Kaposi, Tobias, Joshi, Sushobhan, Hoh, Tobias, Wiengarten, Alissa, Seufert, Knud, Paszkiewicz, Matheusz, Klappenberger, Florian, Ecija, David, Đorđević, Luka, Marangoni, Tomas, Bonifazi, Davide , Barth, Johannes V. and Auwärter, Willi 2016. Supramolecular spangling, crocheting, and knitting of functionalized pyrene molecules on a silver surface. ACS Nano 10 (8) , pp. 7665-7674. 10.1021/acsnano.6b02989

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Supporting Information

Supramolecular Spangling, Crocheting and Knitting of Functionalized Pyrene Molecules on a Silver Surface

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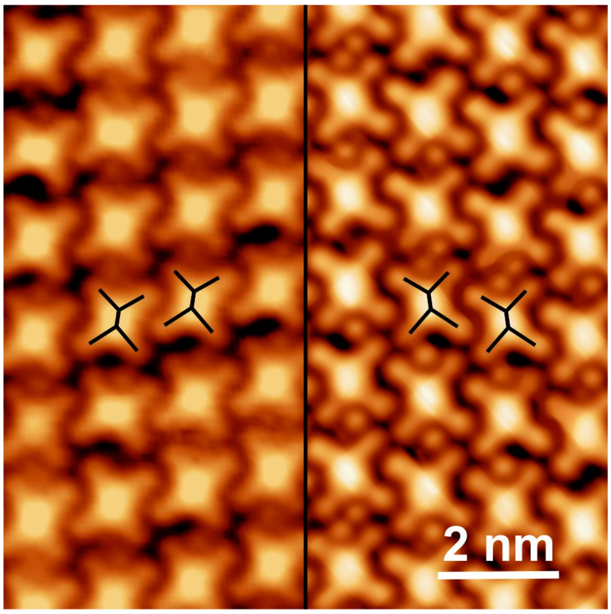


Figure SI1. Supramolecular organizational chirality exhibited by the deposition of species 1 on Ag(111). Left and right panel show high-resolution STM images of two-mirror symmetric domains. The circular protrusions represent iodides guests (see main text for discussion). Tunneling parameters: 50 pA, 1 V.

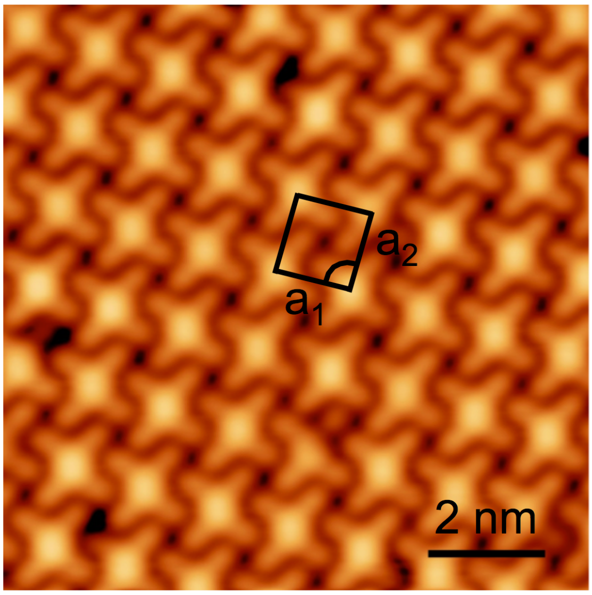


Figure SI2. STM image of a supramolecular array of species 1 on hexagonal boron nitride (*h*-BN) on Cu(111). In a control experiment, species 1 was deposited at room temperature on a single layer of *h*-BN grown by chemical vapour deposition of borazine on a pristine Cu(111) surface.[1] Again, highly regular, densely packed arrays of molecules are observed (cf. Figure 2b), albeit without any noticeable regular cavities, resulting in an even more compact, almost rectangular network with lattice vectors a_1 = (15.5 ± 0.5) Å and a_2 = (16.6 ± 0.5) Å, with an opening angle γ = (92±2)° (0.2 nA, 0.1 V).

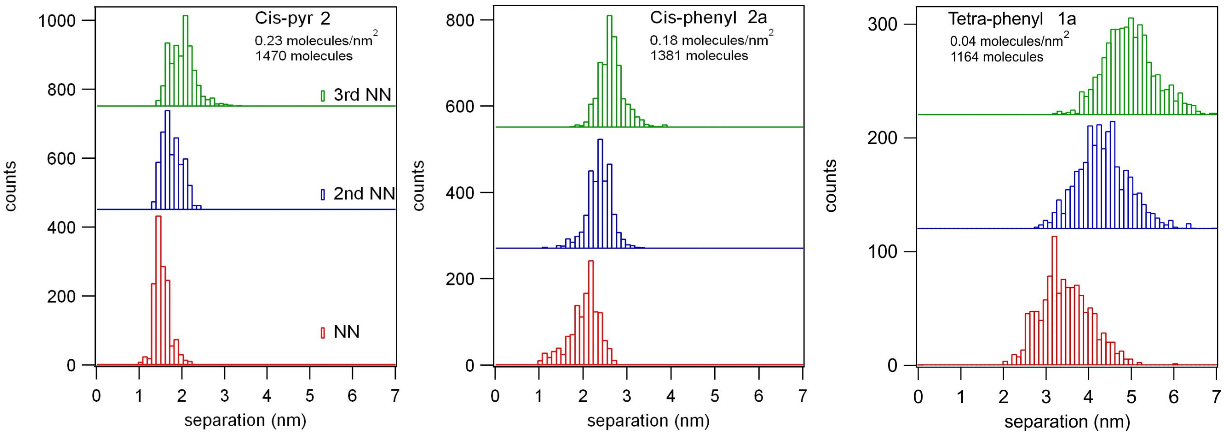


Figure SI3. Statistical analysis of the nearest neighbor separations of the assemblies of species 3, 3a and 1a on Ag(111) (left, middle, and right panel, respectively).

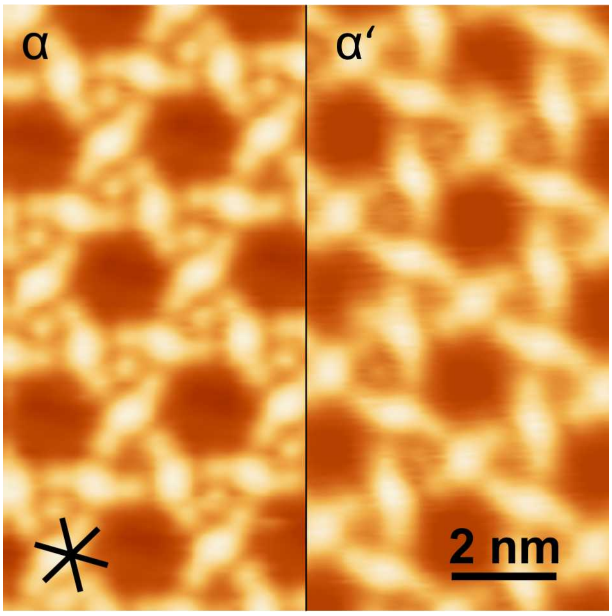


Figure SI4. Supramolecular organizational chirality exhibited by the deposition of species 2 on Ag(111). Left and right panel show high-resolution STM images of two-mirror symmetric domains, labeled α-trans and α’-trans. Tunneling parameters: 0.1 nA, -0.2 V.

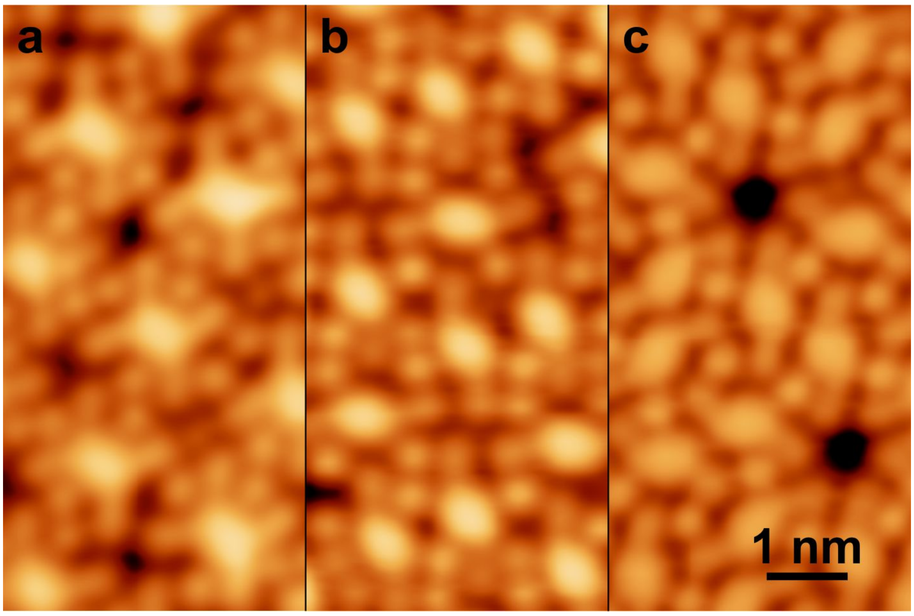


Figure SI5. High iodine coverages lead to different self-assembly patterns. (a) High iodine phase of module 1. Tunneling parameters: 88 pA, 0.1 V. (b, c) Two different high coverage iodine phases of module 2. Tunneling parameters: 0.2 nA, -0.2 V.

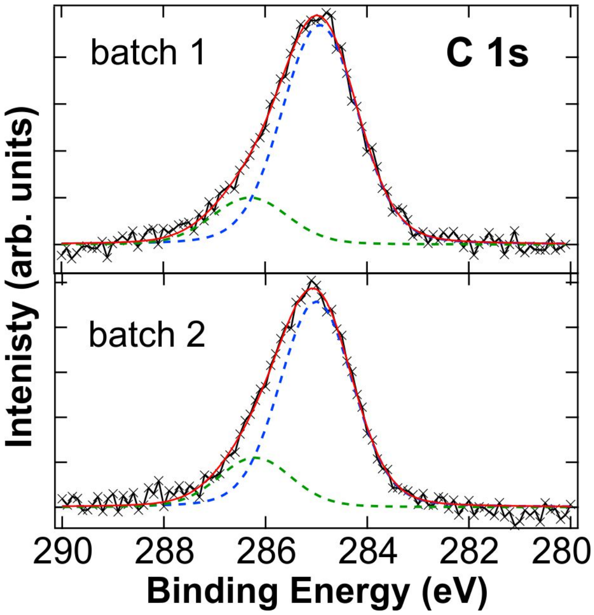


Figure SI6. Carbon 1s XPS signature of two different batches of species 1. The spectra are fitted with two components. The first component with lower binding energy (blue curve) corresponds to tertiary and quaternary carbon atoms of this molecule. The carbon atoms that are directly bound to pyridyl nitrogen atoms result in a second component (green curve) shifted to higher binding energies by 1.3 eV[2-3].

Instrument and materials

Compounds were fully characterized (m.p., ^{1}H and ^{13}C NMR, IR, MS).

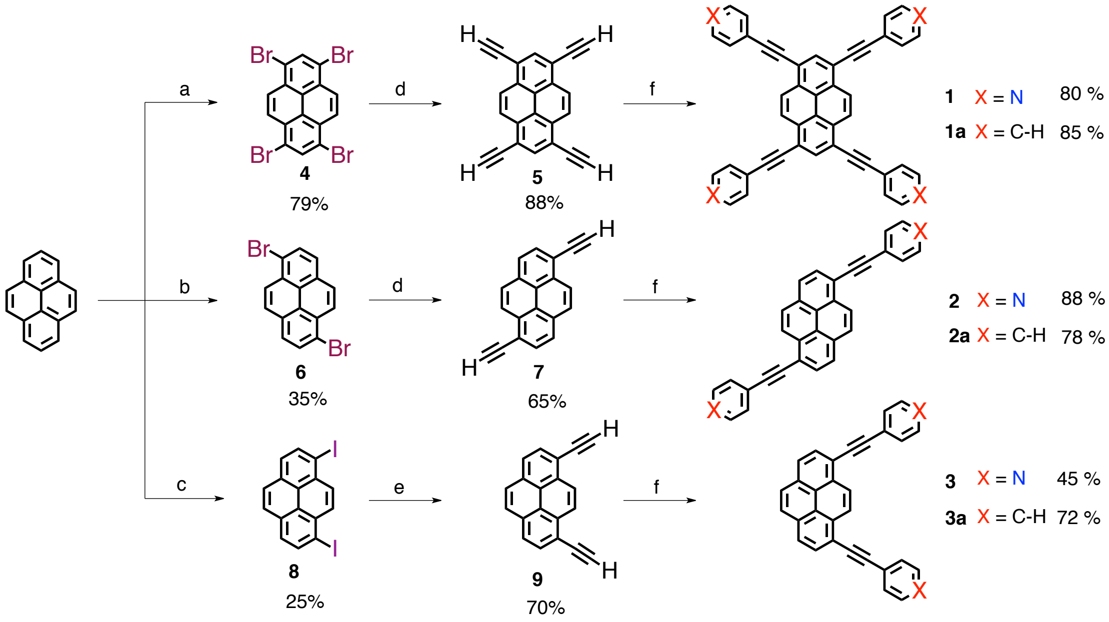
Thin layer chromatography (TLC) was conducted on pre-coated aluminum sheets with 0.20 mm Merck Silica Gel F254. Column chromatography was carried out using Merck silica gel 60 Å (particle size 40-63 µm). Microwave reactions were performed on a CEM Discover Microwave Reactor. Melting points (m.p.) were measured on a SMP-20 in open capillary tubes and have not been corrected.

NMR spectra were obtained on a Varian Inova spectrometer (500 MHz ^{1}H and 125 MHz ^{13}C). Chemical shifts are reported in ppm using the solvent residual signal as an internal reference (Chloroform-*d*: δ_H = 7.26 ppm, δ_C = 77.23 ppm; 1,1,2,2-Tetrachloroethane-d_2: δ_H = 6.00 ppm, δ_C = 73.78 ppm; Pyridine-d_5: δ_H = 8.74, 7.58, 7.22 and δ_C = 150.35, 135.91, 123.81). The resonance multiplicity is described as *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet), *m* (multiplet), *br* (broad signal).

MALDI-MS were recorded using a Waters QToF Premier mass spectrometer equipped with a nitrogen laser, operating at 337 nm with a maximum output of 500 mW delivered to the sample in 4 ns pulses at 20 Hz repeating rate. Time-of-flight analyses were performed in the reflectron mode at a resolution of about 10,000. The matrix solution (1 µl) was applied to a stainless steel target and air dried. Analyte samples were dissolved in a suitable solvent to obtain 1 mg/mL solutions. 1 µl aliquots of these solutions were applied onto the target area already bearing the matrix crystals, and air dried. For the recording of the single-stage MS spectra, the quadrupole (rf-only mode) was set to pass ions from 100 to 1000 THz and all ions were transmitted into the pusher region of the time-of-flight analyzer where they were analyzed with 1 s integration time.

Chemicals were purchased from Sigma Aldrich, TCI, and Acros and used as received. Solvents were purchased from Sigma Aldrich, VWR and Acros, and deuterated solvents from Sigma Aldrich and Cambridge Isotope Laboratories. General solvents such as THF and Et_3N were distilled from Na, Na/benzophenone, and CaH_2 respectively.

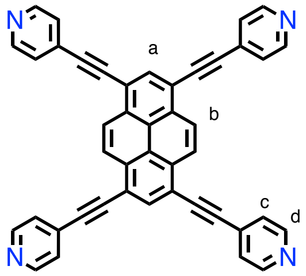
Synthetic procedures and characterizations



Scheme S1. Synthetic pathway adopted for the preparation of compounds **1-9**: a) Br_2, nitrobenzene, 120 °C; b) Br_2, CCl_4, r.t.; c) I_2, KIO_4, H_2SO_4, AcOH, 40 °C; d) 1. TMSA, $[Pd(PPh_3)_2Cl_2]$, CuI, PPh_3, THF, iPr_2NH, 80 °C; 2. KOH, MeOH, THF, r.t.; e) 1. TMSA, $[Pd(PPh_3)_4]$, CuI, THF, Et_3N, r.t.; 2. KOH, MeOH, THF, r.t.; f) 4-iodopyridine, $[Pd(PPh_3)_4]$, CuI, THF, Et_3N.

Characterizations of compounds **4**,[4-5] **5**,[4-5] **6**,[6] **7**,[7] **8**[5] and **9**[7] were in accordance with literature.

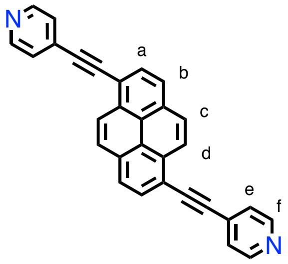
1,3,6,8-Tetrakis(4-pyridylethynyl)pyrene (1)



In a 10-mL microwave-reactor tube containing a stirring bar, 4-iodopyridine (0.121 g, 0.560 mmol), $Pd(PPh_3)_4$ (0.004 g, 0.004 mmol), CuI (0.001 g, 0.007 mmol) were dissolved in DMF/Et_3N (2:2 ml) and was purged with argon. 1,3,6,8-Tetraethynylpyrene (0.022 g, 0.074 mmol) was added and the reaction vessel was sealed and placed into the microwave reactor. The temperature heating profile for the reaction mixture was as follows: RT ⍰ 120 °C over a 2-min period (200-W maximum power), the reaction mixture was held at 120 °C (dynamic, 200-W maximum power) for 60 min. The crude reaction mixture was diluted with MeOH and the dark red solid was filtered and washed extensively with H_2O, Acetone and MeOH. The solid was dissolved in boiling $C_2H_2Cl_4$ and filtered over celite to obtain pure product **1** (0.036 g, 80 % yield) as dark red solid.

m.p. > 250 °C. ^{1}H-NMR (500 MHz, $C_2D_2Cl_4$, 353 K): δ = 8.84 (H_b, *s*, 4*H*), 8.75 (H_d, *d*, *j* = 4.9 Hz, *8*H), 8.58 (H_a, *s*, 2*H*), 7.62 (H_c, *d*, *j* = 4.9 Hz, *8*H). ^{13}C-NMR (125 MHz, $C_2D_2Cl_4$, 353 K): δ = 149.85, 134.43, 132.20, 130.68, 127.24, 125.35, 120.20, 118.30, 93.75, 91.31. IR (KBr): $\tilde{\nu}$ = 2205, 1627, 1601, 1591, 1538, 1471, 1399, 817 cm^{-1}. HRMS-MALDI (dctb matrix): found 606.1847 (M)$^+$, 607.1905 (MH)$^+$ 857.3168 (M+1dctb)$^+$, 1107.4622 (M+2dctb)$^+$, $C_{44}H_{22}N_4$ requires 606.1844.

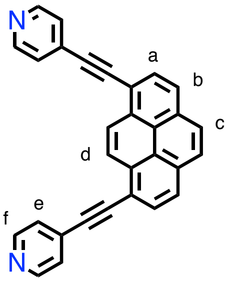
1,6-Bis(4-pyridylethynyl)pyrene (2)



In a 10-mL microwave-reactor tube containing a stirring bar, 4-iodopyridine (0.328 g, 1.600 mmol), $Pd(PPh_3)_4$ (0.009 g, 0.008 mmol), CuI (0.004 g, 0.020 mmol) were dissolved in DMF/Et_3N (2:2 ml) and was purged with argon. 1,6-Diethynylpyrene (0.100 g, 0.400 mmol) was added and the reaction vessel was sealed and placed into the microwave reactor. The temperature heating profile for the reaction mixture was as follows: RT ⍰ 120 °C over a 2-min period (200-W maximum power), the reaction mixture was held at 120 °C (dynamic, 200-W maximum power) for 30 min. The crude reaction mixture was diluted with MeOH and the yellow solid was filtered and washed extensively with H_2O, Acetone and MeOH. The solid was dissolved in boiling $C_2H_2Cl_4$ and filtered over celite to obtain pure product **2** (0.142 g, 88 % yield) as yellow solid.

m.p. > 250 °C. ^{1}H-NMR (500 MHz, $C_2D_2Cl_4$, 298 K): δ = 8.69 (H_f, *d*, *j* = 5.5 Hz, 4H), 8.65 (H_d, *d*, *j* = 9.0 Hz, 2*H*), 8.29 (H_a, *d*, *j* = 8.0 Hz, 2*H*), 8.23-8.21 (*m*, 4H), 7.60 (H_e, *d*, *j* = 6.0 Hz, 4H). ^{13}C-NMR (125 MHz, $C_2D_2Cl_4$, 298 K): δ = 149.63, 132.02, 131.50, 131.30, 130.43, 128.50, 126.27, 125.55, 125.50, 123.75, 117.17, 92.90, 92.75. IR (KBr): $\tilde{\nu}$ = 2203, 1604, 1569, 1483, 1435, 1420, 1215, 1098, 1059, 845, 830, 694 cm^{-1}. HRMS-MALDI (dctb matrix): found 404.1308 $(M)^+$, 405.1369 $(M+H)^+$, 654.3 $(M+1dctb)^+$, 905.5 $(M+2dctb)^+$, $C_{30}H_{16}N_2$ requires 404.1313.

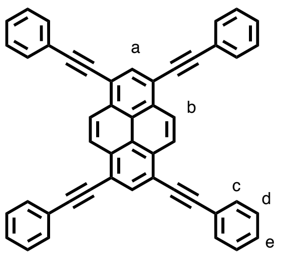
1,8-Bis(4-pyridylethynyl)pyrene (3)



To a degassed solution of dry Et_3N (2.5 mL) and THF (2.5 mL), 4-iodopyridine (0.072 g, 0.35 mmol), $[Pd(PPh_3)_4]$ (0.010 g, 0.008 mmol) and CuI (0.006 g, 0.032 mmol) were added and the mixture degassed a second time. 1,8-Diethynylpyrene (0.040 g, 0.16 mmol) was then added, the reaction mixture degassed one last time, and stirred overnight at room temperature under Ar. After 1 hour an orange precipitate was formed. The precipitate was then separated by centrifugation and washed with copious amount of MeOH, AcCN and Tol and submitted to CC (Tol/Py 85:15) affording the final compound (0.025 g, 45 % yield) as a light orange powder.

m.p. > 250°C ^{1}H-NMR (500 MHz, Pyr-d_5, 298 K): δ = 9.02 (H_d, *s*, 2H), 8.87 (H_f, *d*, *j* = 4.5 Hz, 4H), 8.39 (H_a, *d*, *j* = 8.0 Hz, 2H), 8.28 (H_b, *d*, *j* = 8.0 Hz, 2H), 8.19 (H_c, *s*, 2H), 7.68 (H_e, *d*, *j* = 4.5 Hz, 4H); ^{13}C-NMR (125 MHz, Pyr-d_5, 298 K): δ = 151.11, 132.92, 131.74, 131.38, 129.48, 127.47, 126.69, 126.36, 124.82, 123.53, 118.26, 94.21, 93.56. IR (KBr): $\tilde{\nu}$ = 2202, 1600, 1492, 1443, 1162, 1027, 845, 755, 693, 523 cm^{-1}. HRMS-MALDI (dctb matrix): found 404.1308 $(M)^+$, 405.1369 $(M+H)^+$, 654.3 $(M+1dctb)^+$, 905.5 $(M+2dctb)^+$, $C_{30}H_{16}N_2$ requires 404.1313.

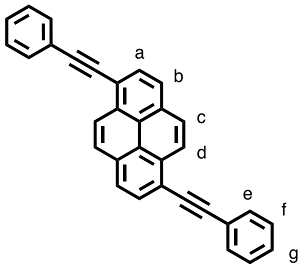
1,3,6,8-Tetrakis(phenylethynyl)pyrene (1a):



In a 10-mL microwave-reactor tube containing a stirring bar, 1,3,6,8-tetrabromopyrene (0.250 g, 0.481 mmol), $Pd(PPh_3)_2Cl_2$ (0.017 g, 0.024 mmol), CuI (0.005 g, 0.026 mmol) were dissolved in DMF/Et_3N (2:2 ml) and was purged with argon. Phenylacetylene (0.317 g, 2.884 mmol) was added and the reaction vessel was sealed and placed into the microwave reactor. The temperature heating profile for the reaction mixture was as follows: RT ⍰ 120 °C over a 2-min period (200-W maximum power), the reaction mixture was held at 120 °C (dynamic, 200-W maximum power) for 60 min. The crude reaction mixture was diluted with MeOH and the solid was filtered and washed extensively with H_2O, Acetone and MeOH to obtain pure product **1a** (0.246 g, 85 % yield) as an orange solid.

m.p. > 250 °C. ^{1}H-NMR (500 MHz, $C_2D_2Cl_4$, 353 K): δ = 8.83 (H_b, *s*, 4*H*), 8.51 (H_a, *s*, 2*H*), 7.81-7.78 (H_c, *m*, 8*H*), 7.52-7.46 (H_{de}, *m*, 12*H*). ^{13}C-NMR (125 MHz, $C_2D_2Cl_4$, 353 K): δ = 133.63, 131.70, 131.68, 128.60, 128.38, 126.79, 123.99, 123.05, 118.98, 96.34, 87.62. IR (KBr): $\tilde{\nu}$ = 2200, 1599, 1499, 1442, 1069, 885, 830, 754, 687 cm^{-1}. MS (ESI): 603 $(M)^+$, 301 $(M)^{2+}$, $C_{48}H_{26}$ requires 602.2.

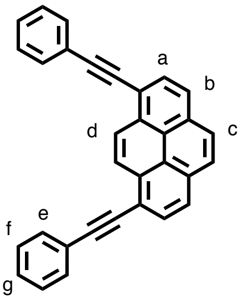
1,6-bis(phenylethynyl)pyrene (2a)



To a degassed solution of dry Et$_3$N (2.5 mL) and THF (2.5 mL), 4-iodobenzene (0.071 g, 0.350 mmol), [Pd(PPh$_3$)$_4$] (0.010 g, 0.008 mmol) and CuI (0.006 g, 0.032 mmol) were added and the mixture degassed a second time. 1,6-Diethynylpyrene (0.040 g, 0.160 mmol) was then added, the reaction mixture degassed one last time, and stirred overnight at room temperature under Ar. The precipitate was then filtered over celite (CHCl$_3$), the solvent was removed under reduced pressure. The crude was purified with CC (CHX/DCM 85:15) affording the final compound 2a (0.046 g, 78 % yield) as a yellow powder.

m.p. > 250°C ^{1}H-NMR (500 MHz, CDCl$_3$, 298 K): δ 8.70 (H$_d$, *d*, *j* = 9.0 Hz, 2H), 8.23 (H$_a$, *d*, *j* = 8.0 Hz, 2H), 8.19-8.16 (H$_{bc}$, *m*, 4H), 7.74 (H$_e$, *m*, 4H), 7.46-7.71 (H$_{fg}$, *m*, 6H); ^{13}C-NMR (125 MHz, CDCl$_3$, 298 K): 132.27, 131.95, 131.40, 130.19, 128.76, 128.73, 128.38, 126.53, 125.39, 124.48, 123.65, 118.71, 95.75, 88.72. IR (KBr): $\tilde{\nu}$ = 2201, 1600, 1492, 1442, 1161, 1071, 1027, 845, 755, 693 cm^{-1}. MS (ESI): found 402.1 (M)$^+$, requires C$_{32}$H$_{18}$ 402.1.

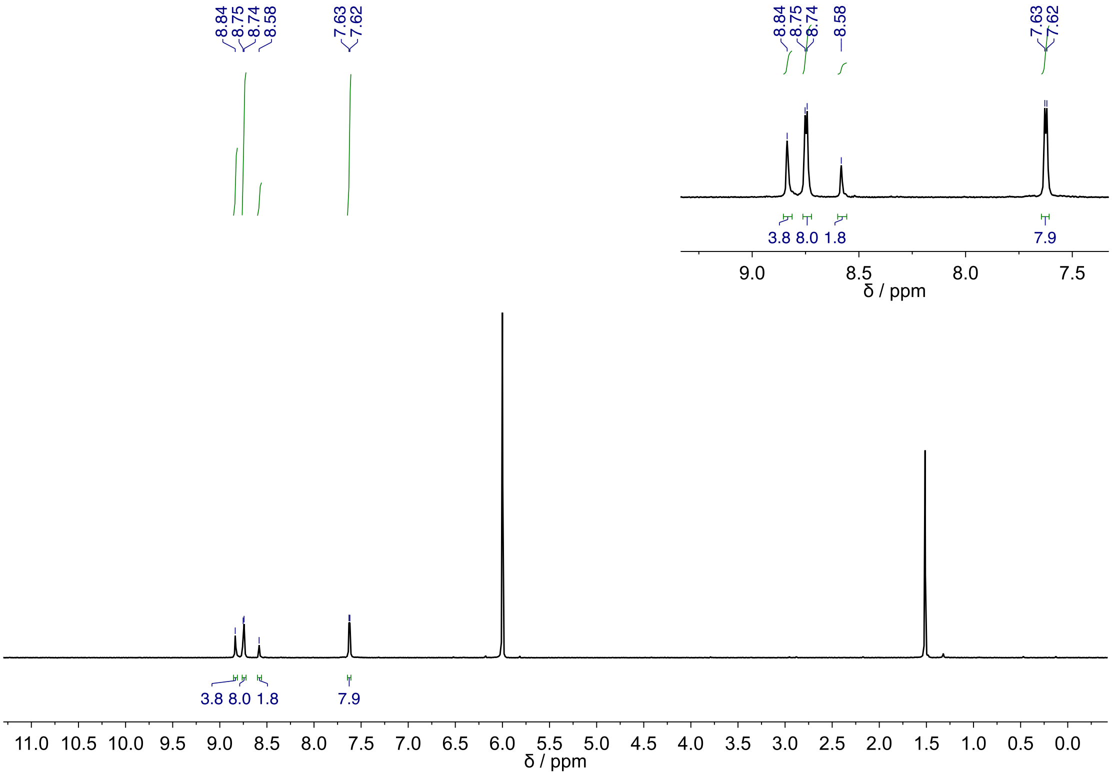
1,8-bis(phenylethynyl)pyrene (3a)

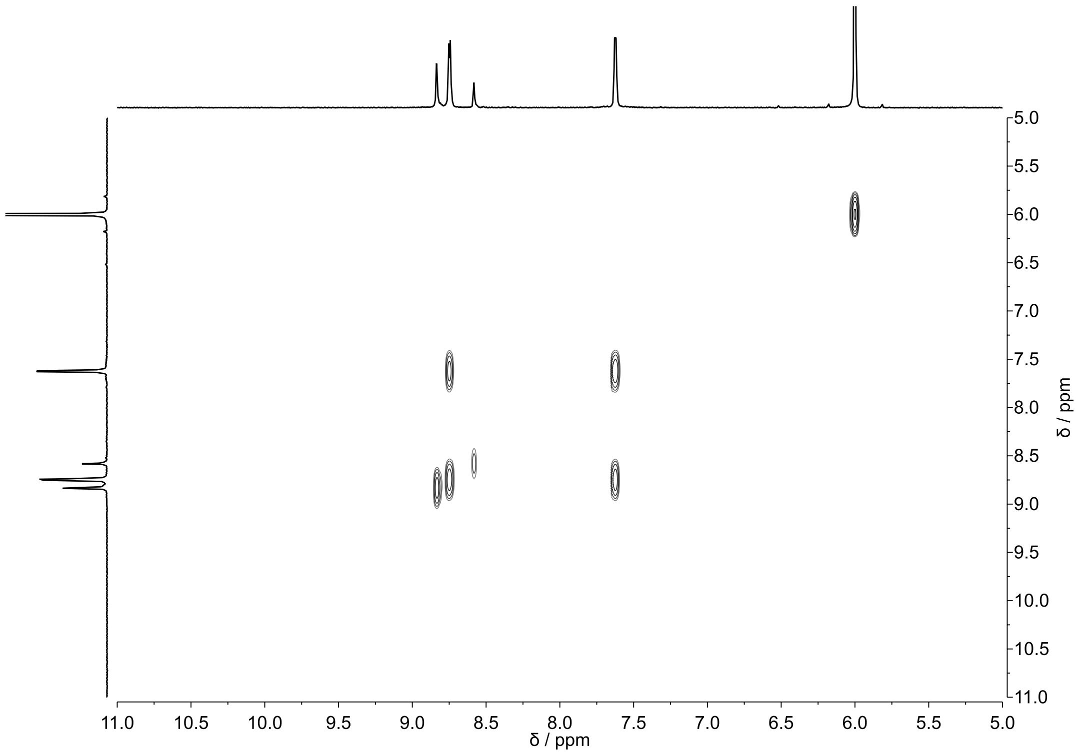


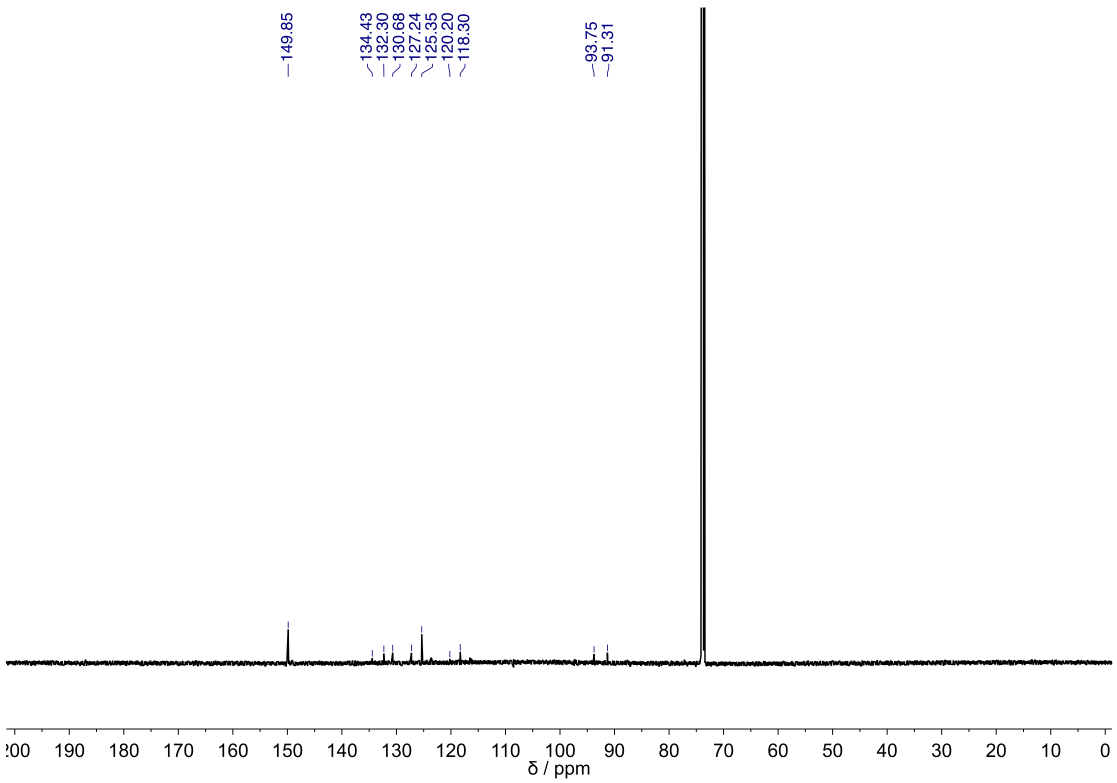
To a degassed solution of dry Et$_3$N (2.5 mL) and THF (2.5 mL), 4-iodobenzene (0.071 g, 0.350 mmol), [Pd(PPh$_3$)$_4$] (0.010 g, 0.008 mmol) and CuI (0.006 g, 0.032 mmol) were added and the mixture degassed a second time. 1,8-Diethynylpyrene (0.040 g, 0.160 mmol) was then added, the reaction mixture degassed one last time, and stirred overnight at room temperature under Ar. The precipitate was then filtered over celite (CHCl$_3$), the solvent was removed under reduced pressure. The crude was purified with CC (CHX/DCM 85:15) affording the final compound (0.046 g, 72 % yield) as a yellow powder.

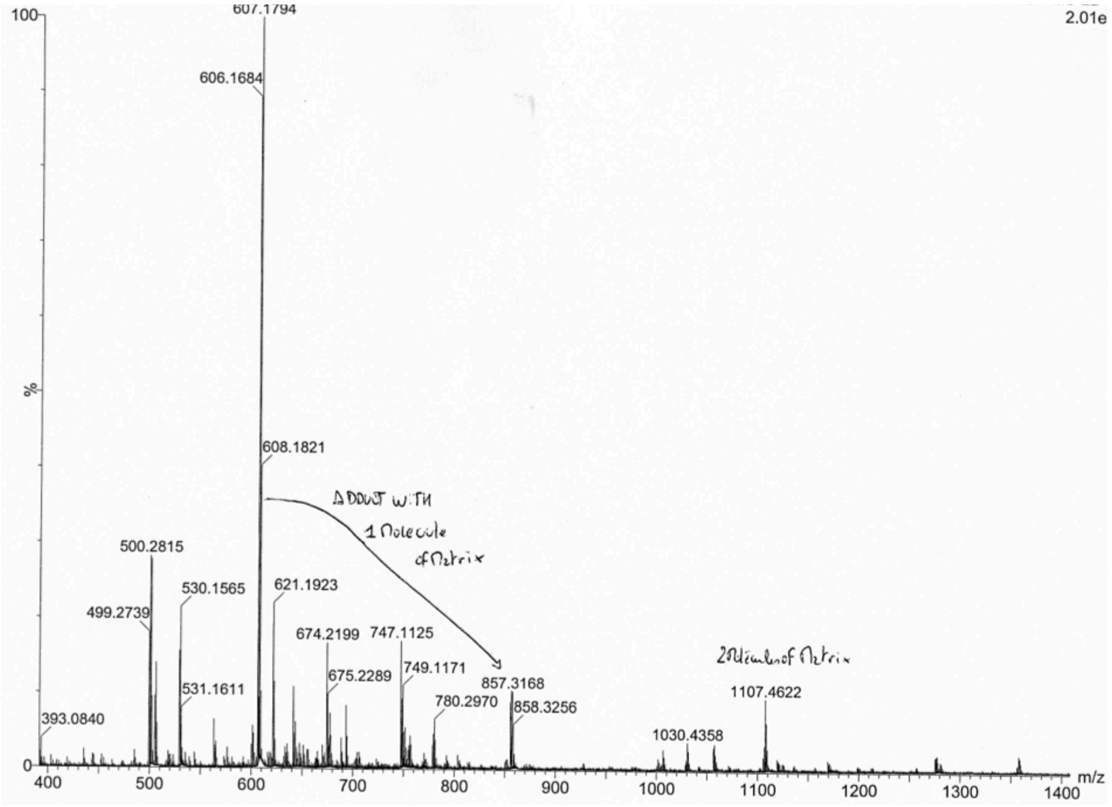
m.p. > 250°C ^{1}H-NMR (500 MHz, CDCl$_3$, 298 K): δ 8.78 (H$_d$, *s*, 2H), 8.22 (H$_a$, *d*, *j* = 8.0 Hz 2H), 8.13 (H$_b$, *d*, *j* = 8.0 Hz, 2H), 8.06 (H$_c$, *s*, 2H), 7.75-7.73 (H$_e$, *m*, 4H), 7.46-7.41 (H$_{fg}$, *m*, 6H); ^{13}C-NMR (125 MHz, CDCl$_3$, 298 K): 132.08, 131.95, 131.56, 130.11, 128.73, 128.71, 128.17, 126.67, 125.32, 124.44, 123.68, 118.74, 95.85, 88.74. IR (KBr): $\tilde{\nu}$ = 2200, 1601, 1495, 1442, 1176, 1159, 1069, 1026, 845, 749, 686 cm^{-1}. MS (ESI): found 402.1 (M)$^+$, requires C$_{32}$H$_{18}$ 402.1.

Selected ^{1}H, HH, ^{13}C and MALDI spectra

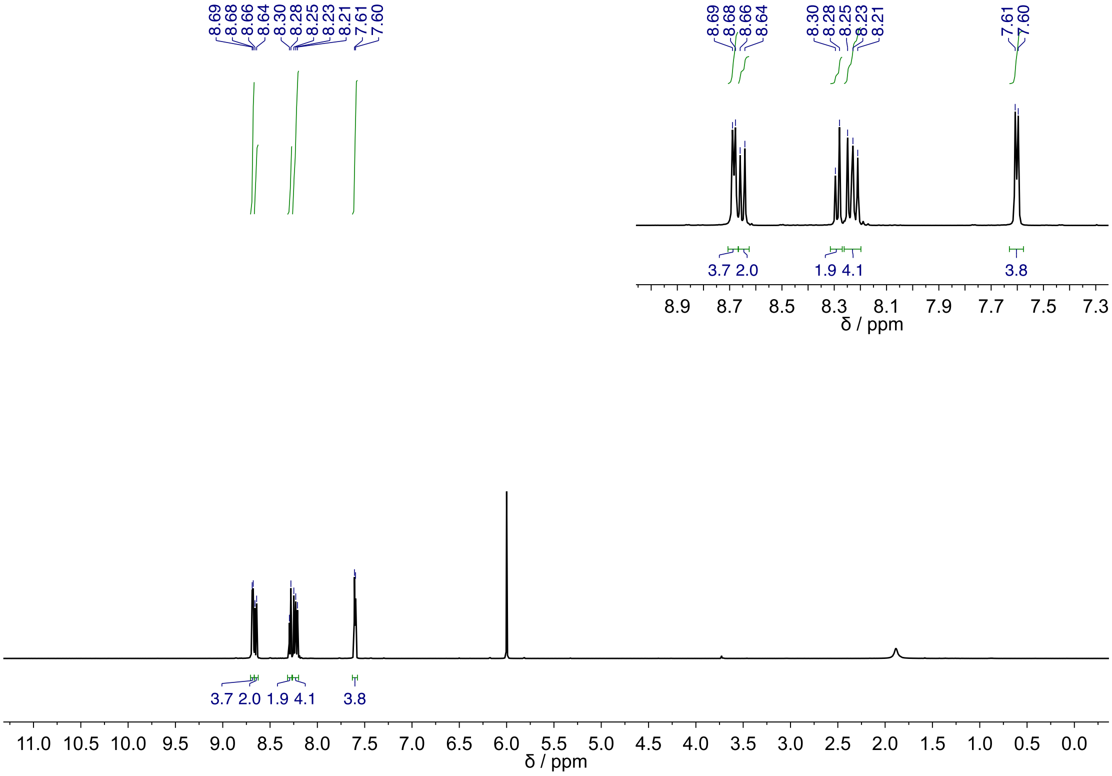


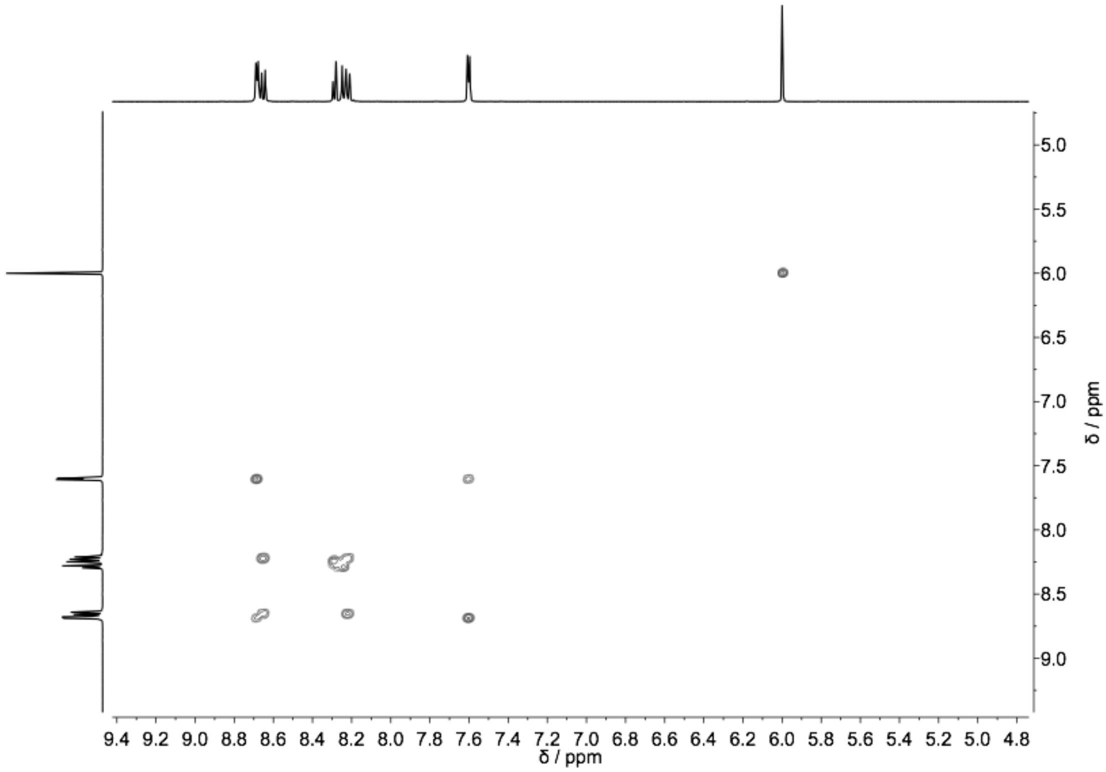


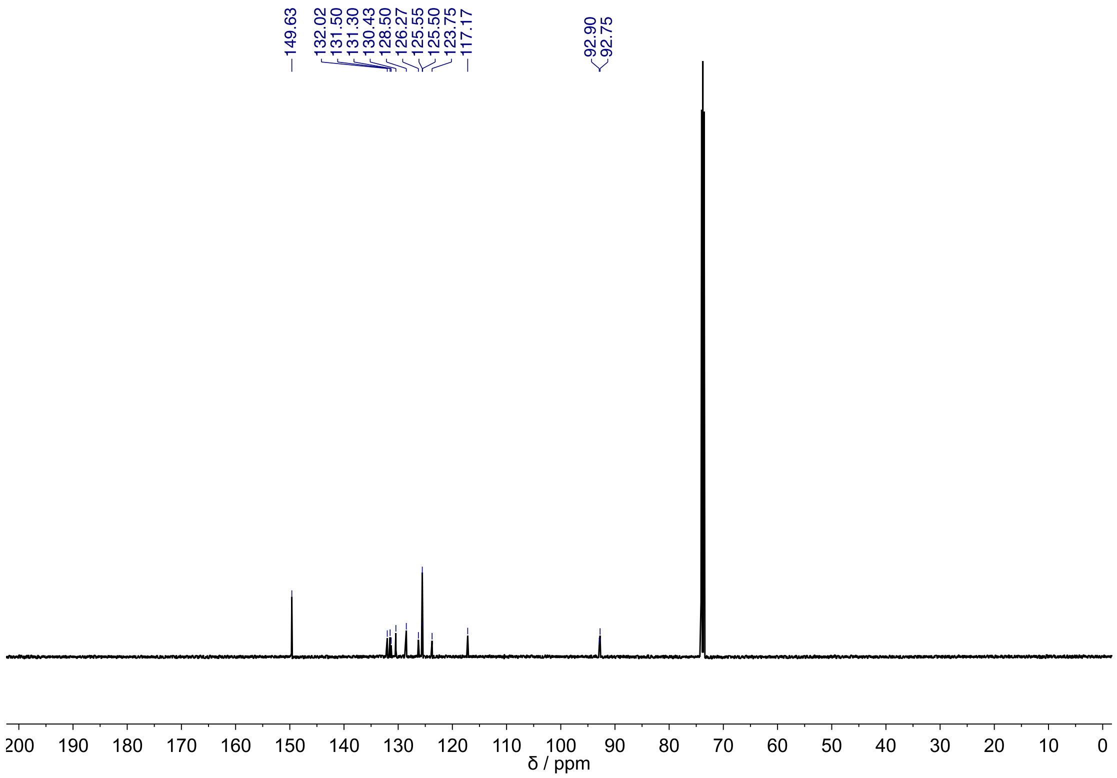


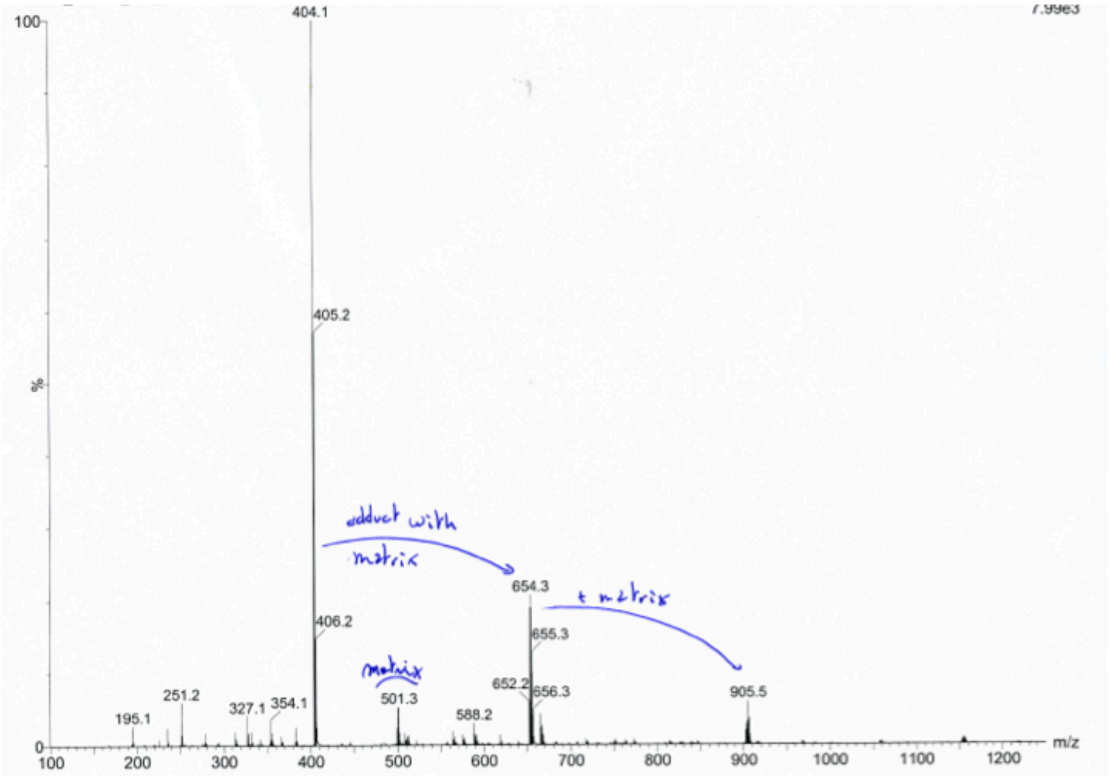


Figures S7-10. ^{1}H, HH and ^{13}C NMR ($C_2D_2Cl_4$, 353 K) and MALDI-MS of 1,3,6,8-tetrakis(4-pyridylethynyl)pyrene **1**.

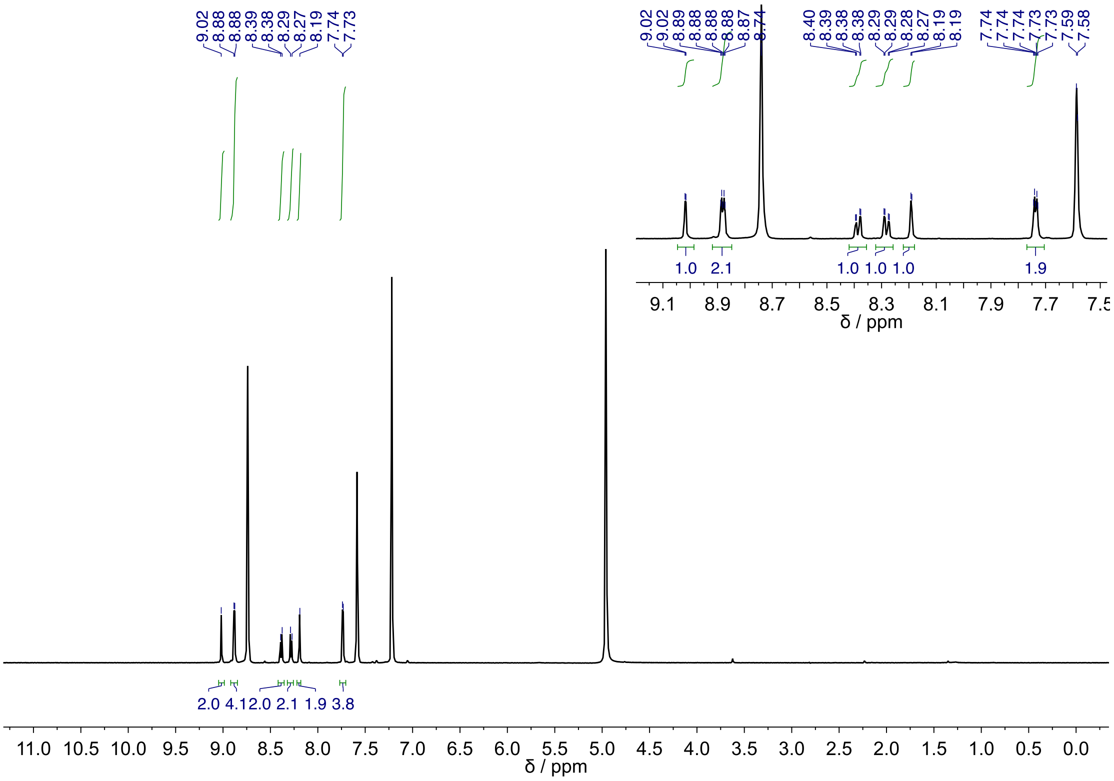

8.69
8.68
8.66
8.64
8.30
8.28
8.25
8.23
8.21
7.61
7.60
3.7 2.0
1.9 4.1
3.8
8.9 8.7 8.5 8.3 8.1 7.9 7.7 7.5 7.3
δ / ppm
3.7 2.0 1.9 4.1 3.8
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ / ppm

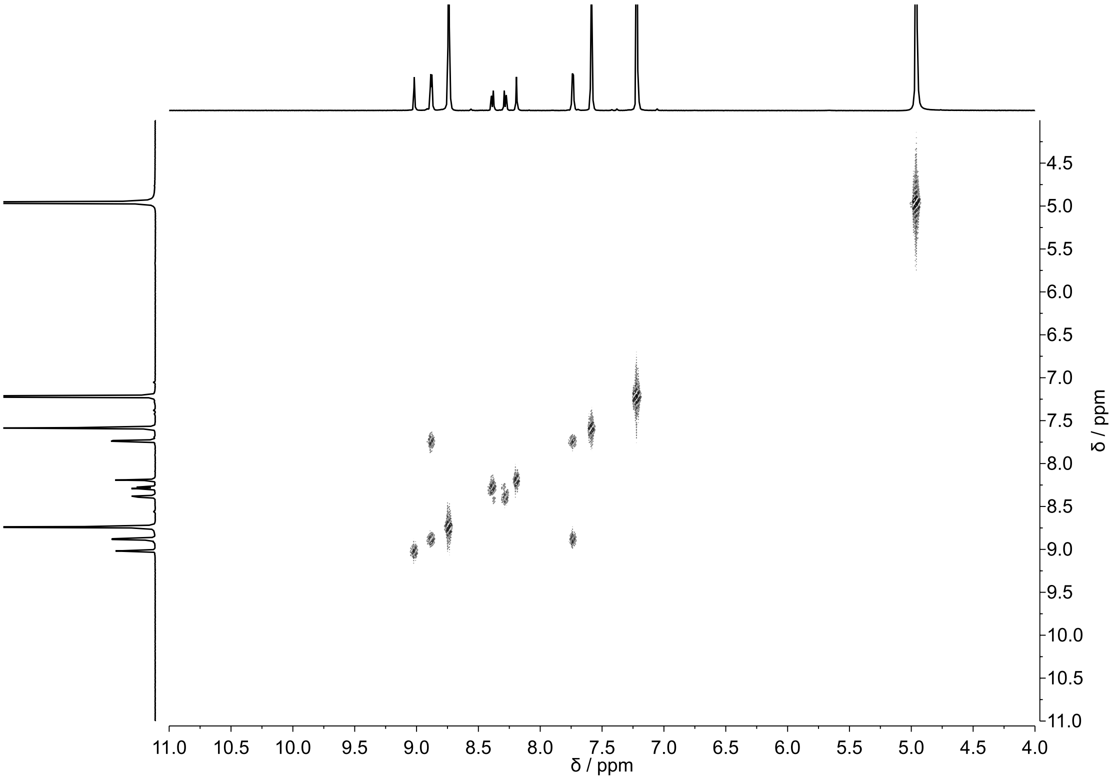

5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
δ / ppm
9.4 9.2 9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8
δ / ppm

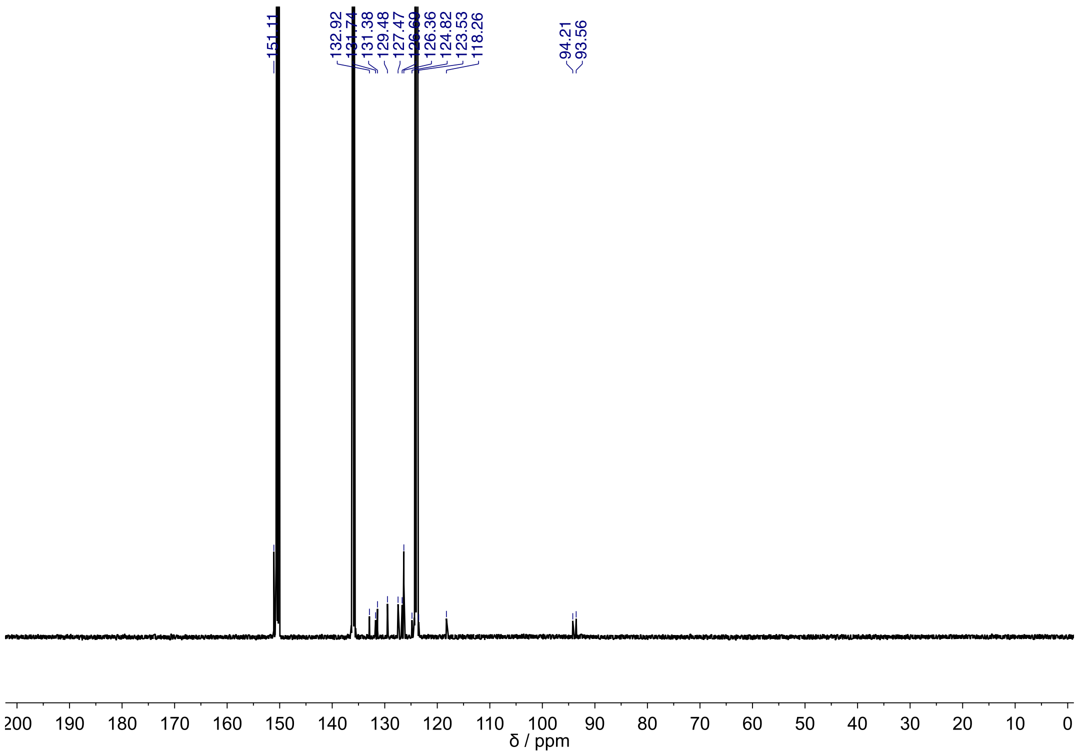


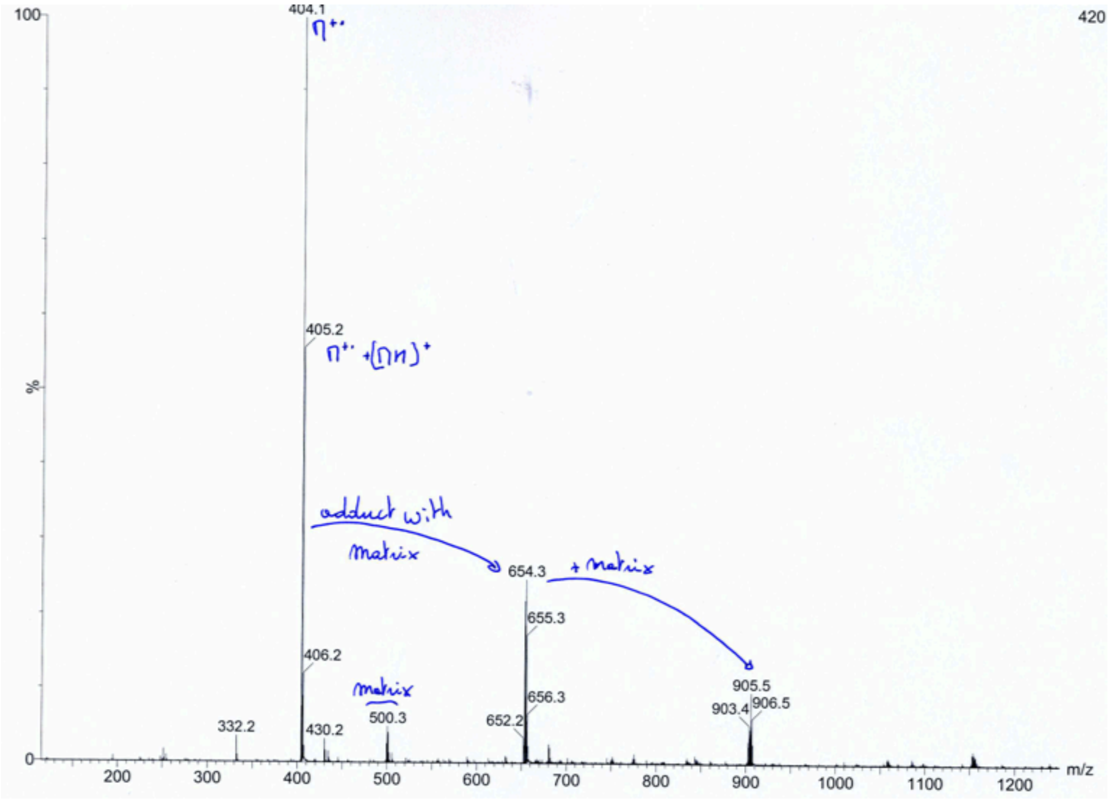


Figures S11-14. ^{1}H, HH and ^{13}C NMR ($C_2D_2Cl_4$, 298 K) and MALDI-MS of 1,6-bis(4-pyridylethynyl)pyrene **2**.

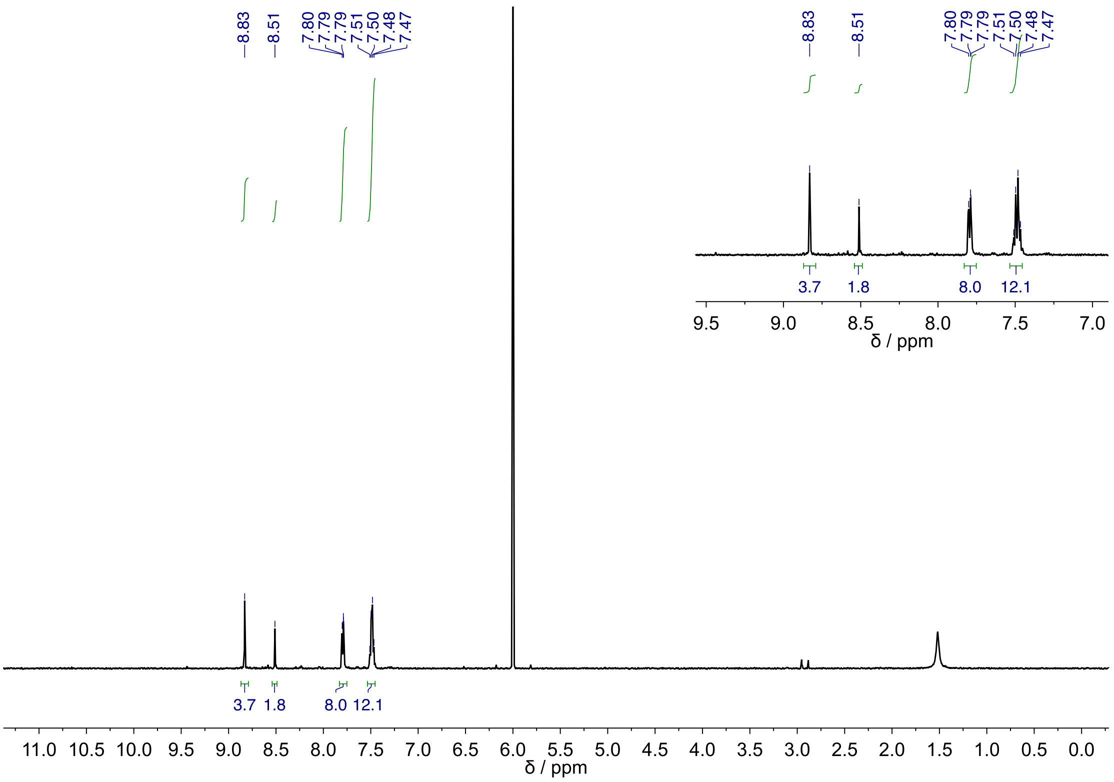

9.02
8.88
8.39
8.38
8.29
8.27
8.19
7.74
7.73
2.0 4.1 2.0 2.1 1.9 3.8
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ / ppm
9.02
9.02
8.89
8.88
8.88
8.88
8.87
8.74
8.40
8.39
8.38
8.38
8.29
8.29
8.28
8.27
8.19
8.19
7.74
7.74
7.74
7.73
7.73
7.59
7.58
1.0 2.1 1.0 1.0 1.0 1.9
9.1 8.9 8.7 8.5 8.3 8.1 7.9 7.7 7.5
δ / ppm

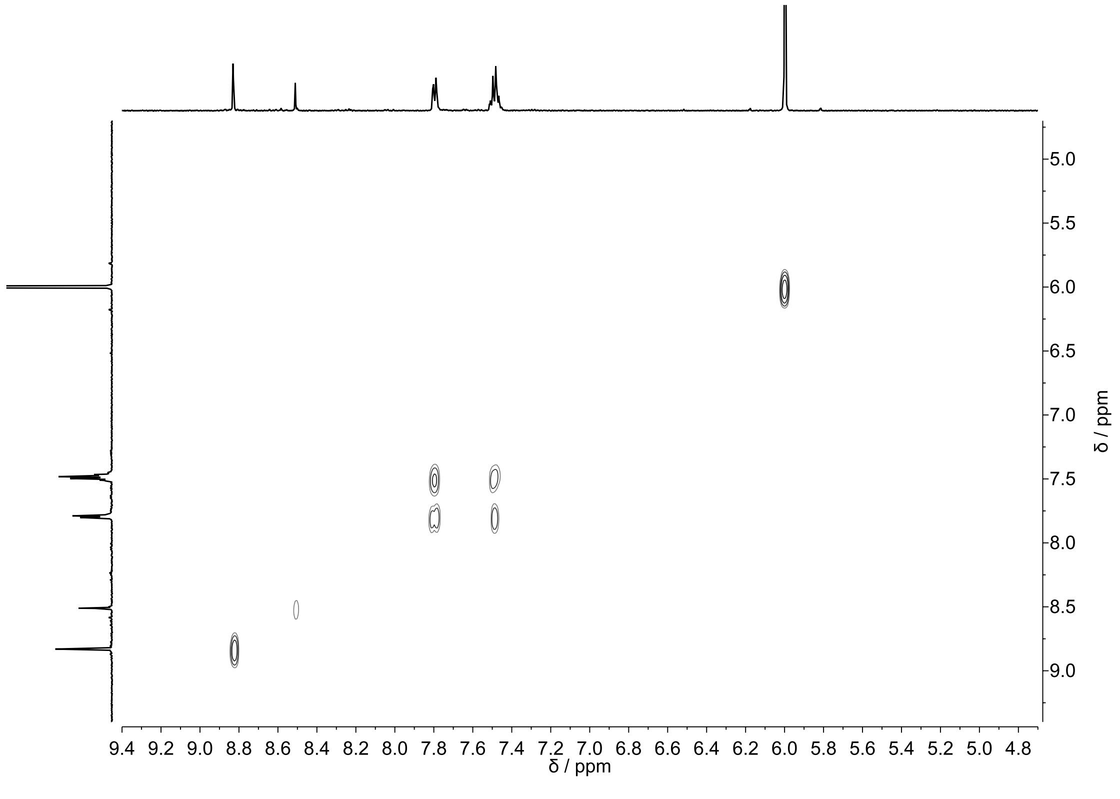

4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
δ / ppm
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0
δ / ppm

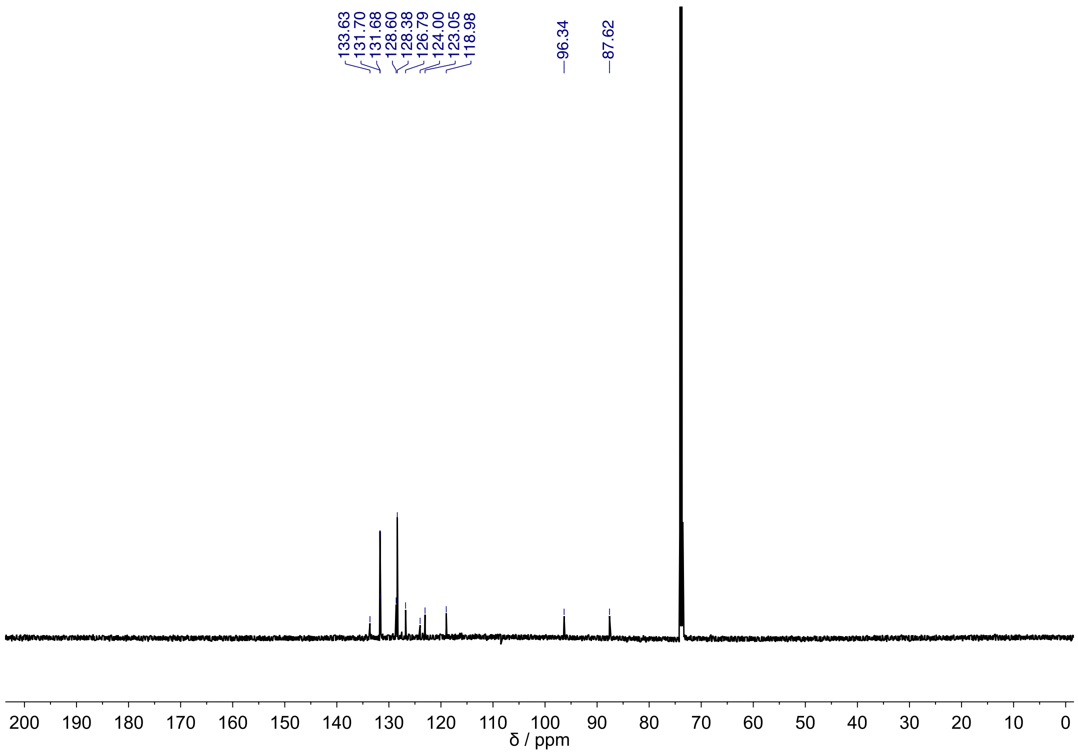




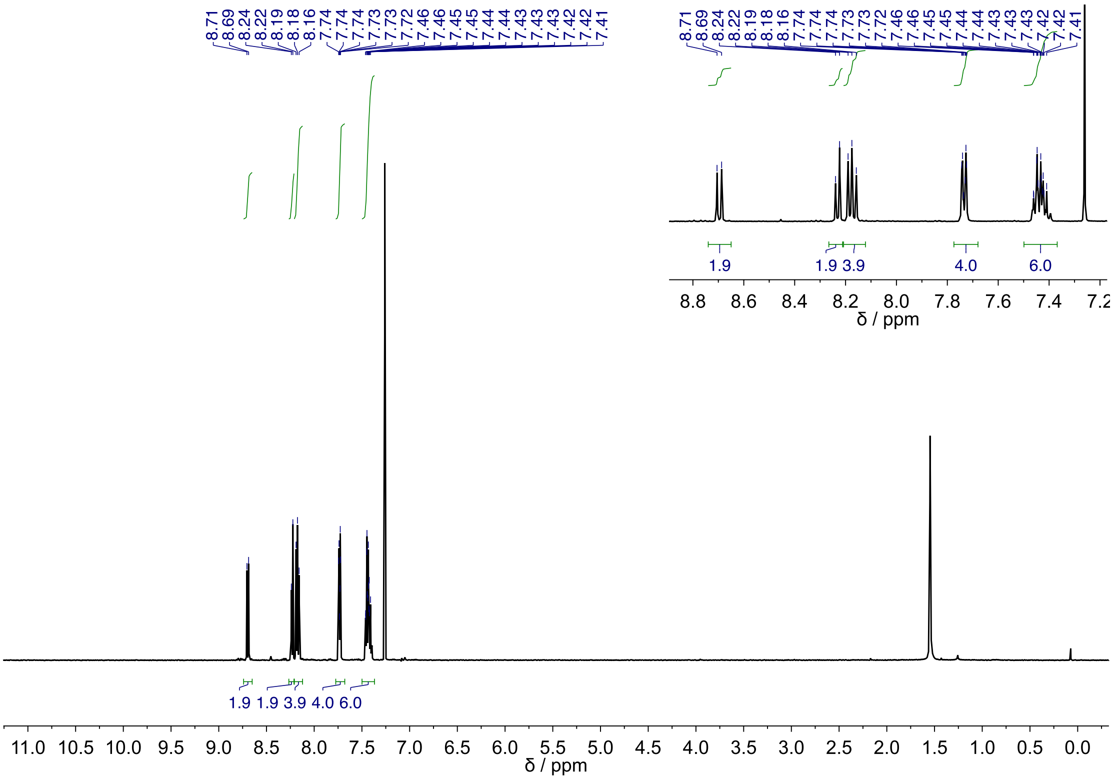
Figures S15-18. ^{1}H, HH and ^{13}C NMR (Pyr-d_5, 298 K) and MALDI-MS of 1,8-bis(4-pyridylethynyl)pyrene **3**.

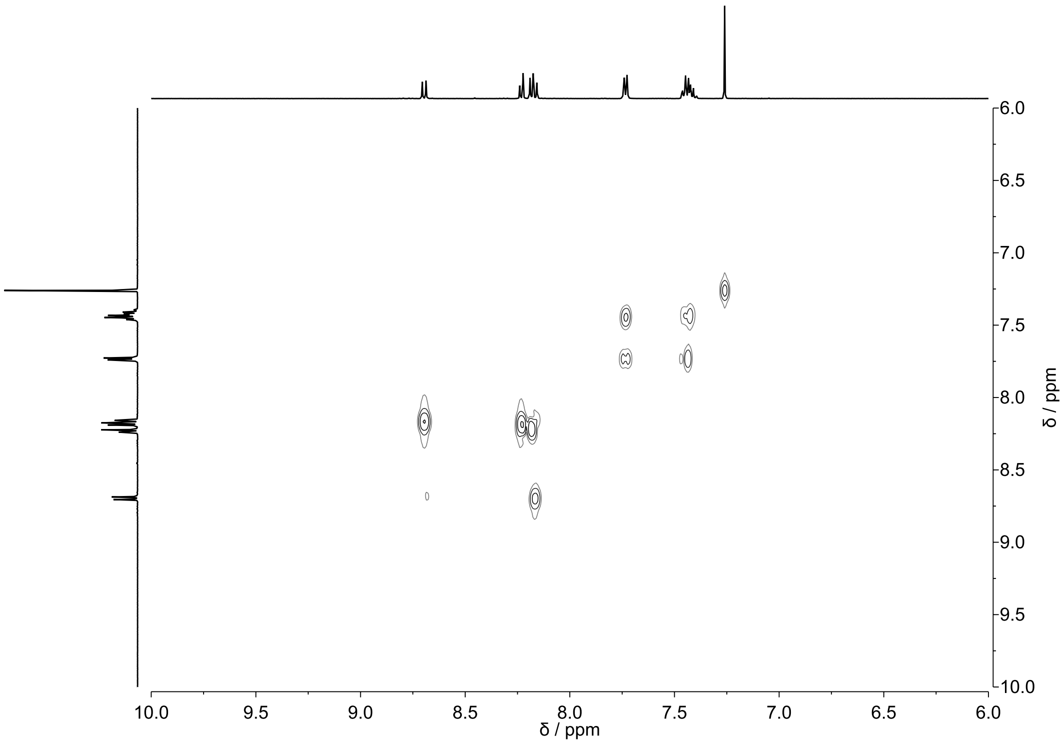

8.83
8.51
7.80
7.79
7.79
7.51
7.50
7.48
7.47
3.7
1.8
8.0
12.1
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ / ppm
9.5 9.0 8.5 8.0 7.5 7.0
δ / ppm

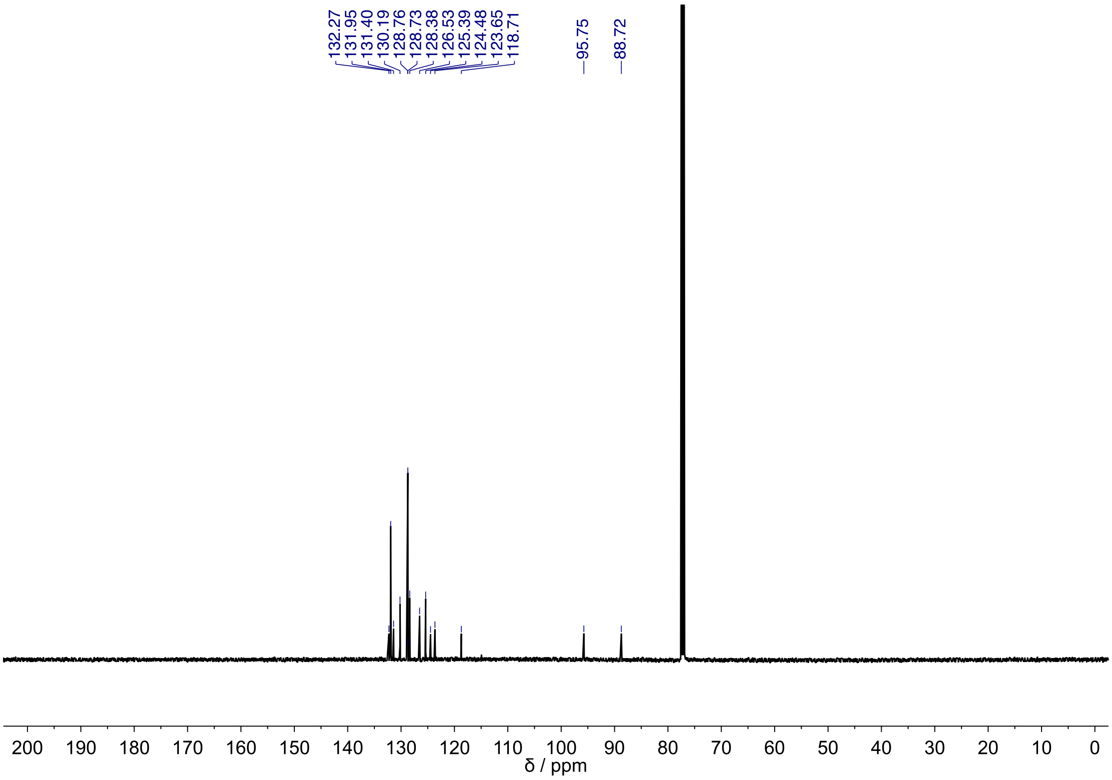

5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
δ / ppm
9.4 9.2 9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8
δ / ppm



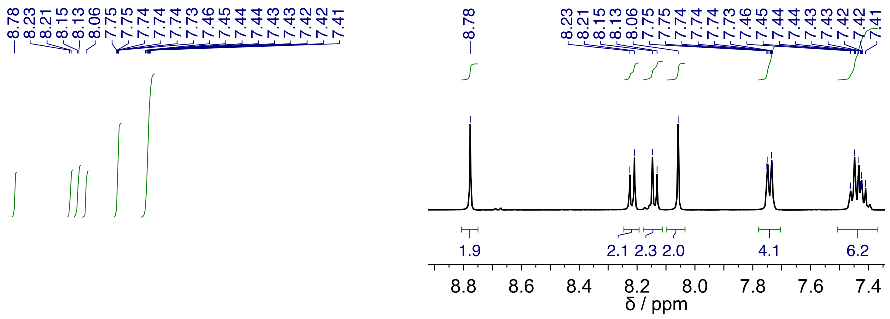
Figures S19-21. ^{1}H, HH and ^{13}C NMR ($C_2D_2Cl_4$, 353 K) of 1,3,6,8-tetrakis(phenylethynyl)pyrene **1a**.

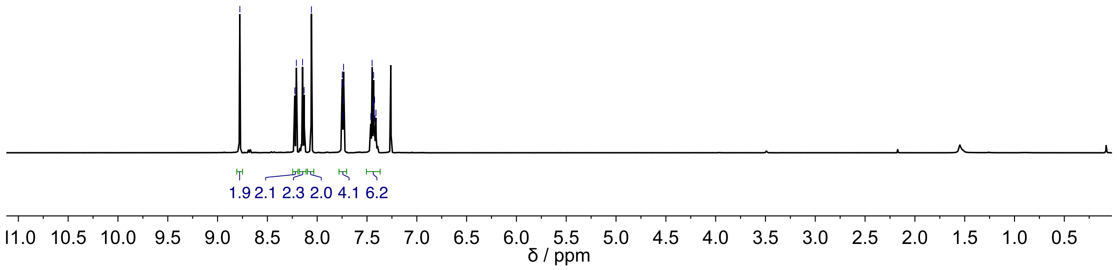


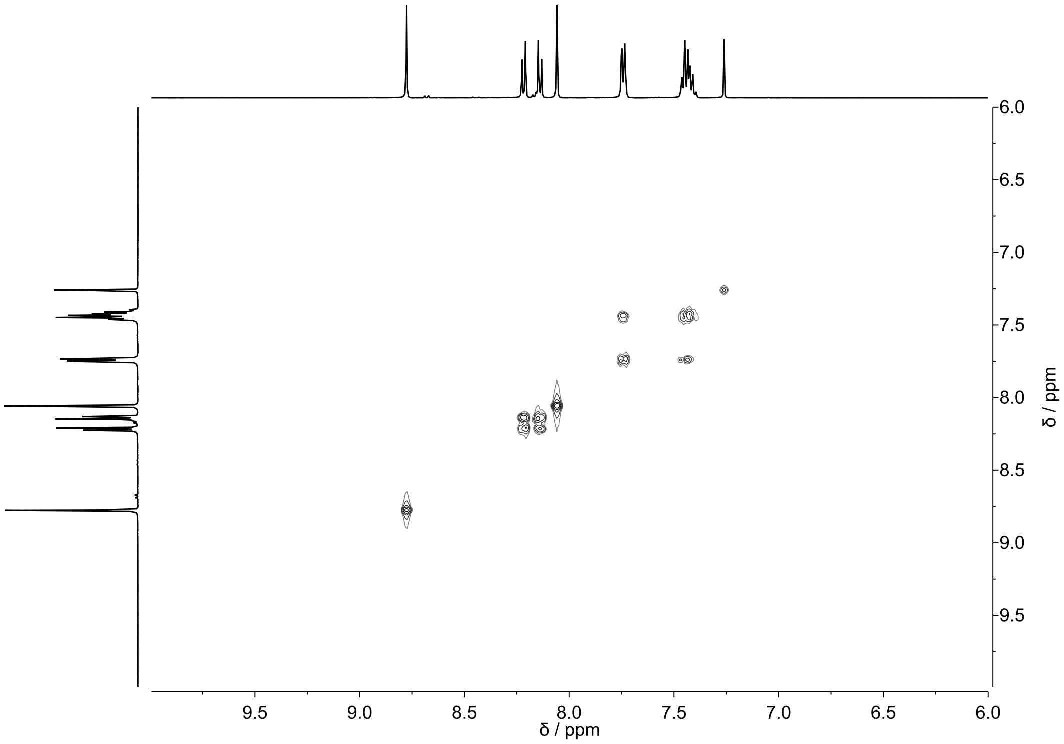


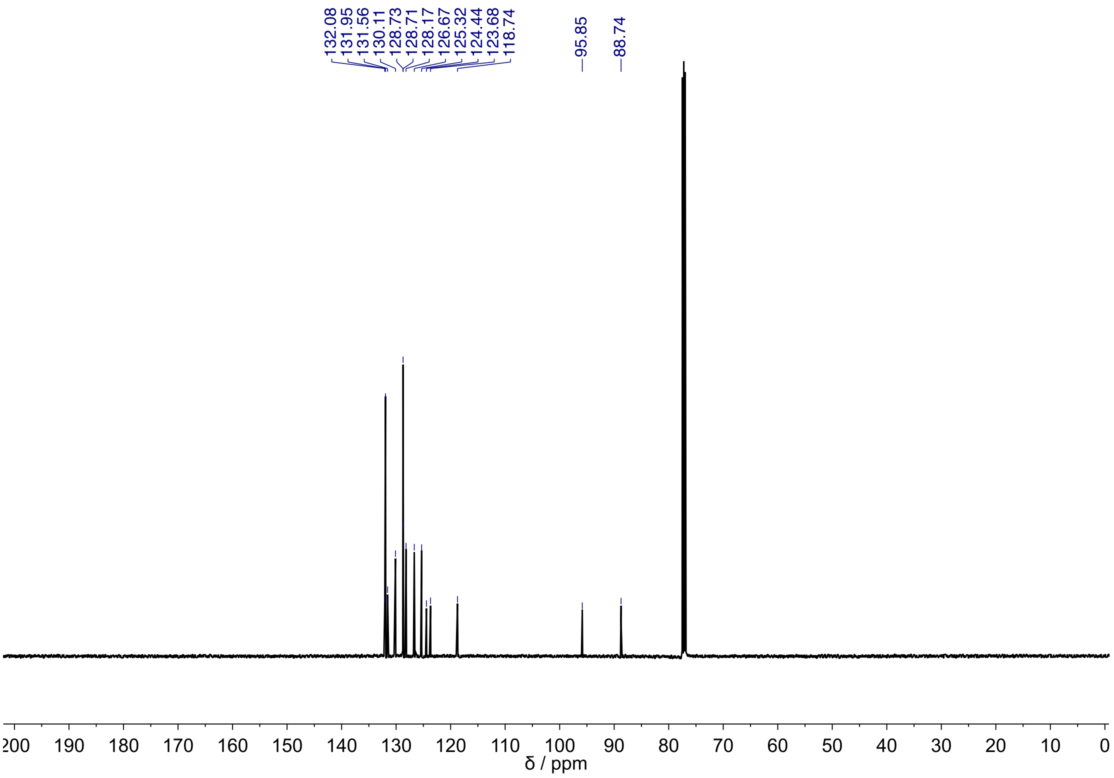


Figures S22-24. ^{1}H, HH and ^{13}C NMR (CDCl$_3$, 298 K) of 1,6-bis(phenylethynyl)pyrene **2a**.


8.78
8.23
8.21
8.15
8.13
8.06
7.75
7.75
7.74
7.74
7.73
7.46
7.45
7.44
7.44
7.43
7.43
7.42
7.42
7.41
8.78
8.23
8.21
8.15
8.13
8.06
7.75
7.75
7.74
7.74
7.74
7.73
7.46
7.45
7.44
7.44
7.43
7.43
7.42
7.42
7.41
1.9
2.1
2.3
2.0
4.1
6.2
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
δ / ppm


1.9
2.1
2.3
2.0
4.1
6.2
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
δ / ppm


6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
δ / ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
δ / ppm



Figures 25-27. ^{1}H, HH and ^{13}C NMR ($CDCl_3$, 298 K) of 1,8-bis(phenylethynyl)pyrene **3a**.

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