

Supporting Information

Dodecacene Generated on Surface: Re-Opening of the Energy Gap

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1 Additional STS data

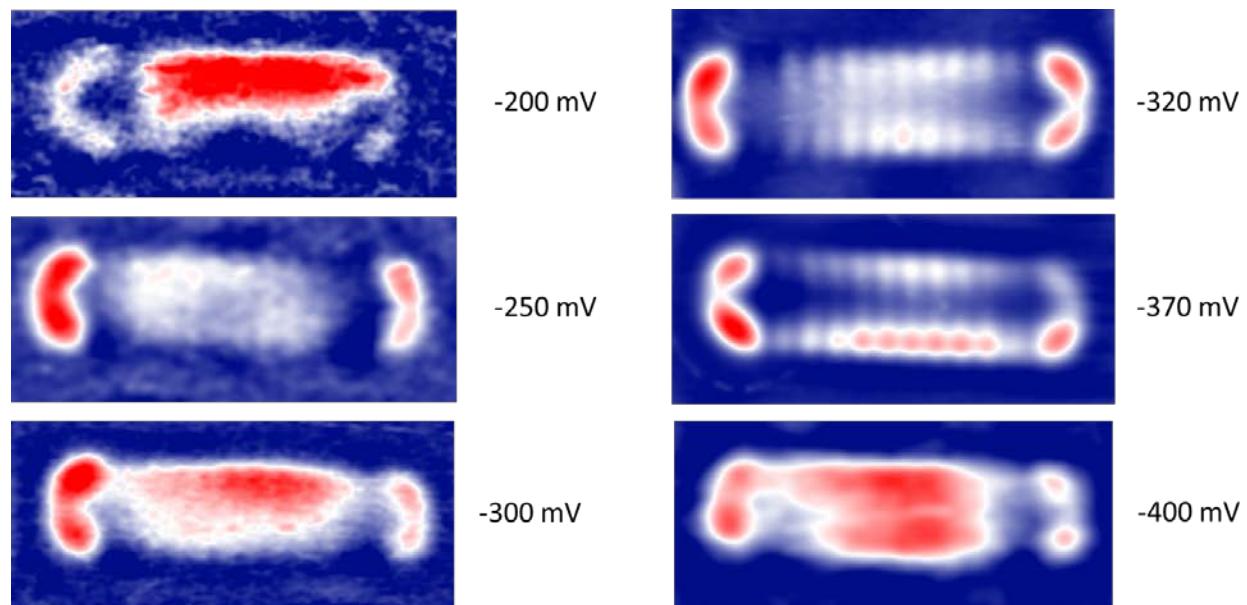


Figure S1. dI/dV maps of the R0 resonance of dodecacene measured by slightly varying the bias voltage. The evolution of the contrast of the resonance features can be clearly followed and shows a maximum of contrast at $V = -320$ mV with the typical HOMO contrast.

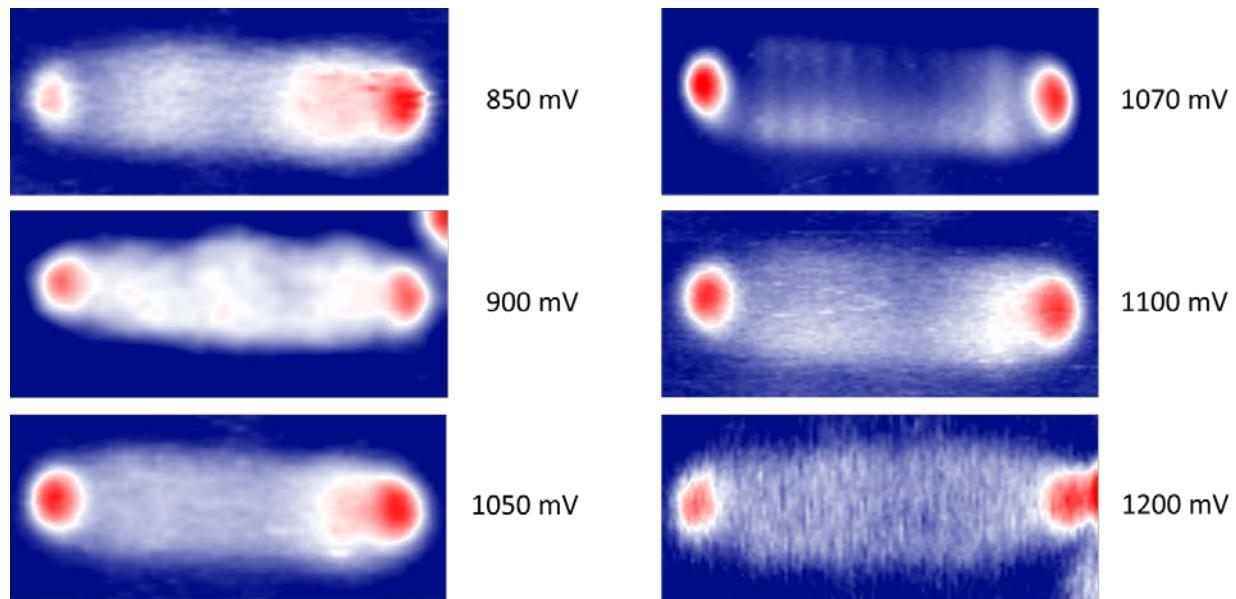
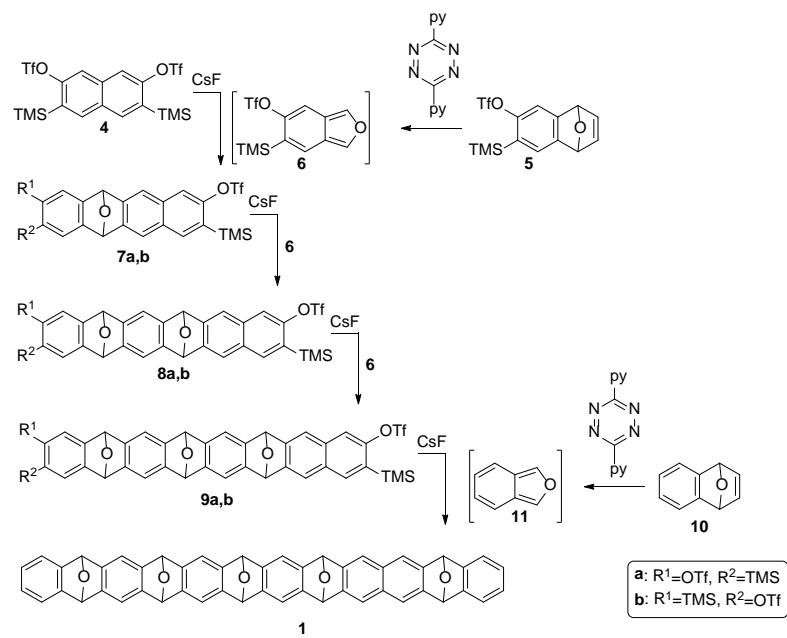


Figure S2. dI/dV maps of the R1 resonance of dodecacene measured by slightly varying the bias voltage. The evolution of the contrast of the resonance features can be clearly followed and shows a maximum of contrast at $V = 1070$ mV with the typical LUMO contrast.

2 Synthetic details

General methods for the synthesis of the precursors

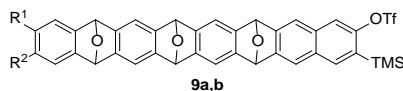
All reactions were carried out under argon using oven-dried glassware. CH_2Cl_2 and CH_3CN were dried using a MBraun SPS-800 Solvent Purification System. Finely powdered CsF was purchased from ABCR GmbH and dried under vacuum at 100 °C, cooled under argon and stored in a glovebox. Furan was purchased from Sigma-Aldrich and filtered through neutral aluminium oxide (Brockmann I) and stored with molecular sieves (3 Å) under argon atmosphere. Other commercial reagents were purchased from ABCR GmbH, Sigma-Aldrich or Acros Organics, and were used without further purification. Deuterated solvents were purchased from Acros Organics. TLC was performed on Merck silica gel 60 F_{254} and chromatograms were visualized with UV light (254 and 365 nm) and/or stained with Hanessian's stain. Column chromatography was performed on Merck silica gel 60 (ASTM 230-400 mesh). ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz (Varian Mercury-300 instrument) or 500 and 125 MHz (Varian Inova 500 or Bruker 500) respectively. APCI high resolution mass spectra were obtained on a Bruker Microtof. The synthesis of the dodecacene precursor (**1**) was made by the following route (Scheme S1).



Scheme S1. Synthesis of dodecacene precursor **1**.

Compounds **4**,¹ **5**,² **7a,b**,² **8a,b**,³ and **10**,⁴ were prepared following reported procedures and showed the same spectroscopic properties as reported therein.

Synthesis of bistriflate **9a,b**



Compound **5** (102 mg, 0.28 mmol), and 3,6-di(pyridin-2-yl)-1,2,4,5-tetrazine (66 mg, 0.28 mmol) were dissolved in 5 mL of dry CH_2Cl_2 under Ar and stirred at 45 °C. The reaction was monitored by TLC until complete consumption of **5** was observed (1.5 hours). Then, the reaction mixture was allowed to warm up to room temperature and the aryne precursor **8a,b** (150 mg, 0.088 mmol) dissolved in MeCN (3 mL) and CsF (19 mg, 0.124 mmol) were added. The reaction mixture was stirred at 45 °C for 16 hours. Then, the solvent was evaporated under reduced pressure and the crude purified by chromatographic column (silica gel, hexane/ CH_2Cl_2 /diethyl ether 1/1/0.5) isolating 14 mg of **9a,b** as a mixture of regio and diastereomers. Yellow solid. Yield: 8%.

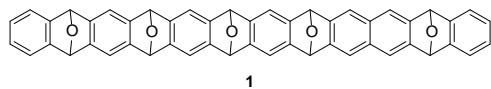
^1H NMR (500 MHz, CDCl_3) δ 7.83-7.77 (singlet group, 1H), 7.63-7.58 (singlet group, 3H), 7.33-7.30 (s, 2H), 7.27 (s, 2H), 7.22 (s group, 2H), 6.11- 6.08 (singlet group, 2H), 5.91 - 5.88 (singlet group, 4H), 0.35, 0.35, 0.18, 0.17. ppm.

^{19}F NMR (282 MHz, CDCl_3) δ -74.25, -74.46, -74.99, -75.09.

^{13}C NMR (126 MHz, CDCl_3) δ 153.1 (C Ar), 152.6 (C Ar), 152.6 (C Ar), 152.3 (C Ar), 152.2 (C Ar), 147.7 (C Ar), 147.6 (C Ar), 147.6 (C Ar), 147.6 (C Ar), 147.5 (C Ar), 147.5 (C Ar), 147.4 (C Ar), 147.3 (C Ar), 146.8 (C Ar), 146.7 (C Ar), 146.4 (C Ar), 146.4 (C Ar), 146.0 (C Ar), 145.9 (C Ar), 145.8 (C Ar), 145.1 (C Ar), 145.1 (C Ar), 137.1 (C Ar), 137.0 (C Ar), 135.7 (C Ar), 133.4 (C Ar), 133.3 (C Ar), 133.2 (C Ar), 131.1 (C Ar), 131.1 (C Ar), 130.8 (C Ar), 130.8 (C Ar), 130.5 (C Ar), 129.6 (C Ar), 129.6 (C Ar), 129.4 (C Ar), 129.4 (C Ar), 128.2 (C Ar), 126.5 (C Ar), 126.4 (C Ar), 125.5 (C Ar), 119.7 (C Ar), 119.7 (C Ar), 119.5 (C Ar), 119.5 (C Ar), 118.5 (CH Ar), 118.5 (CH Ar), 118.4 (CH Ar), 118.4 (CH Ar), 117.2 (C Ar), 117.2 (C Ar), 117.0 (CH Ar), 117.0 (C Ar), 116.8 (C Ar), 114.3 (CH Ar), 114.2 (CH Ar), 114.1 (CH Ar), 114.0 (CH Ar), 113.9 (CH Ar), 113.8 (CH Ar), 113.8 (CH Ar), 113.8 (CH Ar), 112.7 (CH Ar), 112.5 (CH Ar), 82.4 (CH-O), 82.4 (CH-O), 82.2 (CH-O), 82.2 (CH-O), 82.1 (CH-O), 82.0 (CH-O), 81.9 (CH-O), -0.7 (CH₃-TMS), -0.8, -0.9 (CH₃-TMS), -1.0 (CH₃-TMS), -1.0 (CH₃-TMS).

HRMS (APCI): for $\text{C}_{42}\text{H}_{35}\text{F}_6\text{O}_9\text{S}_2\text{Si}_2$ [M+1] calculated 917.1160, observed 917.1159.

Synthesis of the dodecacene precursor



4-Dihydro-1,4-epoxynaphthalene (**10**) (43 mg, 0.30 mmol), and 3,6-di(pyridin-2-yl)-1,2,4,5-tetrazine (70 mg, 0.30 mmol) were dissolved in 2.5 mL of dry CH_2Cl_2 under Ar atmosphere and stirred at 45 °C. The reaction was monitored by TLC until complete consumption of **10** was observed (30 min). Then, highly reactive isobenzofuran **11** was isolated by a short and fast column

chromatography (hexane/CH₂Cl₂ 1/1). Isobenzofuran **11** was added immediately in anhydrous CH₂Cl₂ solution (3 mL) after isolation to a solution of **9a,b** in anhydrous MeCN (3 mL). Afterwards, CsF was added and the reaction mixture was stirred at 40°C for 16 h. Then, the solvent was evaporated under reduced pressure and the crude was purified by chromatographic column (silica gel, hexane/ethyl acetate/diethyl ether 1/1/0.5) isolating two fractions of **1**: the less polar fraction (1 mg) and the more polar fraction (3 mg) as white solids. Combined yield 37%.

Less polar fraction: A mixture of two diastereomers in a 74:26 ratio. NMR data is given for the major isomer.

¹H NMR (500 MHz, CDCl₃) δ 7.50 – 7.47 (m, 2H), 7.34 (s, 2H), 7.33 – 7.30 (m, 2H), 7.25 (s, 2H), 7.23 – 7.20 (m, 2H), 7.15 (s, 2H), 7.03 – 7.00 (m, 2H), 6.97 – 6.93 (m, 2H), 6.07 (s, 2H), 5.99 (s, 2H), 5.86 (s, 2H), 5.79 (d, *J* = 1.5 Hz, 2H), 5.77 (s, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 148.0 (C Ar), 147.5 (C Ar), 147.3 (C Ar), 147.3 (C Ar), 147.1 (C Ar), 146.9 (C Ar), 146.3 (C Ar), 144.9 (C Ar), 144.3 (C Ar), 130.9 (C Ar), 126.2 (CH Ar), 125.7 (CH Ar), 120.3 (CH Ar), 120.1 (CH Ar), 119.1 (CH Ar), 119.1 (CH Ar), 113.7 (CH Ar), 82.5 (CH-O), 82.4 (CH-O), 82.2 (CH-O), 82.2 (CH-O), 82.1 (CH-O).

HRMS (APCI): for C₅₀H₂₉O₅ [M+1] calculated 709.2010, observed 709.2009.

More polar fraction: A mixture of at least 3 different diastereomers. It was not possible to assign the signals; therefore, NMR data is given without integration. This fraction was used for on-surface experiments.

¹H NMR (500 MHz, Chloroform-d) δ 7.58 (s), 7.48 (s), 7.48 (s), 7.42 (s), 7.38 (m), 7.37 – 7.35 (m), 7.33 (s), 7.28 – 7.27 (m), 7.26 (s), 7.21 (s), 7.19 (s), 7.18 (s), 7.17 (s), 7.07 (s), 7.06 – 7.04 (m), 6.99 (m), 6.92 (m), 6.87 (m), 6.72 (m), 6.69 (m), 6.18 (s), 6.14 (s), 6.08 (s), 6.02 (s), 5.95 (s), 5.95 (s), 5.83 (s), 5.82 (s), 5.81 (s), 5.80 (s), 5.79 (s), 5.77 (s), 5.76 (s), 5.72 (s), 5.68 (s), 5.35 (m).

¹³C NMR (126 MHz, CDCl₃) δ 148.4 (C Ar), 147.2 (C Ar), 146.9 (C Ar), 146.7 (C Ar), 146.3 (C Ar), 146.1 (C Ar), 144.7 (C Ar), 144.1 (C Ar), 130.8 (C Ar), 130.8 (C Ar), 126.7 (CH Ar), 126.6 (CH Ar), 126.3 (CH Ar), 126.2 (CH Ar), 125.8 (CH Ar), 125.6 (CH Ar), 120.3 (CH Ar), 120.1 (CH Ar), 120.0 (CH Ar), 119.5 (CH Ar), 119.4 (CH Ar), 119.2 (CH Ar), 119.0 (CH Ar), 119.0 (CH Ar), 118.9 (CH Ar), 114.0 (CH Ar), 113.9 (CH Ar), 113.7 (CH Ar), 113.6 (CH Ar), 113.5 (CH Ar), 82.5 (CH-O), 82.4 (CH-O), 82.3 (CH-O), 82.2 (CH-O), 82.1 (CH-O), 81.9 (CH-O), 77.2 (CH-O).

HRMS (APCI): for C₅₀H₂₉O₅ [M+1] calculated 709.2010, observed 709.2011.

3 NMR data

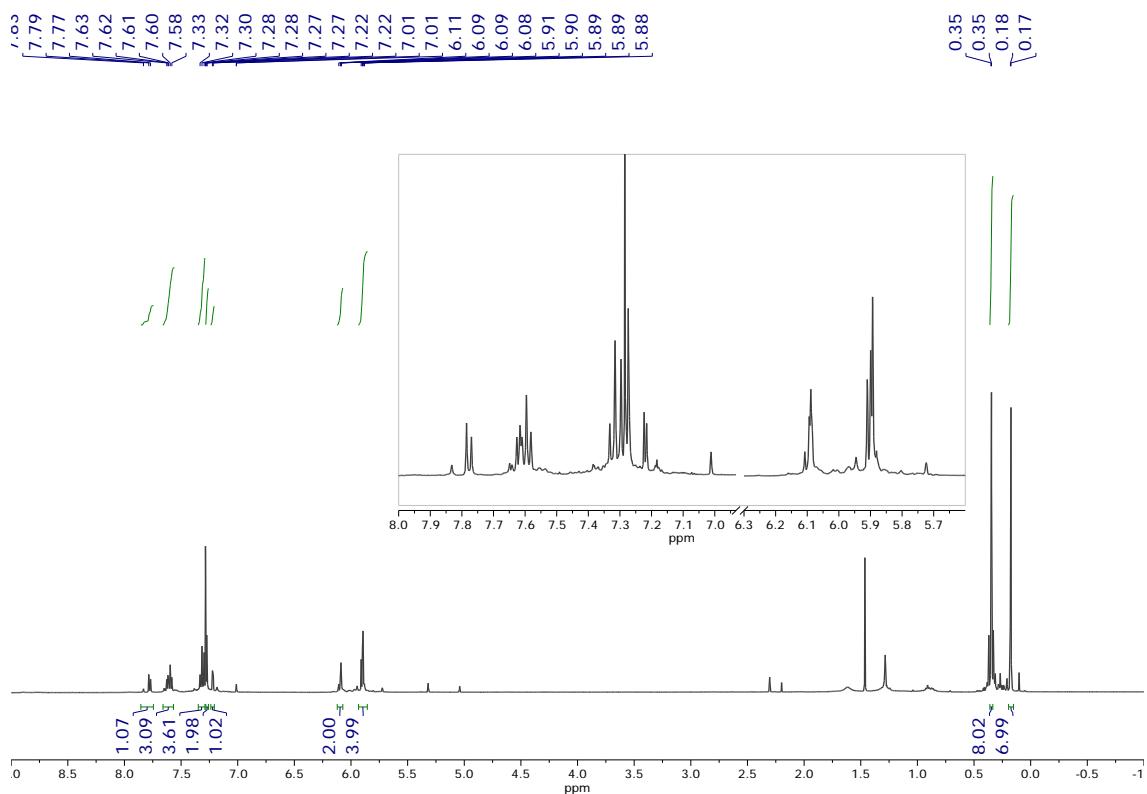


Figure S3. ^1H NMR (500 MHz, CDCl_3) of **9a,b**.

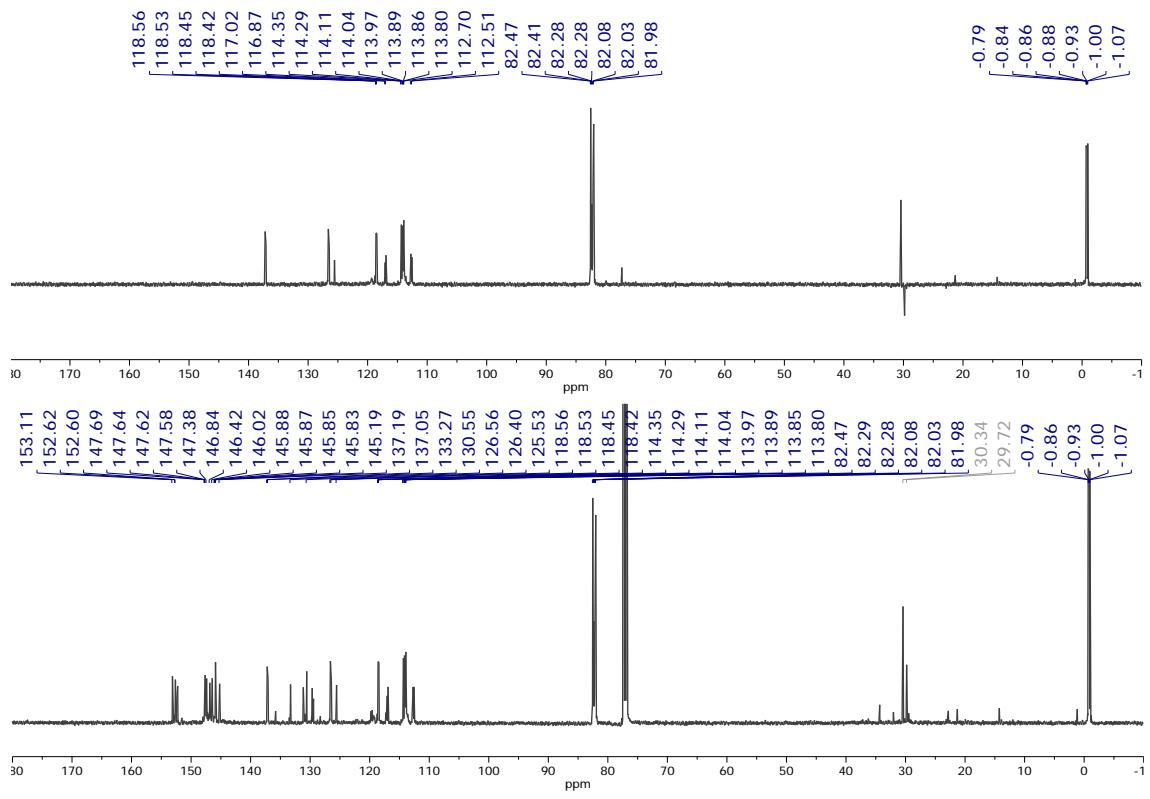


Figure S4. ¹³C (bottom) NMR (126 MHz, CDCl₃) and DEPT 135 (top) of **9a,b**.

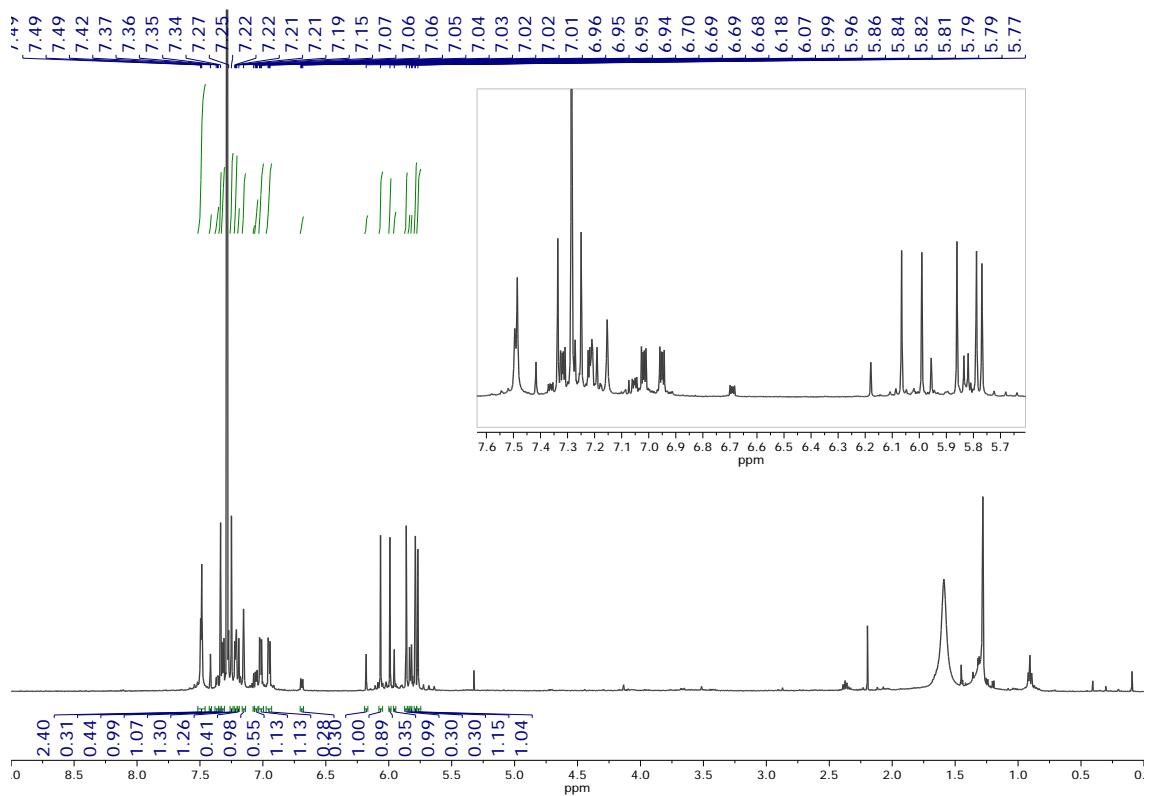


Figure S5. ¹H NMR (500 MHz, CDCl₃) of the less polar fraction of dodecacene precursor **1**.

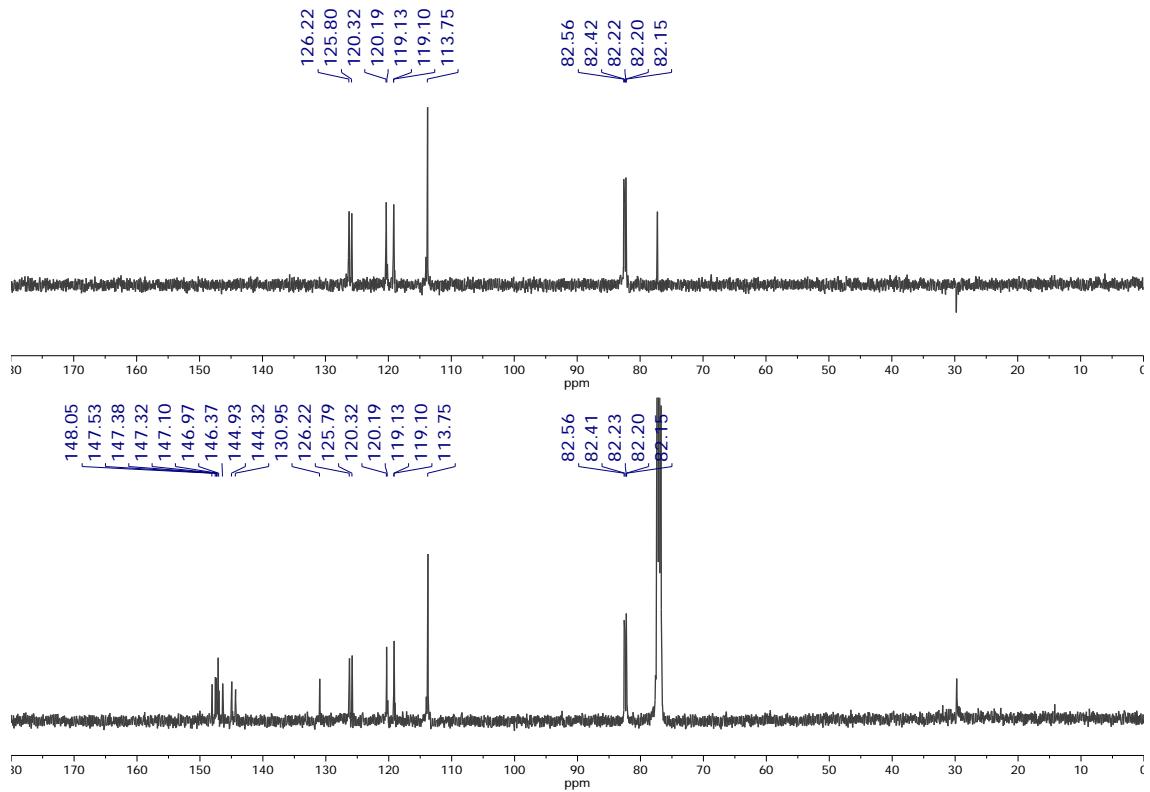


Figure S6. ^{13}C (bottom) NMR (126 MHz, CDCl_3) and DEPT 135 (top) of the less polar fraction of dodecacene precursor **1**.

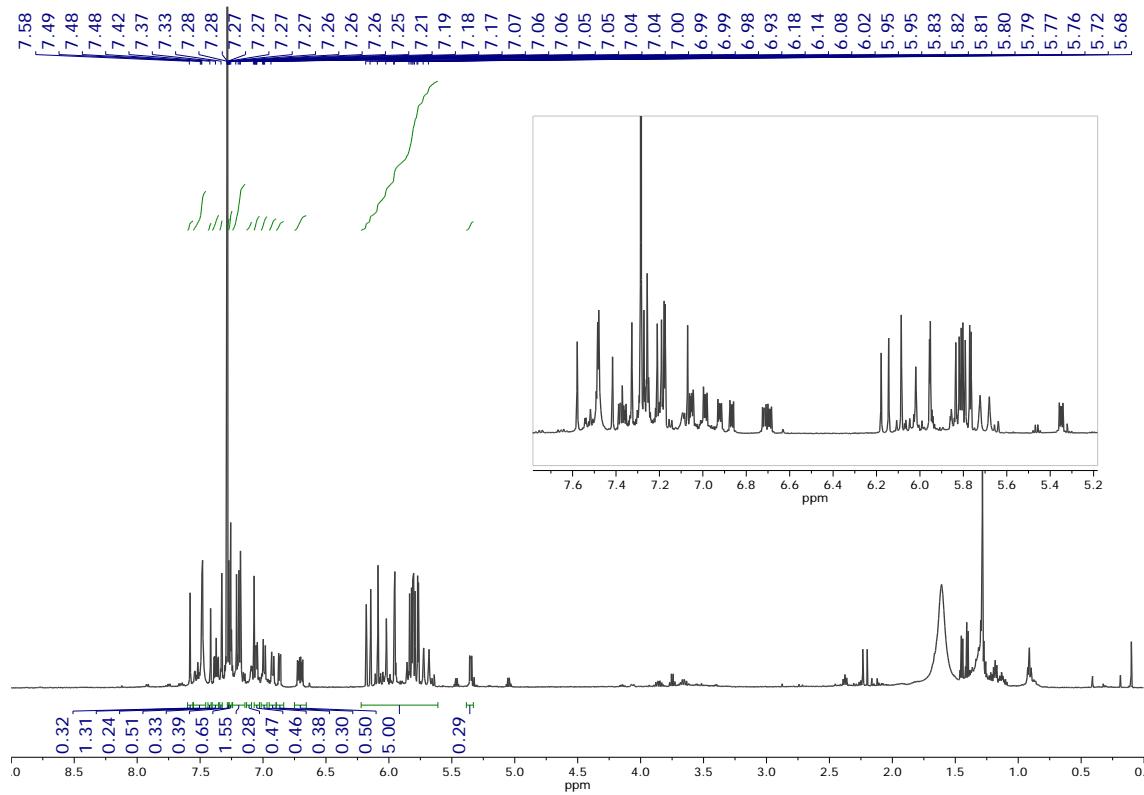


Figure S7. ^1H NMR (500 MHz, CDCl_3) of the more polar fraction of dodecacene precursor **1**.

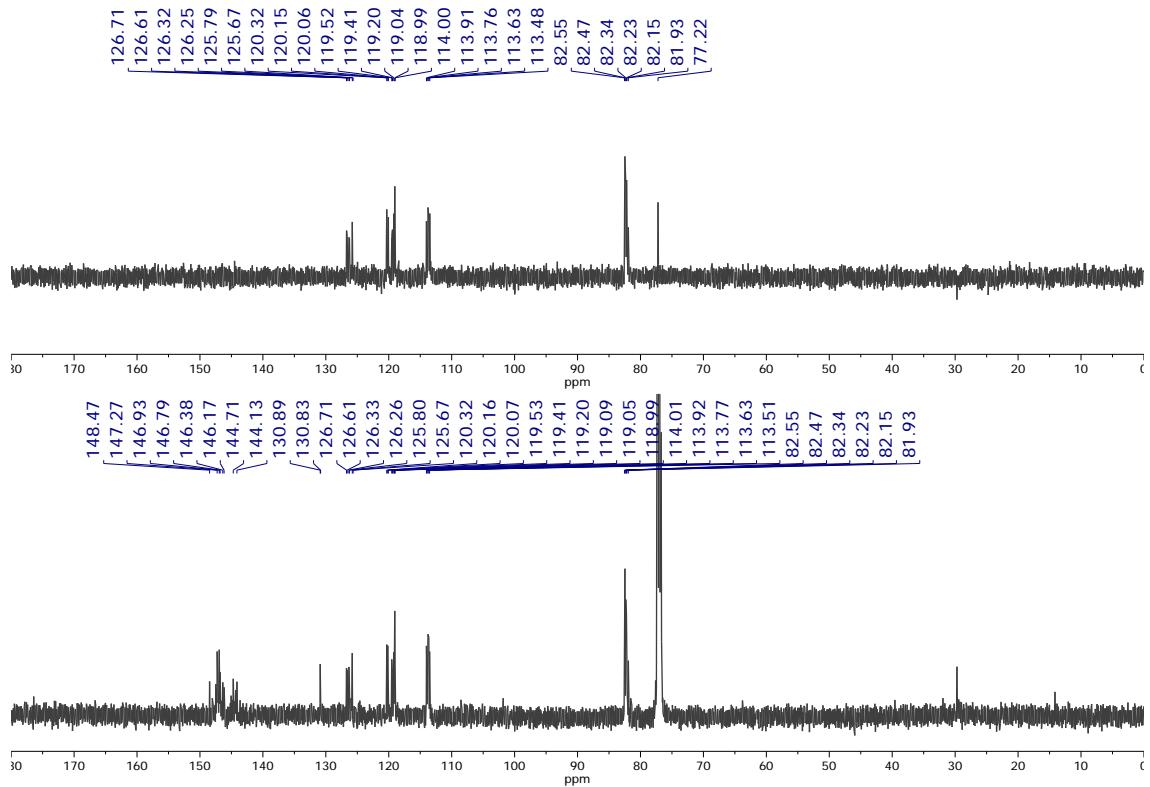


Figure S8. ¹³C (bottom) NMR (126 MHz, CDCl₃) and DEPT 135 (top) of the more polar fraction of dodecacene precursor **1**.

References

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