self-assembled structures due to intramolecular interactions and are characterized by three bright lobes (see also Figure 3a). Such assemblies can be easily separated by STM lateral manipulation. To induce cyclodehydrogenation, we annealed the sample to 200°C and then further to 275°C . After the final annealing (Figure 2b), all molecules reacted and are flat, adopting either the symmetric Y shape of molecular gate **1** or the asymmetric shape of compound **3**, benzodibenzo[7,8,9,10]naphthaceno[2,1-*h*]phenanthro[9,10-*p*]hexaphene. The compound which could be obtained by cyclodehydrogenation of the conformer C is not observed on the surface. The molecules are preferentially aligned along the fcc sites of the Au surface. The analysis of 15 images containing about 300 molecules each reveals that the molecules are equally divided between product **1** and **3** (see SI). Therefore, about 50% of the products are molecular gates **1**, in contrast to the [3,3,2]-nonastarphene (the NAND gate), for which their percentage was more than 90%.^[3] This difference shows that the extension of the polyaromatic system by four phenyl rings increases significantly the adsorption forces so that even more sterically crowded conformation are stable on the surface.

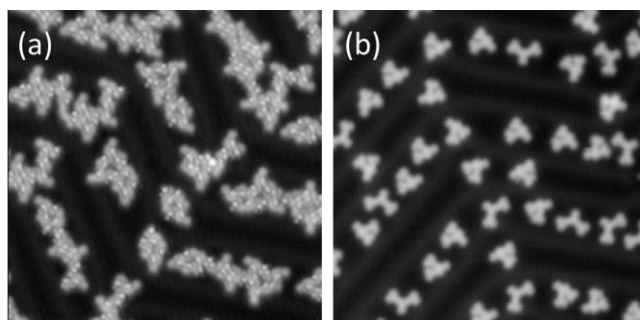


Figure 2. Overview STM images (a) After deposition all molecules are non-flat: each precursor shows three bright lobes. (b) Annealing to 275°C leads to a complete reaction and planarization of all molecules. All images: $U = 0.5\text{ V}$, $I = 100\text{ pA}$, $30\text{ nm} \times 30\text{ nm}$.

The figure 3 below shows STM images of single molecules at the different annealing stages.

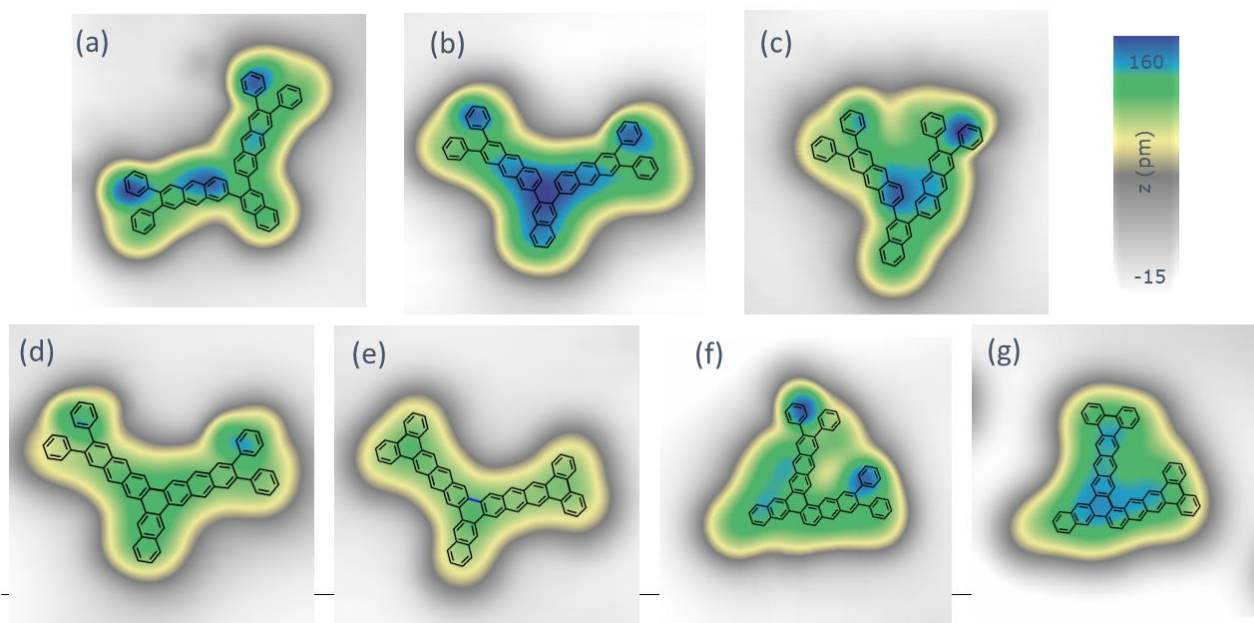


Figure 3. STM images of single molecules at the different reaction steps. (a) and (b): molecule **2** after deposition, in the conformation A, and (c) in the conformation B. After annealing at $T = 200^\circ\text{C}$, in some cases, a partial cyclodehydrogenation can be observed between the anthracene sub-units (d) for the isomer 1; (f) for the isomer 2. (e, molecule **1**) and (g, molecule **3**): after annealing at 275°C , the cyclodehydrogenation is complete, and the images show only planar molecules **1**, and **3**, respectively for the isomer A and B. Imaging parameters: $U = 0.5\text{ V}$, $I = 100\text{ pA}$, image size $3.3\text{ nm} \times 3.3\text{ nm}$.

In Figure 3a-c, a precursor **2** is imaged after sublimation on a surface at room temperature, showing typical non-flat conformations. The conformer A (a and b) shows slightly different contrasts depending on the adsorption sites. The conformer B is shown in Figure 3c. After annealing at 200°C , a partial cyclodehydrogenation can be observed for some molecules, as shown in 3d and 3f, for the conformer A and B respectively. The planarity of the central part indicates that the first cyclodehydrogenation occurs between the anthracene sub-units whereas the steric hindering between the phenyl rings is shown at the end of the molecule branches, with asymmetric contrasts. It corresponds to the formation of the bonds shown in blue in the schemes 1 and 2. Then annealing at 275°C yields a complete cyclodehydrogenation and a full planarization of the conformers (see SI), shown in (e) and (g) with the formation of the bonds shown in red in the schemes 1 and 2. The assignment of the structures is confirmed by the similar experiment performed to obtain the NAND gate.^[3]

We have performed dI/dV spectroscopy to investigate the positions and the geometry of the electronic resonances for the compound **1**. We have identified (Figure 4a) electronic resonances at -1.63 V , -0.93 V , $+1.4\text{ V}$, and $+2.38\text{ V}$. The energy gap is therefore 2.33 eV . The spatial distribution of the frontier electronic resonances probed by dI/dV mapping at -0.93 V and 1.4 V is shown in Figure 4b and 4c, respectively. Compared to the NAND gate [3,3,2]-nonastarphene,^[3] shown in Figure 1, the energy gap has decreased from 2.9 eV to 2.33 eV . This reduction can be explained by the elongation of the two branches which pass from anthracene to dibenzotetracene.

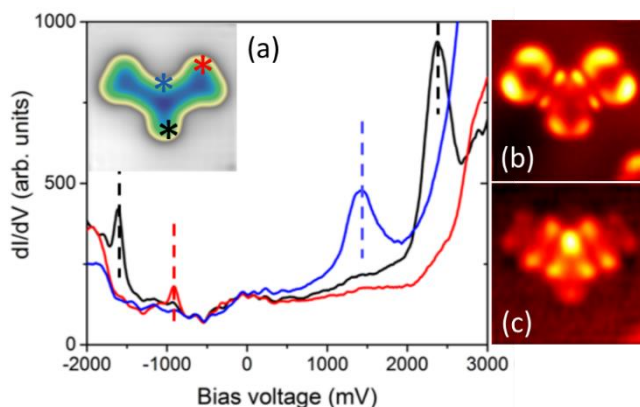


Figure 4. Scanning tunnelling spectroscopy of the product molecule **1**. (a) dI/dV spectrum. In the inset, STM image of a single molecule with stars marking the positions where the spectra were taken. The colour of each spectrum corresponds to the color of the corresponding star. (b-c) dI/dV maps of the frontier resonances recorded at (b) $U = -0.93\text{ V}$ and (c) $U = 1.4\text{ V}$.

Conclusion

To sum up, we have shown that it is possible to prepare large non-fully symmetric polyaromatic hydrocarbons by on-surface multiple cyclodehydrogenations of large, sterically crowded and soluble precursors. Indeed, the design of these precursors has to consider the possibility to observe several on-surface precursor conformers yielding several products, especially when the physisorption energy increases with the size of the molecule.

Experimental Section

General procedure

Solvents were dried over molecular sieves prior to use.^[22] Dry DMF was from Acros Organics or Sigma Aldrich. THF was distilled on sodium/benzophenone. Triethylamine was distilled on CaH₂ under argon atmosphere. Flash column chromatography was performed by using silica gel (60 Å pore size, 40-63 µm Merck). The reactions were monitored by thin layer chromatography (TLC) on silica gel-coated plates (Merck 60 F254). The yields refer to chromatographically and spectroscopically (1H-NMR and 13C-NMR) homogeneous materials, unless otherwise stated. The NMR spectroscopic data were recorded with Bruker Avance 300/400/500 MHz instruments and were calibrated by using the residual undeuterated solvent as an internal reference. Chemical shifts are reported in parts per million (ppm) on the δ scale and coupling constants (J) are in Hertz (Hz). The abbreviations used to describe the multiplicities are s= singlet, bs= broad singlet, d= doublet, t= triplet, dd= doublet of doublets, q= quintuplet, m= multiplet. Mass spectra were recorded at the Service Commun de Spectrométrie de Masse of University Paul Sabatier (Toulouse 3), Toulouse (France). Elemental analyses were done by the Service d'Analyse de l'ICSN (Paris, France). All reagents of high quality were purchased from commercial suppliers, and used without further purification. Solvents were dried on 4°A activated molecular sieves

(3,3'-(4-methoxy-1,2-phenylene)bis(prop-1-yne-3,1-diyl))bis(trimethylsilane) 5. In a three necked round bottom flask equipped with reflux condenser was prepared solution of ethynyltrimethyl silane (1 mL, 6.8 mmol, 4 equiv.) in absolute tetrahydrofuran (20 mL) and cooled to 0°C. A solution of ethyl magnesium bromide (3.0 M in diethyl ether, 2.27 mL, 6.8 mmol, 4 equiv.) was added dropwise and then the reaction mixture was heated to 40°C for 1 hour. Copper chloride (85 mg, 0.85 mmol, 0.5 equiv.) and the dibromide **4** (500 mg, 1.7 mmol, 1 equiv.) were added and the reaction mixture was heated to reflux for 3 h. The reaction mixture was cooled to room temperature and stirred overnight. The reaction was quenched with aq. solution of NH₄Cl and extracted with diethyl ether. The combined organic layers were washed with brine (40 ml) and dried over anhydrous Na₂SO₄. The solvents were removed *in vacuo* and the residue was chromatographed on a silica gel (petroleum ether - ethyl acetate 97 : 3) to get the desired product as a viscous yellow oil. (418 mg, 75%). R_f = 0.61 (petroleum ether/ ethyl acetate = 95/5). ¹H NMR (300 MHz, CDCl₃): 0.17 (9H, s), 0.19 (9H, s), 3.55 (2H, s), 3.62 (2H, s), 3.81 (3H, s), 6.78 (1H, dd, J = 8.4, 2.8), 7.09 (1H, d, J = 2.7), 7.33 (1H, d, J = 8.4). ¹³C NMR (75 MHz, CDCl₃): 0.21 (6C), 23.29, 24.11, 55.29, 87.08, 87.80, 103.51, 104.00, 112.34, 114.50, 126.26, 129.78, 135.50, 158.82. DCI MS: 329 ([M+H]⁺). HR DCI MS: calcd for C₁₉H₂₉OSi₂ 329.1751, found: 329.1776.

4-methoxy-1,2-di(prop-2-ynyl)benzene 6. The protected diyne **5** (400 mg, 1.22 mmol) was dissolved in tetrahydrofuran (20 ml) under argon and cooled to 0°C. A solution of *n*-tetrabutylammonium fluoride trihydrate (1 M in tetrahydrofuran, 2.7 ml, 2.7 mmol, 2.2 equiv.) was added dropwise and the reaction mixture was stirred at room temperature for 6h. Then the reaction mixture was quenched by water (20 ml) and extracted with diethyl ether. The combined organic portions were dried over anhydrous Na₂SO₄. The evaporation of the solvents afforded an orange oil, which was chromatographed on silica gel (petroleum ether - ethyl acetate 95:5) to get the desired product (157 mg, 70%) as a yellow viscous oil. ¹H NMR (300 MHz, CDCl₃): 2.18 (1H, t, J = 2.7), 2.22 (1H, t, J = 2.7), 3.54 (2H, d, J = 2.7), 3.61 (2H, d, J = 2.7), 3.81 (3H, s), 6.79 (1H, dd, J = 8.4, 2.8), 7.07 (1H, d, J = 2.8), 7.35 (1H, d, J = 8.4). ¹³C NMR (75 MHz, CDCl₃): 21.78, 22.66, 55.33, 70.65, 71.22, 80.99, 81.56, 112.25, 114.83, 125.97, 129.87, 135.18, 158.92. DCI MS: 185 ([M+H]⁺). HR DCI MS: calcd for C₁₃H₁₃O 185.0961, found 185.0961.

6-methoxy-2,3-diphenyl-9,10-dihydroanthracene 7. A well dried flask equipped with a reflux condenser was charged with the diyne **6** (1.24 g, 6.74 mmol), diphenylacetylene (12 g, 67.4 mmol, 10 equiv.) and (Ph₃P)₂Ni(CO)₂ (0.43 g, 0.674 mmol, 0.1 mol%) under argon. The absolute toluene (125 mL) was added and the reaction mixture was placed into a preheated oil bath (135°C) for 1 h. After cooling to room temperature, the solvent was removed *in vacuo* and the residue was chromatographed on silica gel (cyclohexane – ethyl acetate 95 : 5) to afford the desired product (1.28 g, 22%) as a yellow amorphous solid. ¹H NMR (300 MHz, CD₂Cl₂): 3.80 (3H, s), 3.96 (2H, s), 4.00 (2H, s), 6.77 (1H, dd, J = 8.3, 2.7), 6.89 (1H, d, J = 2.5), 7.12 - 7.27 (11H, m), 7.34 (2H, s). ¹³C NMR (75 MHz, CDCl₃): 35.04, 36.22, 55.55, 111.99, 113.09, 126.44 (2C), 127.96 (4C), 128.44, 128.69, 129.74 (2C), 130.05 (4C), 135.86, 136.46, 137.81, 138.58, 138.64, 141.61 (2C), 158.31. DCI MS: 363 ([M+H]⁺). HR DCI MS: calcd for C₂₇H₂₃O calc: 363.1743, found 363.1735.

6-methoxy-2,3-diphenylanthracene 8. A well dried Schlenk flask was charged with dihydroanthracene **7** (1.2 g, 3.3 mmol, 1 equiv.), DDQ (1.13 g, 4.97 mmol, 1.5 equiv.) under argon. The absolute toluene (100 mL) was added and the reaction mixture was stirred at 120°C for 3h. After cooling to room temperature, the solvent was removed *in vacuo* and the residue was chromatographed on silica gel (hexane – chloroform 4:1) to afford the desired product (833 mg, 70%) as a yellow crystalline solid. ¹H NMR (300 MHz, CD₂Cl₂): 3.98 (3H, s), 7.18 (1H, dd, J = 9.2, 2.5), 7.25-7.30 (11H, m), 7.93 (1H, d, J = 9.3), 8.01 (1H, s), 8.02 (1H, s), 8.34 (1H, s), 8.40 (1H, s). ¹³C NMR (75 MHz, CD₂Cl₂): 55.85, 104.16, 121.22, 124.50, 126.63, 127.03, 127.10, 128.36 (4C), 129.23, 129.52, 130.15, 130.21, 130.34, 130.49 (4C), 132.07, 133.77, 138.57, 139.66, 142.19, 142.23, 157.97. DCI MS: 361 ([M+H]⁺). HR DCI MS: calcd for C₂₇H₂₁O 361.1587, found 361.1509.

6,7-diphenylanthracen-2-ol 9. A methoxy derivative **8** (770 mg, 2.14 mmol) was dissolved in dry dichloromethane (70 mL) under argon and cooled to 0°C. A solution of BBr₃ (1M solution in dichloromethane, 6.41 mL, 6.41 mmol, 3 equiv.) was added dropwise and the reaction mixture was stirred at 0°C for 30 min. Then temperature was allowed to increase to room temperature and stirring continued for another 8 h. The reaction mixture was quenched with cold water and then extracted with DCM. The combined organic portions were dried over anhydrous MgSO₄. The solvents were removed *in vacuo* and the residue was chromatographed on a short plug (4cm) of silica gel (hexane-chloroform 1:4) to get the desired product (730 mg, 99%) as a brown amorphous solid. ¹H NMR (300 MHz, CD₂Cl₂): 5.67 (1H, s), 7.18 (1H, dd, J = 9.1, 2.5), 7.26 - 7.28 (11H, m), 7.96 (1H, d, J = 9.2), 7.98 (1H, s), 8.01 (1H, s), 8.26 (1H, s), 8.41 (1H, s). ¹³C NMR (75 MHz, CD₂Cl₂): 108.07, 120.07, 124.09, 126.82, 127.04, 127.12, 128.36 (4C), 129.05, 129.51, 130.19 (2C), 130.48 (4C), 130.92, 132.13, 133.68, 138.60, 139.74, 142.16, 142.18, 153.85. DCI MS: 347 ([M+H]⁺). HR DCI MS: calcd for C₂₆H₁₉O 347.1430; found 347.1423.

6,7-diphenylanthracen-2-yl trifluoromethanesulfonate 10. In a dry Schlenk flask was dissolved previous hydroxyl compound **9** (730 mg, 2.11 mmol) in dichloromethane (30 mL) under argon and cooled to 0°C. Triethyl amine (879 µL, 6.32 mmol, 3 equiv.) was added dropwise and the yellow solution was stirred for 5 min. A solution of triflic anhydride (1M solution in dichloromethane, 2.74 mL, 2.74 mmol, 1.3 equiv.) was added dropwise. The reaction was stirred 1 hour at 0°C and then 1 hour at room temperature. The colour of the reaction mixture turn slowly to brown. The reaction mixture was adsorbed on silica gel and the volatiles were removed *in vacuo* and the residue was chromatographed on silica gel (hexane - dichloromethane 5:1) to get the desired product (950 mg, 94%) as a yellow amorphous solid. ¹H NMR (300 MHz, CD₂Cl₂): 7.26-7.30 (10H, m), 7.37 (1H, dd, *J* = 9.3, 2.5), 7.94 (1H, d, *J* = 2.4), 8.06 (1H, s), 8.07 (1H, s), 8.11 (1H, d, *J* = 10.0), 8.49 (1H, s), 8.52 (s, 1H). ¹³C NMR (75 MHz, CD₂Cl₂): 119.62, 119.65 (*J* = 321 Hz, CF₃), 119.90, 127.13, 127.18, 127.49 (2C), 128.58 (4C), 129.85, 130.09, 130.50 (4C), 130.75, 131.36, 131.82, 132.02, 132.12, 140.38, 140.55, 141.71 (2C), 147.32. DCI MS: 479 ([M+H]⁺). HR DCI MS: calcd for C₂₇H₁₈F₃O₃S 479.0923, found 479.0942.

2-(6,7-diphenylanthracen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 11. A well dried Schlenk flask was charged with previous triflate **10** (940 mg, 1.97 mmol), PdCl₂(dppf) (58 mg, 78.6 µmol, 4 mol%), dppf (44 mg, 78.6 µmol, 4 mol%), bis(pinacolato)diboron (748 mg, 2.95 mmol, 1.5 equiv.) and potassium acetate (578 mg, 5.89 mmol, 3 equiv.) under argon. The absolute dioxane (50 ml) was added and the reaction mixture was stirred at 80°C for 24 h. The reaction mixture was evaporated and chromatographed on silica gel (gradient hexane - dichloromethane 4:1 to dichloromethane) to get the desired product (820 mg, 91%) as a foam yellowish compound. ¹H NMR (300 MHz, CD₂Cl₂): 1.44 (12H, s), 7.30 (10H, s), 7.81 (1H, d, *J* = 8.5), 8.03 (1H, d, *J* = 8.6), 8.07 (1H, s), 8.10 (1H, s), 8.47 (1H, s), 8.56 (1H, s), 8.60 (1H, s). ¹³C NMR (75 MHz, CD₂Cl₂): 25.36 (4C), 84.57 (2C), 126.38, 127.19, 127.22, 127.67, 127.85, 128.41 (4C), 129.88, 130.03, 130.35, 130.49 (4C), 131.59, 132.07, 132.32, 133.67, 137.79, 139.55, 140.04, 142.04 (2C). DCI MS: 457 ([M+H]⁺). HR DCI MS: calcd for C₃₂H₃₀BO₂ 457.2333, found 457.2350.

2,3-bis(6,7-diphenylanthracen-2-yl)naphthalene 2. A Schlenk flask was charged with **11** (480 mg, 1.05 mmol, 3 equiv.), potassium phosphate tribasic (297 mg, 1.40 mmol, 4 equiv.), XPhos Pd G2 (27 mg, 35 µmol, 10 mol%) and 2,3-dibromonaphthalene (100 mg, 0.35 mmol, 1 equiv.) under argon. The freshly distilled THF (10 mL) and water (2.8 mL) was added and the reaction mixture was degassed and stirred at room temperature for 24 h. The reaction mixture was evaporated and chromatographed on silica gel (hexane - chloroform 4:1) to get the desired product (200 mg, 73%) as a yellow crystalline compound. ¹H NMR (300 MHz, CD₂Cl₂): 7.21 – 7.26 (20 H, m), 7.31 (2H, dd, *J* = 6.2, 3.3), 7.60 (2H, dt, *J* = 6.2, 3.3), 7.75 (2H, d, *J* = 9.0), 7.97 (2H, s), 7.98 (2H, s), 8.01 (2H, dt, *J* = 6.2, 3.3), 8.13 (2H, dd, *J* = 1.7, 0.8), 8.16 (2H, s), 8.35 (2H, s), 8.37 (2H, s). ¹³C NMR (126 MHz, CD₂Cl₂): 126.32, 126.72, 127.10, 127.13 (2C), 127.91, 128.35 (4C), 128.37, 128.93, 129.13, 129.98, 130.03, 130.45 (4C), 130.50, 131.42, 131.66, 131.75, 132.68, 133.57, 139.43, 139.49, 139.51, 139.59, 142.04 (2C). HR MALDI: calcd for C₆₂H₄₀: 784.3130, found 784.3136.

Experimental details. The STM experiments were performed with a low-temperature (*T* = 5 K) STM under ultrahigh vacuum conditions (base pressure <10⁻¹⁰ mbar). The Au(111) substrate was cleaned by repeated cycles of sputtering with Ar ions and annealing at 723 K. The precursors **2** were sublimated from a Knudsen cell at a temperature of 340°C onto the Au(111) surface kept at room temperature. The on-surface reaction was induced by annealing the sample to 275 °C. After sublimation and annealing, the sample was cooled to cryogenic temperature and transferred to the STM without breaking the vacuum. Scanning tunneling spectroscopy measurements were performed using a lock-in technique with a bias modulation amplitude of 40 mV at a frequency of 707 Hz. Voltages are applied to the surface respect to the tip.

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