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6 REFERENCES......................................ERROR! BOOKMARK NOT DEFINED.
1 General Aspects

All chemicals and solvents were purchased in reagent grade from commercial suppliers (Acros®, Sigma-Aldrich® or Fluka®, Fluorochem®, Merck®, chemPur®) and used as received, unless otherwise specified. Solvents in HPLC grade were purchased from Fisher Chemicals®.

Flash column chromatography was performed on a Interchim PuriFlash 430 using flash grade silica gel from Machery-Nagel 60 M (40–63 mm, deactivated).

NMR spectra were recorded on a Bruker Avance 400, a Bruker Avance Neo 400 or a Joel JNM EX-400, all operating at 400 MHz (1H NMR) and 100 MHz (13C NMR), and on a Bruker Avance 300 operating at 282 MHz (19F NMR) at room temperature. Furthermore, a Bruker Avance Neo 500, operating at 500 MHz (1H NMR), 125 MHz (13C NMR) and 470 MHz (19F NMR) at room temperature or 30 °C and a Bruker Avance Neo 600, operating at 600 MHz (1H NMR) and 150 MHz (13C NMR) at room temperature, were used. The signals were referenced to residual solvent peaks (in parts per million (ppm)) 1H: CDCl₃, 7.24 ppm; CD₂Cl₂, 5.32 ppm; C₂D₂Cl₄, 5.91 ppm; DMSO-d₆, 2.05 ppm; 13C: CDCl₃, 77.0 ppm; CD₂Cl₂, 53.8 ppm; C₂D₂Cl₄, 74.2 ppm; DMSO-d₆, 39.5 ppm). Coupling constants were assigned as observed. The obtained spectra were evaluated with the program MestReNova 11.0.4.

LDI-MS spectra were recorded on a Shimadzu Biotech AXIMA Confidence MALDI-TOF instrument (MALDI-MS was recorded for precursor P4 using AgOTf and trans-2-[3-(4-t-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrix).

High resolution APPI spectra were recorded on a Bruker ESI TOF maXis 4G instrument. The data was evaluated with the program Bruker Compass DataAnalysis 4.2.

Analytical HPLC measurements were performed on a Shimadzu Prominence Liquid Chromatograph LC-20AT with communication bus module CBM-20A, diode array detector SPD-M20A, and column oven CTO-20AC. Preparative HPLC was performed on a Shimadzu Prominence Liquid Chromatograph LC-20AT with communication bus module CBM-20A, diode array detector SPD-M20A, degassing unit DGU-20A 5R, column oven CTO-20A, auto sampler SIL-20A HT and fraction collector FRC-10A. For analysis a Cosmosil 5PYE column (4.6 x 250 mm) and a Cosmosil PBr column (4.6ID x 250 mm), both from Nacalai Tesque, were used. For separation a Cosmosil PBr column (10ID x 250 mm) and a Cosmosil Buckyprep column (10 x 250 mm) were used. As eluent a DCM/MeOH mixture was used (UV-vis detection). The data (HPLC chromatograms and UV/vis spectra) were evaluated with the programs Shimadzu LCsolution and Shimadzu LabSolutions, respectively.

Microwave-assisted reactions were performed using Discover SP Microwave Synthesizer, CEM.
**TLC analysis** was carried out with TLC sheets coated with silica gel with fluorescent indicator 254 nm from Machery-Nagel (ALUGRAM® SIL G/UV254) and visualized via UV-light of 254nm or 366 nm.
Overview

Synthesized Building Blocks

| B1 | B2 | B3 | B4 |
|----|----|----|----|
| ![Image](image1.png) | ![Image](image2.png) | ![Image](image3.png) | ![Image](image4.png) |

Synthesized Oligophenylenes

| P1 | P2 | P3 | P4 |
|----|----|----|----|
| ![Image](image5.png) | ![Image](image6.png) | ![Image](image7.png) | ![Image](image8.png) |

Synthesized Carbon-Based Nanostructures

1. By Condensation of P1

| N1 | N2 | N3 |
|----|----|----|
| ![Image](image9.png) | ![Image](image10.png) | ![Image](image11.png) |
2. By Condensation of \( \textbf{P2} \)

3. By Condensation of \( \textbf{P3} \)

4. By Condensation of \( \textbf{P4} \)
2 Experimental Procedures

General Procedure for Suzuki-Cross-Coupling Reaction:

A single neck round-bottom flask equipped with a magnetic stirring bar was charged with aryl halide (1 equiv.), boronic acid/ester (1.1–2.2 eq), K₂CO₃/Cs₂CO₃ or K₃PO₄ (2 eq/4 eq) and a mixture of toluene/MeOH 2:1, toluene/H₂O 5:1, or THF/H₂O 5:1. The mixture was degassed under dynamic vacuum for 5 min under vigorous stirring. Under nitrogen atmosphere Pd(PPh₃)₄/Pd(dppf)Cl₂ (5 mol%, 0.05 equiv.) was added as catalyst and the suspension again degassed for 1 min under stirring. The reaction mixture was stirred at reflux for 18–24 h under nitrogen atmosphere. After cooling to room temperature water was added, phases were separated and the aqueous layer extracted with CH₂Cl₂ three times. The combined organic fractions were dried over Na₂SO₄, filtered and the solvent removed in vacuo. The crude material was filtered through silica gel with CH₂Cl₂/hexanes 1:1 and after removal of the solvent the product was purified by precipitation with hexanes from DCM solution or by flash column chromatography on silica gel which yielded the pure cross-coupled product.

2.1 Synthesis of the Building Blocks

2-Bromo-2’-fluoro-1,1’-biphenyl (B1). 1-Bromo-2-iodo-benzene (10.0 g, 4.54 mL, 35.4 mmol, 1 eq), 2-fluorophenylboronic acid (5.44 g, 38.9 mmol, 1.1 eq), Cs₂CO₃ (23.0 g, 70.7 mmol, 2 eq), and Pd(dppf)Cl₂ (517 mg, 707 µmol, 0.02 eq) in THF/H₂O 5:1 (100 mL/20 mL) were reacted according to the general procedure (100 °C, 18 h).

The product was isolated by flash column chromatography on silica gel (hexanes) as colorless oil which crystallized as hard white solid by scratching (7.63 g, 86 %).

Rₛ = 0.47 (SiO₂, hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.67 (dd, J = 8.0, 1.2 Hz, 1H), 7.41–7.34 (m, 2H), 7.32–7.18 (m, 4H), 7.17–7.12 (ddd, J = 9.5, 8.3, 1.1 Hz, 1H) ppm.

¹³C NMR (100 MHz, CDCl₃) δ 160.7, 158.3, 137.1, 132.9, 131.6, 131.6, 131.5, 129.9, 129.8, 129.5, 128.9, 128.7, 127.2, 123.9, 123.8, 123.8, 115.8, 115.6 ppm.

¹⁹F NMR (282 MHz, CDCl₃) δ -113.76 – -114.84 (m, 1F) ppm.
HPLC (PBr column (anal.), 1.0 mL/min, 35 °C, MeOH/DCM 9:1) \( t_R = 4.36 \) min.

UV/vis (DCM/MeOH) \( \lambda_{max} \) 267 (sh), 226 nm.

\(^1\)H and \(^{13}\)C NMR spectra were consistent with those reported in literature.\(^1\)

(2'-Fluoro-[1,1'-biphenyl]2-yl)boronic acid (B2). A two-necked round-bottom flask equipped with a magnetic stirring bar and a rubber septum was charged with 2-bromo-2'-fluoro-1,1'-biphenyl (1.50 g, 6.97 mmol, 1 eq) and THF (10 mL) and the clear solution was cooled to -78 °C. n-BuLi (765 mg, 5.97 mL, 2.5 M in hexanes, 14.9 mmol, 2.5 equiv) was added dropwise via a syringe and the yellow solution stirred for 30 minutes at -78 °C. Trimethyl borate (3.10 g, 3.39 mL, 29.9 mmol, 5 equiv) was added in one portion via a syringe and the mixture allowed to reach room temperature over a period of 3 h. A 1 M aqueous solution of HCl (5 mL) was added to quench the reaction and stirring at room temperature was continued for further 30 minutes. Water (10 mL) and CH\(_2\)Cl\(_2\) (10 mL) were added, layers were separated and the aqueous phase extracted with CH\(_2\)Cl\(_2\) (3 x 20 mL). The combined organic phases were dried over Na\(_2\)SO\(_4\), filtered and the solvent evaporated to dryness. After short column chromatography over silica gel using a solvent gradient (hexanes/CH\(_2\)Cl\(_2\) 5:1 \( \rightarrow \) CH\(_2\)Cl\(_2\) \( \rightarrow \) CH\(_2\)Cl\(_2\)/MeOH 20:1) and precipitation with hexanes product B2 was obtained as white solid (722 mg, 56%).

\( R_f = 0.28 \) (SiO\(_2\), CH\(_2\)Cl\(_2\)/EtOAc 20:1).

\(^1\)H NMR (500 MHz, 30 °C, DMSO-\(d_6\)) \( \delta \) 7.73 (s, 2H, -B(OH)\(_2\)), 7.57 (dd, \( J = 7.4 \), 1.5 Hz, 1H), 7.41 (td, \( J = 7.6 \), 1.6 Hz, 1H), 7.36–7.32 (m, 3H), 7.27 (d, \( J = 7.5 \) Hz, 1H), 7.22–7.15 (m, 2H) ppm.

\(^{13}\)C NMR (125 MHz, proton and fluorine decoupled, 30 °C, DMSO-\(d_6\)) \( \delta \) 159.5, 139.1, 133.3, 131.7, 131.0, 129.78, 129.2, 129.0, 127.0, 124.4, 115.6 ppm (signal of C-B not observed).

\(^{19}\)F NMR (470 MHz, proton decoupled, 30 °C, DMSO-\(d_6\)) \( \delta \) -116.72 (s, 1F) ppm.

HPLC (PBr column (anal.), 1.0 mL/min, 35 °C, MeOH/DCM 9:1) \( t_R = 4.17 \) min.

UV/vis (DCM/MeOH) \( \lambda_{max} \) 275 (sh), 240, (219) nm.
1,3,5-Tris(2'-bromophenyl)benzene (B3). In a 100 mL round-bottom flask equipped with a magnetic stirring bar 2'-bromoacetophenone (2.00 g, 1.36 mL, 10.1 mmol, 1 eq) was dissolved in EtOH (15 mL) and the solution cooled to 0 °C in an ice bath. SiCl₄ (5.12 g, 3.45 mL, 30.1 mmol, 3 eq) was added quickly. After 2 min of stirring the ice bath was removed and the mixture stirred at room temperature overnight. The reaction was quenched with water (40 mL), the yellow precipitate collected by filtration and washed with water. After drying in vacuum 1,3,5-tris(2'-bromophenyl)benzene (B3) was obtained as yellow solid (1.78 g, 99 %).

Rᵣ = 0.49 (SiO₂, hexanes/CH₂Cl₂ 5:1).

¹H NMR (400 MHz, CDCl₃) δ 7.67 (dd, J = 8.0, 1.2 Hz, 3H), 7.49 (s, 3H), 7.45 (dd, J = 7.6, 1.7 Hz, 3H), 7.36 (td, J = 7.5, 1.3 Hz, 3H), 7.20 (td, J = 7.7, 1.8 Hz, 3H) ppm;

¹³C NMR (100 MHz, CDCl₃) δ 142.0, 140.4, 133.2, 131.5, 129.6, 128.9, 127.4, 122.7 ppm.

HPLC (PBr column (anal.), 1.0 mL/min, 35 °C, MeOH/CH₂Cl₂ 6:4) tᵣ = 6.29 min.

UV/vis (MeOH/CH₂Cl₂) λₘₐₓ 241 nm.

The spectral data were consistent with those reported in literature.²,³

2',2''-Dibromo-1,1':4',1''-terphenyl (B4). 1,4-Diodobenzene (1.50 g, 4.55 mmol, 1 eq), 2-Bromophenylboronic acid (2.01 g, 10.0 mmol, 2.2 eq), K₂CO₃ (2.51 g, 18.2 mmol, 4 eq), and Pd(PPh₃)₄ (263 mg, 227 μmol, 0.05 eq) in toluene/H₂O 2:1 (20 mL/10 mL) were reacted according to the general procedure (reflux, 18 h). After filtration through silica gel the resulting white solid was taken up in a small amount of DCM (1 mL) and hexanes (5–10 mL) was added. The mixture was stored in a refrigerator overnight and the resulting white precipitate collected by suction filtration. After drying in vacuo 2',2''-dibromo-1,1':4',1''-terphenyl (B4) was afforded as white solid (1.44 mg, 82 %).

Rᵣ = 0.28 (SiO₂, hexanes).

¹H NMR (400 MHz, CDCl₃) δ 7.68 (dd, J = 8.0, 0.8 Hz, 2H), 7.47 (s, 4H), 7.41–7.34 (m, 4H), 7.24–7.18 (ddd, J = 8.0, 6.9, 2.3 Hz, 2H) ppm.
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 142.2, 140.2, 133.2, 131.4, 129.0, 128.8, 127.4, 122.6 ppm (one signal coincident or not observed).

HPLC (PBr column (anal.), 1.0 mL/min, 35 °C, MeOH/CH$_2$Cl$_2$ 7:3) $t_R = 5.67$ min.

UV/vis (MeOH/CH$_2$Cl$_2$) $\lambda_{max}$ 254, 226 nm.

$^1$H and $^{13}$C NMR spectra in CDCl$_3$ matched previously published data.$^4$

The synthesis of 2',5'-dibromo-1,1':4',1''-terphenyl and (2,2'-difluoro-[1,1'-biphenyl]-3-yl)boronic acid has already been described previously.$^5$
2.2 Synthesis of the Oligophenylenes

1,3,5-Tris[2''-(2'''-fluoro-1'',1''''-biphenyl)]benzene (P1).

1,3,5-Tris(2''-bromophenyl)benzene (150 mg, 276 µmol, 1 eq), 2-fluorophenyloboric acid (232 mg, 1.66 mmol, 6 eq), K3PO4 (352 mg, 1.66 mmol, 6 eq), and Pd(dppf)Cl2 (10.1 mg, 13.8 µmol, 0.05 eq) in toluene/H2O 10:1 (10 mL/1 mL) were reacted according to the general procedure (100 °C, 24 h). The product was isolated by flash column chromatography on silica gel (solvent gradient hexanes/DCM 95:5 → 8:2) as light yellow solid (107 mg, 68 %).

Rf = 0.19 (SiO2, hexanes/CH2Cl2 5:1).

1H NMR (400 MHz, CD2Cl2) δ 7.39–7.27 (m, 12H), 7.07 (td, J = 7.5, 1.2 Hz, 3H), 7.02 (ddd, J = 9.6, 8.3, 1.2 Hz, 3H), 6.91 (td, J = 7.6, 1.8 Hz, 3H), 6.82 (dt, J = 7.1, 1.3 Hz, 3H), 6.76 (s, 3H) ppm.

13C NMR (100 MHz, CD2Cl2) δ 161.3, 158.8, 141.6, 140.7, 134.6, 132.9, 132.9, 131.2, 131.2, 130.4, 129.6, 129.5, 129.2, 129.2, 129.1, 128.4, 127.4, 124.2, 124.1, 115.9, 115.7 ppm.

19F NMR (377 MHz, CD2Cl2) δ -115.55 – -115.61 ppm (m, 3F).

HPLC (PBr column (anal.), 1.0 mL/min, 35 °C, MeOH/CH2Cl2 6:4) tR = 5.38 min.

UV/vis (MeOH/CH2Cl2) λmax 230, 255 (sh) nm.

HR MS (APPI) calcd. for C42H27F3 (M+•, 100) m/z 588.2070, found 588.2063.

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2-Fluoro-1,1':2',1''':2'',1''''-quaterphenyl (P2). 2-Bromo-2''-fluoro-1,1''-biphenyl (150 mg, 597 µmol, 1 eq), 2-biphenyloboric acid (237 mg, 1.19 mmol, 2 eq), K3PO4 (254 mg, 1.19 mmol, 2 eq), and Pd(dppf)Cl2 (21.9 mg, 29.9 µmol, 0.05 eq) in toluene/H2O 5:1 (12 mL/2.4 mL) were reacted according to the general procedure (100 °C, 18 h). Final flash column chromatography on silica gel (solvent gradient hexanes/CH2Cl2 100:0 → 9:1) afforded the product as white solid (123 mg, 63 %).

Rf = 0.43 (SiO2, hexanes/CH2Cl2 5:1).
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.42–7.28 (m, 6H), 7.20–7.04 (m, 6H), 6.81–6.72 (m, 4H), 6.51 (td, \(J = 7.7, 1.8\) Hz, 1H) ppm.

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 160.7, 158.3, 141.0, 140.9, 140.7, 139.5, 135.0, 132.0, 132.0, 131.6, 131.6, 130.7, 130.7, 129.9, 129.3, 128.6, 128.4, 128.3, 128.2, 127.6, 127.5, 127.5, 127.0, 126.8, 126.2, 123.2, 123.2, 115.2, 115.0 ppm.

\(^{19}\)F NMR (470 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) -114.94 (br s) ppm.

HPLC (PBr column, 1.0 mL/min, 35 °C, MeOH/CH\(_2\)Cl\(_2\) 6:4) \(t_R = 4.36\) min.

HR MS (APPI) calcd. for C\(_{24}\)H\(_{17}\)F (M\(^+\), 100) \(m/z\) 324.1309, found 324.1314.

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2,2''''-Difluoro-2'',5''-diphenyl-1,1':2',1'':4'',1''':2''',1''''-quinquephenyl (P3). 2',5'-Dibromo-1,1':4'',1'''-terphenyl (100 mg, 258 \(\mu\)mol, 1 eq), (2'-Fluoro-[1,1'-biphenyl]2-yl)boronic acid (223 mg, 1.03 mmol, 4 eq), K\(_3\)PO\(_4\) (219 mg, 1.03 mmol, 4 eq), and Pd(dppf)Cl\(_2\) (9.40 mg, 12.9 \(\mu\)mol, 0.05 eq) in toluene/H\(_2\)O 5:1 (10 mL/2 mL) were reacted according to the general procedure (100 °C, 18 h). Final flash column chromatography on silica gel (solvent gradient hexanes/CH\(_2\)Cl\(_2\) 9:1 \(\rightarrow\) 8:2) afforded the product as white solid (140 mg, 95 %).

\(R_f = 0.25\) (SiO\(_2\), hexanes/CH\(_2\)Cl\(_2\) 5:1).

\(^1\)H NMR (500 MHz, CD\(_2\)Cl\(_2\), fluorine decoupled) \(\delta\) 7.43 (vis d, \(J = 7.3\) Hz, 1H), 7.38–7.32 (m, 2H), 7.22–7.13 (m, 5H), 7.07 (vis t, \(J = 7.5\) Hz, 3H), 6.91 (vis t, \(J = 7.6\) Hz, 1H), 6.83 (vis d, \(J = 8.3\) Hz, 1H), 6.76–6.69 (m, 3H), 6.57 (vis d, \(J = 7.6\) Hz, 1H) ppm (all signals very broad due to different possible conformers).

\(^{13}\)C NMR (125 MHz, CD\(_2\)Cl\(_2\), proton and fluorine decoupled) \(\delta\) 159.8, 141.0, 140.9, 139.7, 139.0, 135.5, 133.9, 132.4, 132.0, 131.1, 129.6, 129.0, 128.8, 128.1, 128.0, 127.5, 126.7, 123.9, 115.7 ppm.

\(^{19}\)F NMR (470 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) -114.9 (br s), -115.3 (br s) ppm (two different conformers).

HPLC (5PYE column, 1.0 mL/min, 35 °C, MeOH/CH\(_2\)Cl\(_2\) 6:4) \(t_R = 4.98\) min.

UV/vis (CH\(_2\)Cl\(_2\)/MeOH) \(\lambda_{\text{max}}\) 238 nm.

HR MS (APPI) calcd. for C\(_{42}\)H\(_{28}\)F\(_2\) (M\(^+\), 100) \(m/z\) 570.2154, found 570.2162.
2',2''-Bis(2,2'-difluoro-[1,1'-biphenyl]-3-yl)-1,1':4',1''-terphenyl (P4). 2,2'-Dibromo-1,1':4',1''-terphenyl (100 mg, 258 μmol, 1 eq), 2,2'-difluoro-[1,1'-biphenyl]-3-yl)boronic acid (241 mg, 1.03 mmol, 4 eq), K$_3$PO$_4$ (219 mg, 1.03 mmol, 4 eq), and Pd(dppf)Cl$_2$ (9.43 mg, 12.9 μmol, 0.05 eq) in toluene/H$_2$O 5:1 (10 mL/2 mL) were reacted according to the general procedure (100 °C, 18 h). Final flash column chromatography on silica gel (solvent gradient hexanes/DCM 9:1 → 8:2) afforded the product as white solid (137 mg, 88 %).

$R_f = 0.18$ (SiO$_2$, hexanes/DCM 5:1).

$^1$H NMR (500 MHz, CD$_2$Cl$_2$, fluorine decoupled) δ 7.49–7.41 (m, 8H), 7.35 (ddd, $J = 8.3, 6.9, 2.3$ Hz, 2H), 7.24 (dd, $J = 7.6, 1.8$ Hz, 2H), 7.20–7.14 (m, 4H), 7.13–7.10 (m, 4H), 7.04 (s, 4H), 7.01 (t, $J = 7.6$ Hz, 2H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 159.8 (d, $^{1}$$J_{C-F} = 248.9$ Hz), 156.6 (d, $^{1}$$J_{C-F} = 249.4$ Hz), 141.5, 139.6, 134.4, 132.1, 132.0, 131.7, 131.0, 130.5, 130.1, 129.7, 129.6, 129.5, 128.8, 128.2, 127.1, 124.0, 123.9, 123.8, 123.7, 123.6, 123.5, 115.7 (d, $^{2}$$J_{C-F} = 22.3$ Hz) ppm.

$^{19}$F NMR (470 MHz, CD$_2$Cl$_2$, proton decoupled) δ -115.26 (d, $J = 16.1$ Hz; 2F, F$_{out}$), -117.17 (d, $J = 16.0$ Hz, 2F,F$_{in}$) ppm.

HPLC (5PYE column (anal.), 1.0 mL/min, 35 °C, MeOH/DCM 1:1) $t_R = 4.47$ min.

UV/vis (DCM/MeOH) $\lambda_{max}$ 270 (sh), 235 nm.

MALDI MS (DCTB, AgOTf) $m/z$ 714 and 716 ([M + Ag]$^+$, 100).

HR MS (APPI) calcd. for C$_{42}$H$_{26}$F$_4$ (M$^+$, 100) $m/z$ 606.1965, found 606.1976.
2.3 Synthesis of the PAHs

General Procedure: Al₂O₃-Mediated HF Elimination in Microwave

Typically, a Schlenk ampule was charged with γ-Al₂O₃ (5–6 g) which was activated by annealing at 250 °C for 30 min in air. Afterwards, it was activated by annealing at 590 °C under vacuum (3 x 10⁻² mbar) for 1 h. During cooling to room temperature a heated and nitrogen flushed microwave vial (2–5 mL) was filled with the respective fluoroarene and o-DCB (4 mL). Under N₂ atmosphere previously activated γ-Al₂O₃ was added and the vial closed. The condensation was carried out at 200–250 °C for the indicated time in the microwave. Al₂O₃ was extracted with hot toluene. The crude product mixture was analyzed by HPLC and pure product was obtained after preparative HPLC.

Condensation of P1

1,3,5-Tris[2''-(2''-fluoro-1',1''-biphenyl)]benzene (P1) was reacted on activated Al₂O₃ (1.5–2 g) in o-DCB (4 mL) according to the general procedure (200 °C, 5 h). The reaction outcome was monitored by HPLC (PBr column (anal.), 1.0 mL/min, 35 °C, MeOH/DCM 6:4) which showed eight product peaks. All products formed were isolated by preparative HPLC (PBr column (semiprep), 1.0 mL/min, 40 °C, MeOH/DCM 6:4).

![HPLC chromatogram of the reaction mixture (PBr (semiprep), 5.0 ml/min, 40 °C, MeOH/DCM 6:4).](image)

**Figure S1**: HPLC chromatogram of the reaction mixture (PBr (semiprep), 5.0 ml/min, 40 °C, MeOH/DCM 6:4).
F1 turned out to be residual starting material according to NMR and HPLC/UV-vis studies. (1H NMR (400 MHz, CDCl₃) δ 7.33–7.20 (m, 12H), 7.01–6.96 (m, 6H), 6.84–6.78 (m, 6H), 6.73 (s, 3H) ppm; 13C NMR (100 MHz, CDCl₃) δ 159.7 (d, 1J_C-F = 247.0 Hz), 141.2, 140.25, 134.1, 132.5, 132.5, 130.8, 130.8, 130.1, 129.3, 129.1, 128.8, 128.6, 128.5, 127.8, 126.9, 123.6, 123.5, 115.5 (d, 2J_C-F = 22.5 Hz) ppm; 19F NMR (377 MHz, CDCl₃) δ -114.98 – -115.04 (m, 3F) ppm. HPLC (PBr column (anal.), 1.0 mL/min, 35 °C, MeOH/DCM 6:4) tᵣ = 5.38 min. UV/vis (DCM/MeOH) λ_max 230, 255 (sh) nm.)

1,3-Bis(2'-fluoro-[1,1'-biphenyl]-2-yl)triphenylene (F2).

1H NMR (400 MHz, C₂D₂Cl₄) δ 8.35–8.31 (m, 2H), 8.06 (d, J = 1.9 Hz, 1H), 7.86 (d, J = 7.8 Hz, 1H), 7.65 (d, J = 8.1, 1H), 7.48–7.27 (m, 12H), 7.18–7.12 (m, 2H), 7.06–7.00 (m, 2H), 6.91–6.86 (m, 1H), 6.80–6.74 (m, 1H), 6.53–6.47 (m, 3H) ppm.

19F NMR (377 MHz, C₂D₂Cl₄) δ -114.64 (s, 1F), -114.77 (s, 1F) ppm.

HPLC (PBr column (anal.), 1.0 mL/min, 35 °C, MeOH/DCM 6:4) tᵣ = 7.45 min.

UV/vis (DCM/MeOH) λ_max 314 (sh), 268, 227 nm.

LDI MS m/z 568 (M⁺, 100).

Product of 2 HF eliminations (F3).

1H NMR (400 MHz, C₂D₂Cl₄) δ 8.44–8.42 (m, 1H), 8.35–8.30 (m, 3H), 7.58–7.51 (m, 3H), 7.45–7.28 (m, 6H), 7.25–7.21 (m, 2H), 7.13–7.05 (m, 2H), 7.02 (dd, J = 7.26, 1.09 Hz, 1H), 6.98 (td, J = 7.6, 1.8 Hz, 1H), 6.93 (td, J = 7.5, 1.5 Hz, 1H), 6.82–6.78 (m, 1H), 6.70–6.66 (m, 1H), 6.62 (d, J = 1.7 Hz, 1H), 6.50 (dd, J = 7.6, 1.3 Hz, 1H), 6.00 (dd, J = 7.7, 1.2 Hz, 1H) ppm.

19F NMR (377 MHz, C₂D₂Cl₄) δ -114.90 – -114.96 (m, 1F) ppm.

HPLC (PBr column (anal.), 1.0 mL/min, 35 °C, MeOH/DCM 4:6) tᵣ = 7.94 min.

UV/vis (DCM/MeOH) λ_max 277, 227 nm.
**LDI MS** $m/z$ 548 ($M^+$, 100).

**Product of 1 HF elimination (F4).**

$^1$H NMR (400 MHz, C$_2$D$_2$Cl$_4$) $\delta$ 8.59 (d, $J = 8.1$ Hz, 2H), 8.52–8.44 (m, 2H), 8.34 (s, 2H), 7.63–7.54 (m, 4H), 7.23 (vis t, $J = 7.6$ Hz, 2H), 7.11 (d, $J = 7.6$ Hz, 2H), 7.06–6.98 (m, 4H), 6.72–6.65 (m, 4H), 6.52 (m, 2H), 6.41 (m, 2H) ppm (very weak and poor resolved signals).

$^{19}$F NMR (377 MHz, C$_2$D$_2$Cl$_4$) $\delta$ -114.64 ppm (very weak and poor resolved signal).

**HPLC** (PBr column (anal.), 1.0 mL/min, 35 °C, MeOH/DCM 4:6) $t_R = 9.98$ min.

**UV/vis** (DCM/MeOH) $\lambda_{max}$ 267 nm.

**LDI MS** $m/z$ 568 ($M^+$, 100).

**F5** seemed to contain a mixture of twofold HF elimination products (see part Spectroscopic Analysis and Characterization). **F6–F8** were fully condensed products (three HF eliminations). **F6** and **F7** were obtained as mixture by separation with PBr column. Thus, this mixture was again separated with a Buckyprep column (semiprep) to yield pure **F6** and **F7** (see Figure S69).

Since the reaction was obviously not finished (**F2–F5** were products of one and twofold HF elimination, respectively), a second reaction was carried out with improved reaction conditions (210 °C, 18 h). The reaction outcome was again analyzed by HPLC/UV-vis studies (PBr column (anal.), 1.0 mL/min, 35 °C, MeOH/DCM 6:4), which indicated the formation of only three fully condensed products (threefold HF elimination). The overall yield after extraction was 75 %. The yield of each product was determined by NMR spectrum of the mixture. All products formed were isolated by preparative HPLC and characterized by NMR, HPLC/UV-vis and MS studies.
Separation of the reaction mixture with a PBr column (semiprep) yielded a mixture of $N_1$ and $N_2$ as first fraction and pure $N_3$ as second fraction (see Figure S87–S89). Thus, fraction 1 ($N_1 + N_2$) was afterwards separated with a Buckyprep column (semiprep) to yield pure $N_1$ and $N_2$, respectively.

In a second attempt the reaction mixture was first separated with a Buckyprep column (semiprep) to yield pure $N_2$ as first fraction and the mixture of $N_1$ and $N_3$ as second fraction (see Figure S90–S92). $N_1$ and $N_3$ were finally isolated by separation with PBr column (semiprep).
Hexabenzotriphenylene (N1). Yield: 9 % (from NMR).

$^1$H NMR (400 MHz, C$_2$D$_2$Cl$_4$) $\delta$ 8.47 (d, $J = 7.6$ Hz, 1H), 8.07 (d, $J = 7.9$ Hz, 1H), 7.49 (ddd, $J = 8.1, 6.9, 0.9$ Hz, 1H), 7.16 (ddd, $J = 8.2, 6.9, 1.0$ Hz, 1H) ppm.

HPLC (PBr column (anal.), 1.0 mL/min, 35 °C, MeOH/DCM 4:6) $t_R = 14.48$ min.

UV/vis (DCM/MeOH) $\lambda_{max}$ 467 (sh), 439 (sh), 381 (sh), 361, 298, 235 nm.

LDI MS $m/z$ 528 (M$^+$, 100).

HR MS (APPI) calcd. for C$_{42}$H$_{24}$ (M$^+$, 100) $m/z$ 528.1873, found 528.1855.

Spectroscopic data were consistent with those previously reported. 6-8

Naphtho[1,2,3,4-def]phenanthro[9,10-a]tetraphenylene (N2). Yield: 35 % (from NMR).

$^1$H NMR (400 MHz, C$_2$D$_2$Cl$_4$) $\delta$ 9.55 (s, 1H), 8.73 (d, $J = 8.1, 2$H), 8.48–8.42 (m, 3H), 8.37 (d, $J = 7.5$ Hz, 1H), 7.68–7.46 (m, 9H), 7.38–7.29 (m, 3H), 7.16 (td, $J = 7.5, 1.3$ Hz, 1H), 7.11–7.07 (m, 2H), 6.87 (td, $J = 7.5, 1.4$ Hz, 1H), 6.78 (dd, $J = 7.6, 1.2$ Hz, 1H), 6.05 (dd, $J = 7.7, 1.2$ Hz, 1H) ppm.

HPLC (PBr column (anal.), 1.0 mL/min, 35 °C, MeOH/DCM 4:6) $t_R$ 15.38 min.

UV/vis (DCM/MeOH) $\lambda_{max}$ 338 (sh), 310, 274, 255 nm.

LDI MS $m/z$ 528 (M$^+$, 100).

HR MS (APPI) calcd. for C$_{42}$H$_{24}$ (M$^{100}$, 100) $m/z$ 528.1873, found 528.1873.
Naphtho[1,2,3,4-\textit{def}]phenanthro[9,10-\textit{b}]tetraphenylen (N3). Yield: 31 % (from NMR).

$^1$H NMR (400 MHz, C$_2$D$_2$Cl$_4$) δ 8.60–8.58 (m, 3H), 8.51–8.38 (m, 6H), 8.24 (d, $J = 8.3$ Hz, 1H), 8.01 (s, 1H), 7.63–7.54 (m, 3H), 7.49–7.45 (m, 1H), 7.43–7.34 (m, 4H), 7.27 (td, $J = 7.5$, 1.3 Hz, 1H), 7.22–7.07 (m, 5H), 6.86–6.84 (d, $J = 7.5$ Hz, 1H), 6.71–6.69 (dd, $J = 7.9$, 1.2 Hz, 1H) ppm.

HPLC (PBr column (anal.), 1.0 mL/min, 35 ºC, MeOH/DCM 4:6) $t_R = 16.70$ min.

UV/vis (DCM/MeOH) $\lambda_{max}$ 409 (sh), 363 (sh), 317, 291, 261 (sh), 238 nm.

LDI MS $m/z$ 528 ($M^+$, 100).

HR MS (APPI) calcd. for C$_{42}$H$_{24}$ ($M^+$, 100) $m/z$ 528.1873, found 528.1870.
Condensation of P2

2-Fluoro-1,1':2',1''-2',1'''-quaterphenyl (P2) (10.0 mg, 30.8 µmol) was reacted on activated Al₂O₃ (1.5–2 g) in o-DCB (4 mL) according to the general procedure (250 °C, 4 h). The reaction outcome was monitored by HPLC (PBr column (anal.), 1.0 mL/min, 35 °C, MeOH/DCM 9:1) which indicated the formation of three products. All products formed were isolated by preparative HPLC (PBr column (semiprep), 5.0 mL/min, 40 °C, MeOH/DCM 1:1).

Figure S3: HPLC chromatogram of the reaction mixture (250 °C, 4 h) (PBr (anal.), 1.0 ml/min, 35°C, MeOH/DCM 9:1).

Tetraphenylene (N4). Yield: 3 % (from NMR).

¹H NMR (400 MHz, CD₂Cl₂) δ 7.34–7.30 (m, 8H), 7.20–7.16 (m, 8H) ppm.

¹³C NMR (100 MHz, CD₂Cl₂) δ 141.9, 129.5, 127.8 ppm.

HPLC (PBr column (anal.), 1.0 ml/min, 35°C, MeOH/DCM 8:2) tᵣ = 5.49 min.

UV/vis (DCM/MeOH) λ_max 275 (sh), 227, (216) nm.

HR MS (APPI) calcd. for C₂₄H₁₆ (M⁺, 100) m/z 304.1247, found 304.1243.
The spectral data were consistent with those reported.\(^9\)

1-Phenyltriphenylene (**N5**). White solid. Yield: 4.1 mg (44\%, isolated).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.65–8.57 (m, 3H), 8.54–8.51 (m, 1H), 7.72–7.69 (m, 1H), 7.67–7.61 (m, 3H), 7.50 (dd, \(J = 7.3, 1.3\) Hz, 1H), 7.46–7.34 (m, 6H), 7.03 (ddd, \(J = 8.4, 7.0, 1.4\) Hz, 1H) ppm.

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 145.4, 140.7, 131.6, 131.4, 131.0, 130.3, 130.1, 130.0, 129.7, 129.1, 129.0, 128.7, 127.3, 127.3, 126.9, 126.6, 126.3, 125.0, 123.6, 123.13, 123.1, 122.3 ppm.

HPLC (PBr column (anal.), 1.0 ml/min, 35°C, MeOH/DCM 1:1) \(t_R = 5.62\) min.

UV/vis (DCM/MeOH) \(\lambda_{\text{max}} 291\) (sh), 262 nm.

LDI MS \(m/z 304\) (\(M^+\), 100).

The spectral data were consistent with those reported.\(^{10}\)

2-Phenyltriphenylene (**N6**). White solid. Yield: 3.5 mg (38\%, isolated).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.84 (d, \(J = 1.9\) Hz, 1H), 8.76–8.64 (m, 5H), 7.89 (dd, \(J = 8.5, 1.9\) Hz, 1H), 7.81–7.78 (m, 2H), 7.69–7.64 (m, 4H), 7.55–7.50 (m, 2H), 7.43–7.39 (m, 1H) ppm.

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 141.2, 139.9, 130.1, 130.0, 129.8, 129.8, 129.6, 128.9, 128.9, 127.5, 127.4, 127.4, 127.3, 127.3, 127.2, 126.4, 123.9, 123.4, 123.3, 123.3, 121.8 ppm.

HPLC (PBr column (anal.), 1.0 ml/min, 35°C, MeOH/DCM 1:1) \(t_R = 7.22\) min.

UV/vis (DCM/MeOH) \(\lambda_{\text{max}} 305\) (sh), 288 (sh), 268 nm.

LDI MS \(m/z 304\) (\(M^+\), 100).

The spectral data were consistent with those reported.\(^{11}\)
Condensation of P3

2,2”,5”-Difluoro-2”,5”-diphenyl-1”,1’:2”,1’’:4”,1’’’:2’’,1’’’’-quinquephenyl (P3) (20.0 mg, 35.1 µmol) was reacted on activated Al₂O₃ (1.5–2 g) in o-DCB (4 mL) according to the general procedure (200 °C, 12 h). The reaction outcome was monitored by HPLC (PBr column (anal.), 1.0 mL/min, 35 °C, MeOH/DCM 6:4) which indicated the formation of five products. All products formed were isolated by preparative HPLC (PBr column (semiprep), 5.0 mL/min, 40 °C, MeOH/DCM 6:4).

![HPLC chromatogram of the reaction mixture](image)

**Figure S4:** HPLC chromatogram of the reaction mixture (200 °C, 12 h) (PBr (semiprep), 5.0 mL/min, 40°C, MeOH/DCM 6:4). F1: t_R = 6.69 min, F2: t_R = 7.40 min, F3: t_R = 9.58 min, F4 + F5: t_R = 10.21 min, F6: t_R = 11.28 min.

2-(2’-Fluoro-[1,1’-biphenyl]-2-yl)-1,4-diphenyltriphenylene (F1).

**1H NMR** (400 MHz, CD₂Cl₂) δ 8.32–8.27 (m, 2H), 7.62 (d, J = 8.1 Hz, 1H), 7.57 (s, 1H), 7.52–7.49 (m, 1H), 7.38–7.16 (m, 11H), 7.08–7.01 (m, 5H), 6.89–6.82 (m, 3H), 6.62–6.57 (m, 2H), 6.38 (vis t, 1H) ppm (all signals very broad due to different conformers).

**19F NMR** (377 MHz, CD₂Cl₂) δ -114.50 (br s, 1F) ppm.
HPLC (PBr column (anal.), 1.0 ml/min, 35°C, MeOH/DCM 6:4) $t_R = 6.95$ min.

UV/vis (DCM/MeOH) $\lambda_{max}$ 287 nm.

LDI MS $m/z$ 550 (M+, 100).

HR MS (APPI) calcd. for $C_{42}H_{27}F$ (M++, 100) $m/z$ 550.2097, found 550.2095.

Since the reaction was not finished (F1 is product of one HF elimination reaction), a second reaction was carried out with improved reaction conditions (210 °C, 18 h). The reaction outcome was again analyzed by HPLC/UV-vis studies (PBr column (anal.), 1.0 mL/min, 35 °C, MeOH/DCM 6:4) and LDI MS, which indicated the formation of only fully condensed products (twofold HF elimination). All products formed were isolated by preparative HPLC (PBr column (semiprep), 5.0 mL/min, 40 °C, MeOH/DCM 6:4) and characterized by NMR, HPLC/UV-vis and MS studies.

Figure S5: HPLC chromatogram of the reaction mixture (210 °C, 18 h) (PBr (semiprep), 5.0 ml/min, 40°C, MeOH/DCM 6:4). N7: $t_R = 6.37$ min, N8: $t_R = 6.71$ min, N9: $t_R = 7.47$ min, N10: $t_R = 9.63$ min, N11 + N12: $t_R = 10.25$ min, N13: $t_R = 11.32$ min.
trans-Tribenzo[3,4:5,6:7,8]cycloocta[1,2-b]tetraphenylen (N7). 0.5 mg (2.7 %).

$^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ 7.44–7.39 (m, 4H), 7.32–7.22 (m, 12H), 7.18 (dd, $J = 7.5, 1.4$ Hz, 4H), 7.06 (dd, $J = 7.5, 1.3$ Hz, 4H), 7.01 (s, 2H) ppm.

HPLC (PBr column (anal.), 1.0 ml/min, 35°C, MeOH/DCM 6:4) $t_R = 6.62$ min.

UV/vis (DCM/MeOH) $\lambda_{\text{max}}$ 233 nm.

LDI MS $m/z$ 530 (M$^+$, 100).

HR MS (APPI) calcd. for C$_{42}$H$_{26}$ (M$^+$, 100) $m/z$ 530.2029, found 530.2021.

cis-Tribenzo[3,4:5,6:7,8]cycloocta[1,2-b]tetraphenylen (N8). 0.8 mg (4.3 %).

$^1$H NMR (400 MHz, C$_2$D$_2$Cl$_4$) $\delta$ 7.32–7.16 (m, 12H), 7.05–7.01 (m, 8H), 6.90–6.86 (m, 4H), 6.85 (s, 2H) ppm.

HPLC (PBr (anal.), 1.0 ml/min, 35°C, MeOH/DCM 6:4) $t_R = 6.91$ min.

UV/vis (DCM/MeOH) $\lambda_{\text{max}}$ 233 nm.

HR MS (APPI) calcd. for C$_{42}$H$_{26}$ (M$^{11}$, 100) $m/z$ 530.2029, found 530.2030.

5-Phenylphenanthro[9,10-a]tetraphenylene (N9). 3.0 mg (16 %).

$^1$H NMR (400 MHz, C$_2$D$_2$Cl$_4$) $\delta$ 8.35–8.31 (m, 2H), 7.65 (dd, $J = 8.5, 1.2$ Hz, 1H), 7.46–7.42 (m, 3H), 7.38–7.17 (m, 16H), 7.08 (ddd, $J = 8.4, 7.0, 1.3$ Hz, 1H), 7.03 (ddd, $J = 8.4, 7.0, 1.3$ Hz, 1H), 6.98 (ddd, $J = 7.7, 6.9, 1.9$ Hz, 1H), 6.67 (dd, $J = 7.5, 1.1$ Hz, 1H) ppm.

$^{13}$C NMR (100 MHz, C$_2$D$_2$Cl$_4$) $\delta$ 144.4, 143.1, 142.5, 142.2, 141.9, 141.6, 141.5, 138.6, 136.7, 132.3, 131.6, 131.2, 131.0, 130.8, 130.3, 130.2, 130.0,
129.8, 129.5, 129.4, 128.8, 128.2, 128.0, 127.9, 127.7, 127.5, 127.5, 126.9, 126.7, 126.0, 125.8, 123.6, 123.5 ppm.

**HPLC** (PBr column (anal.), 1.0 ml/min, 35°C, MeOH/DCM 6:4) \( t_R = 7.62 \) min.

**UV/vis** (DCM/MeOH) \( \lambda_{\text{max}} \) 284, (227) nm.

**LDI MS** \( m/z \) 530 (M\(^+\), 100).

**HR MS (APPI)** calcd. for C\(_{42}\)H\(_{26}\) (M\(^+\), 100) \( m/z \) 530.2035, found 530.2031.

![](image)

6-Phenylphenanthro[9,10-a]tetraphylene (N10).

1.9 mg (10 %).

\(^1\text{H NMR}\) (400 MHz, C\(_2\)D\(_2\)Cl\(_4\)) \( \delta \) 8.58–8.54 (d, \( J = 5.6 \) Hz, 2H), 8.52–8.48 (m, 1H), 8.43 (d, \( J = 7.8 \) Hz, 1H), 7.60–7.56 (m, 2H), 7.47–7.43 (m, 2H), 7.40–7.21 (m, 6H), 7.19–6.96 (m, 9H), 6.74 (td, \( J = 7.5, 1.4 \) Hz, 1H), 6.69 (d, \( J = 7.5 \) Hz, 1H), 6.54 (dd, \( J = 7.7, 1.2 \) Hz, 1H) ppm.

**HPLC** (PBr column (anal.), 1.0 ml/min, 35°C, MeOH/DCM 6:4) \( t_R = 9.96 \) min.

**UV/vis** (DCM/MeOH) \( \lambda_{\text{max}} \) 257, (228) nm.

**LDI MS** \( m/z \) 530 (M\(^+\), 100).

**HR MS (APPI)** calcd. for C\(_{42}\)H\(_{26}\) (M\(^+\), 100) \( m/z \) 530.2035, found 530.2023.

The next product peak (orange, **N11 + N12**) contained two products according to NMR studies. Since it was not possible to separate them with PBr column, a Buckyprep column (semiprep) was used for separation afterwards to obtain pure fractions of **N11** and **N12** (see respective chromatogram below, Figure S6).
**Figure S6:** HPLC chromatogram of mixture N11 + N12 (Buckyprep (anal.), 1.0 ml/min, 35°C, MeOH/DCM 7:3).

9,18-Diphenylphenanthro[9,10-b]triphenylene (N11). 3.6 mg (19%).

**HPLC** (Buckyprep (anal.), 1.0 mL/min, 35°C, MeOH/DCM 7:3) \( t_R = 10.91 \) min.

**UV/vis** (DCM/MeOH) \( \lambda_{max} \) 322, 227, 237 nm.

**LDI MS** m/z 530 (M⁺, 100).

Spectroscopic data were consistent with those reported previously.\(^\text{12,13}\)
17,18-Diphenyl dibenzof[4,5]picene (N12). 1.0 mg (5.4 %).

$^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ 8.56 (dd, $J = 8.2$, 1.4 Hz, 2H), 8.50 (dd, $J = 8.2$, 1.2 Hz, 2H), 8.12 (dd, $J = 8.3$, 1.2 Hz, 2H), 7.52–7.46 (m, 4H), 7.37 (dd, $J = 8.5$, 1.1 Hz, 2H), 7.24–7.17 (m, 6H), 7.14–7.08 (m, 4H), 7.02 (ddd, $J = 8.4$, 7.0, 1.4 Hz, 2H), 6.95–6.93 (m, 1H) ppm.

$^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) $\delta$ 142.9, 138.7, 132.4, 132.4, 132.3, 132.0, 131.7, 130.4, 130.2, 129.6, 129.4, 129.1, 128.6, 128.3, 127.3, 126.7, 126.7, 126.5, 125.8, 123.7, 123.6 ppm.

HPLC (Buckyprep (anal.), 1.0 ml/min, 35°C, MeOH/DCM 6:4) $t_R = 12.29$ min.

UV/vis (DCM/MeOH) $\lambda_{max}$ 369, 320, 292, 236 nm.

LDI MS $m/z$ 530 ($M^+$, 100).

Spectroscopic data were consistent with those reported previously.

9-Phenylphenanthro[9,10-b]tetraphenylene (N13). 2.6 mg (14 %).

$^1$H NMR (400 MHz, C$_2$D$_2$Cl$_4$) $\delta$ 8.57–8.55 (m, 1H), 8.49–8.47 (m, 1H), 8.43–8.39 (m, 2H), 7.59–7.56 (m, 2H), 7.50 (d, $J = 7.4$ Hz, 1H), 7.40–7.22 (m, 7H), 7.17–7.01 (m, 6H), 6.95–6.83 (m, 4H), 6.67 (t, $J = 7.5$ Hz, 1H), 6.29 (d, $J = 7.7$ Hz, 1H) ppm.

HPLC (PBr (anal.), 1.0 ml/min, 35°C, MeOH/DCM 6:4) $t_R = 11.67$ min.

UV/vis (DCM/MeOH) $\lambda_{max}$ 271 nm.

LDI MS $m/z$ 530 ($M^+$, 100).

HR MS (APPI) calcd. for C$_{42}$H$_{26}$ ($M^+$, 100) $m/z$ 530.2035, found 530.2032.
Condensation of P4

Oligophenylen P4 (10.0 mg, 16.5 µmol) was reacted on activated Al₂O₃ (1.5–2 g), in o-DCB (4 mL) according to the general procedure (200 °C, 15 h). The reaction outcome was monitored by HPLC (PBr column (anal.), 1.0 mL/min, 35 °C, MeOH/DCM 4:6) which showed a mixture of several products. The main product N14 and desired nanostructure N15 were isolated by preparative HPLC (PBr column (semiprep), 1.0 mL/min, 40 °C, DCM/MeOH 6:4).

Figure S7: HPLC chromatogram of the reaction mixture (200 °C, 15 h) (PBr (anal.), 1.0 ml/min, 35 °C, DCM/MeOH 6:4).

Benzo[4,10]anthra[3,2,1,9-vwxa]naphtho[1,2,3,4-def]tetraphenylen (N14). Light yellow solid. Yield: 1.5 mg (17 %, isolated).

1H NMR (400 MHz, CD₂Cl₂) δ 9.37 (s, 1H), 8.62–8.52 (m, 6H), 8.34 (dd, J = 8.4, 1.3 Hz, 1H), 8.29–8.26 (m, 1H), 7.84 (t, J = 7.9 Hz, 1H), 7.79–7.69 (m, 3H), 7.67–7.63 (m, 1H), 7.54–7.47 (m, 2H), 7.37–7.34 (m, 2H), 7.23 (td, J = 7.4, 1.5 Hz, 1H), 7.18 (td, J = 7.5, 1.6 Hz, 1H), 6.79–6.77 (m, 1H), 6.70–6.67 (m, 1H) ppm.
**$^{13}$C NMR** (150 MHz, CD$_2$Cl$_2$) δ 143.6, 143.5, 142.1, 142.0, 132.41, 132.3, 131.5, 131.2, 131.0, 130.8, 130.8, 129.9, 129.8, 129.8, 129.6, 129.3, 129.0, 128.8, 128.8, 128.4, 128.2, 127.9, 127.7, 127.7, 127.5, 127.5, 127.4, 126.5, 125.3, 125.1, 124.3, 124.0, 123.3, 122.9, 122.9, 122.0, 121.4, 120.8, 119.4 ppm (three signals coincident or not observed).

**HPLC** (PBr column (anal.), 1.0 mL/min, 35 °C, DCM/MeOH 6:4) $t_R = 8.43$ min.

**UV/vis** (DCM/MeOH) $\lambda_{max}$ 400 (sh), 369 (sh), 350 (sh), 322, 296 (sh), 284 (sh), 236 nm.

**LDI MS** $m/z$ 526 (M$^+$, 100).

**HR MS (APPI)** calcd. for C$_{42}$H$_{22}$ (M$^{++}$, 100) $m/z$ 526.1716, found 526.1719.

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**Hexabenzo[a,cdf,ijlm,o]perylene (N15).** Orange solid. Yield: 0.3 mg (4 %, isolated).

**$^1$H NMR** (400 MHz, C$_2$D$_2$Cl$_4$) δ 8.60–8.58 (m, 3H), 8.51–8.38 (m, 6H), 8.24 (d, $J = 8.3$ Hz, 1H), 8.01 (s, 1H), 7.63–7.54 (m, 3H), 7.49–7.45 (m, 1H), 7.43–7.34 (m, 4H), 7.27 (td, $J = 7.5$, 1.3 Hz, 1H), 7.22–7.07 (m, 5H), 6.86–6.84 (d, $J = 7.5$ Hz, 1H), 6.71–6.69 (dd, $J = 7.9$, 1.2 Hz, 1H) ppm.

**HPLC** (PBr column (anal.), 1.0 mL/min, 35 °C, MeOH/DCM 7:3) $t_R = 8.74$ min.

**UV/vis** (DCM/MeOH) $\lambda_{max}$ 462, 437, 352, 335, 308, 282 nm.

**LDI MS** $m/z$ 526 (M$^+$, 100).

**HR MS (APPI)** calcd. for C$_{42}$H$_{22}$ (M$^{++}$, 100) $m/z$ 526.1716, found 526.1712.

Spectroscopic data were consistent with those previously reported.$^{15,16}$
3 Spectroscopic Analysis and Characterization

3.1 Building Blocks

Figure S8: $^1$H NMR spectrum of 2-bromo-2'-fluoro-1,1'-biphenyl (B1) (in CDCl$_3$).

Figure S9: $^{13}$C NMR spectrum of 2-bromo-2'-fluoro-1,1'-biphenyl (B1) (in CDCl$_3$).
**Figure S10:** $^{19}$F NMR spectrum of 2-bromo-2'-fluoro-1,1'-biphenyl (B1) (in CDCl$_3$).

**Figure S11:** HPLC chromatogram of 2-bromo-2'-fluoro-1,1'-biphenyl (B1) (PBr column (anal.), 1.0 mL/min, 35 °C, MeOH/DCM 9:1), $t_R = 4.36$ min, (inset) UV/vis spectrum.
Figure S12: $^1$H NMR spectrum of (2'-fluoro-[1,1'-biphenyl]2-yl)boronic acid (B2) (in DMSO-$d_6$, 30 °C).

Figure S13: $^{13}$C NMR spectrum (fluorine decoupled) of (2'-fluoro-[1,1'-biphenyl]2-yl)boronic acid (B2) (in DMSO-$d_6$, 30 °C).
Figure S14: HSQC of (2'-fluoro-[1,1'-biphenyl]2-yl)boronic acid (B2) (in DMSO-d$_6$, 30 °C).

Figure S15: $^{19}$F NMR spectrum (proton decoupled) of (2'-fluoro-[1,1'-biphenyl]2-yl)boronic acid (B2) (in DMSO-d$_6$, 30 °C).
Figure S16: HPLC chromatogram of (2'-fluoro-[1,1'-biphenyl][2-yl])boronic acid (B2) (PBr column (anal.), 1.0 mL/min, 35 °C, MeOH/DCM 9:1), $t_R = 4.17$ min, (inset) UV/vis spectrum.

Figure S17: $^1$H NMR spectrum of 1,3,5-tris(2'-bromophenyl)benzene (B3) (in CDCl$_3$).
Figure S18: $^{13}$C NMR spectrum of 1,3,5-tris(2'-bromophenyl)benzene (B3) (in CDCl$_3$).

Figure S19: HPLC chromatogram of 1,3,5-tris(2'-bromophenyl)benzene (B3) (PBr column (anal.), 1.0 mL/min, 35 °C, MeOH/DCM 6:4), $t_R = 6.29$ min, (inset) UV/vis spectrum.
Figure S20: $^1$H NMR spectrum 2',2''-dibromo-1,1':4',1''-terphenyl (B4) (in CDCl$_3$).

Figure S21: $^{13}$C NMR spectrum 2',2''-dibromo-1,1':4',1''-terphenyl (B4) (in CDCl$_3$).
Figure S22: HPLC chromatogram 2',2''-dibromo-1,1':4',1''-terphenyl (B4) (PBr column (anal.), 1.0 mL/min, 35 °C, MeOH/DCM 7:3), $t_R = 5.67$ min, (inset) UV/vis spectrum.
3.2 Oligophenylenes

**Figure S23**: $^1$H NMR spectrum of 1,3,5-tris[2’-(2”-fluoro-1’,1”-biphenyl)]benzene (P1) (in CD$_2$Cl$_2$).

**Figure S24**: $^{13}$C NMR spectrum of 1,3,5-tris[2’-(2”-fluoro-1’,1”-biphenyl)]benzene (P1) (in CD$_2$Cl$_2$).
Figure S25: $^{19}$F NMR spectrum of 1,3,5-tris[2''-(2'''-fluoro-1',1''-biphenyl)]benzene (P1) (in CD$_2$Cl$_2$).

Figure S26: HPLC chromatogram of 1,3,5-tris[2''-(2'''-fluoro-1',1''-biphenyl)]benzene (P1) (PBr column (anal.), 1.0 mL/min, 35 °C, MeOH/DCM 6:4), $t_R = 5.38$ min, (inset) UV/vis spectrum.
Figure S27: HR MS (APPI) spectrum 1,3,5-tris[2''-(2''-fluoro-1',1''-biphenyl)]benzene (P1), m/z 588.2063 (M⁺, 100%).

Figure S28: ¹H NMR spectrum of 2-fluoro-1,1':2',1''-quaterphenyl (P2) (in CDCl₃).
Figure S29: $^{13}$C NMR spectrum of 2-fluoro-1,1':2',1''-quaterphenyl (P2) (in CDCl$_3$).

Figure S30: $^{19}$F NMR spectrum of 2-fluoro-1,1':2',1''-quaterphenyl (P2) (in CDCl$_3$).
Figure S31: HPLC chromatogram of 2-fluoro-1,1’:2’,1”-quaterphenyl (P2) (PBr column (anal.), 1.0 mL/min, 35 °C, MeOH/DCM 6:4), t_R = 4.36 min, (inset) UV/vis spectrum.

Figure S32: HR MS (APPI) spectrum of 2-fluoro-1,1':2',1''-quaterphenyl (P2), m/z 324.1314 (M+, 100%).
Figure S33: $^1$H NMR spectrum of 2,2''''-difluoro-2''-5''-diphenyl-1,1':2',1''':4'',1'''':2'''',1''''''-quinquephenyl (P3) (in CD$_2$Cl$_2$, fluorine decoupled).

Figure S34: $^{13}$C NMR spectrum of 2,2''''-difluoro-2''-5''-diphenyl-1,1':2',1''':4'',1'''':2'''',1''''''-quinquephenyl (P3) (in CD$_2$Cl$_2$, proton and fluorine decoupled).
**Figure S35:** $^{19}$F NMR spectrum of 2,2''-difluoro-2''-5''-diphenyl-1,1''-2',1'',4',1''',2''',1'''-quinquephenyl (P3) (in CD$_2$Cl$_2$).

**Figure S36:** HPLC chromatogram of 2,2'''-difluoro-2''-5''-diphenyl-1,1''-2',1'',4',1''',2''',1'''-quinquephenyl (P3) (5PYE column (anal.), 1.0 mL/min, 35 °C, MeOH/DCM 6:4), $t_R = 4.98$ min, (inset) UV/vis spectrum.
**Figure S37:** HR MS (APPI) spectrum of 2,2''-difluoro-2''-5''-diphenyl-1,1':2',1''-terphenyl (P3), m/z 570.2162 (M+, 100%).

**Figure S38:** ¹H NMR spectrum of 2',2''-bis(2,2'-difluoro-[1,1'-biphenyl]-3-yl)-1',1''-terphenyl (P4) (in CD₂Cl₂, fluorine decoupled).
Figure S39: $^{13}$C NMR spectrum of $2',2''$-bis($2,2'$-difluoro-$[1,1'$-biphenyl]-3$-yl)-1,1'$:4',1''-terphenyl (P4) (in CDCl$_3$).

Figure S40: $^{19}$F NMR spectrum of $2',2''$-bis($2,2'$-difluoro-$[1,1'$-biphenyl]-3$-yl)-1,1'$:4',1''-terphenyl (P4) (in CD$_2$Cl$_2$, proton decoupled).
Figure S41: HPLC chromatogram of 2',2''-bis(2,2'-difluoro-[1,1'-biphenyl]-3-yl)-1,1':4',1''-terphenyl (P4) (5PYE column (anal.), 1.0 mL/min, 35 °C, MeOH/DCM 1:1), t_R = 4.47 min, (inset) UV/vis spectrum.

Figure S42: MALDI MS spectrum (DCTB, AgOTf) of 2',2''-bis(2,2'-difluoro-[1,1'-biphenyl]-3-yl)-1,1':4',1''-terphenyl (P4), m/z 714 and 716 ([M + Ag]^+), 100.
Figure S43: HR MS (APPI) spectrum 2',2''-bis(2,2'-difluoro-[1,1'-biphenyl]-3-yl)-1,1':4',1''-terphenyl (P4), m/z 606.1976 (M+, 100%).
3.3 Condensation of P1

**Figure S44:** HPLC chromatogram of the reaction mixture (200 °C, 5 h) (PBr (semiprep), 5.0 ml/min, 40 °C, MeOH/DCM 6:4).

**Figure S45:** $^1$H NMR spectrum of F1 (in CDCl$_3$).
Figure S46: Expanded $^1$H NMR spectrum of F1 (in CDCl$_3$).

Figure S47: $^{13}$C NMR spectrum of F1 (in CDCl$_3$).
Figure S48: $^{19}$F NMR spectrum of F1 (in CDCl$_3$).

Figure S49: HPLC chromatogram of F1 (PBr (anal.), 1.0 ml/min, 35°C, MeOH/DCM 6:4), $t_R = 5.38$ min, (inset) UV/vis spectrum.
Figure S50: $^1$H NMR spectrum of F2 (in C$_2$D$_2$Cl$_4$).

Figure S51: Expanded $^1$H NMR spectrum of F2 (in C$_2$D$_2$Cl$_4$).
Figure S52: $^{19}$F NMR spectrum of F2 (in C$_2$D$_2$Cl$_4$).

Figure S53: HPLC chromatogram of F2 (PBr (anal.), 1.0 ml/min, 35°C, MeOH/DCM 6:4), $t_R = 7.45$ min, (inset) UV/vis spectrum.
Figure S54: LDI MS spectrum of F2, m/z 568 (M⁺, 100).

Figure S55: ¹H NMR spectrum of F3 (in C₂D₂Cl₄).
Figure S56: Expanded $^1$H NMR spectrum of F3 (in C$_2$D$_2$Cl$_4$).

Figure S57: $^{19}$F NMR spectrum of F3 (in C$_2$D$_2$Cl$_4$).
Figure S58: HPLC chromatogram of F3 (PBr (anal.), 1.0 ml/min, 35°C, MeOH/DCM 6:4), t_R = 7.94 min, (inset) UV/vis spectrum.

Figure S59: LDI MS spectrum of F3, m/z 548 (M⁺, 100).
Figure S60: $^1$H NMR spectrum of F4 (in C$_2$D$_2$Cl$_4$).

Figure S61: Expanded $^1$H NMR spectrum of F4 (in C$_2$D$_2$Cl$_4$).
Figure S62: $^1$H NMR spectrum of F4 (in C$_2$D$_2$Cl$_4$).

Figure S63: HPLC chromatogram of F4 (Buckyprep (anal.), 1.0 ml/min, 35°C, MeOH/DCM 6:4), $t_R = 6.81$ min, (inset) UV/vis spectrum.
Figure S64: LDI MS spectrum of F4, m/z 568 (M⁺, 100).

Figure S65: ¹H NMR spectrum of F5 (in C₂D₂Cl₄).
Figure S66: Expanded $^1\text{H}$ NMR spectrum of F5 (in C$_2$D$_2$Cl$_4$).

Figure S67: HPLC chromatogram of F5 (Buckyprep (anal.), 1.0 ml/min, 35°C, MeOH/DCM 6:4), $t_R = 8.12$ min, (inset) UV/vis spectrum.
Figure S68: LDI MS spectrum of F5, m/z 548 (M+, 100).

Figure S69: HPLC chromatogram of mixture of N1 and N2 (Buckyprep (semiprep), 5.0 ml/min, 40 °C, MeOH/DCM 6:4).
Nanostructure N1

Figure S70: $^1$H NMR spectrum of hexabenzotriphenylene (N1) (in C$_2$D$_2$Cl$_4$).

Figure S71: Expanded $^1$H NMR spectrum of hexabenzotriphenylene (N1) (in C$_2$D$_2$Cl$_4$).
Figure S72: HPLC chromatogram of hexabenzotriphenylene (N1) (PBr (anal.), 1.0 ml/min, 35°C, MeOH/DCM 6:4), t<sub>R</sub> = 14.48 min, (inset) UV-vis spectrum.

Figure S73: LDI MS spectrum of hexabenzotriphenylene (N1), m/z 528 (M<sup>+</sup>, 100).
Figure S74: HR MS (APPI) spectrum of hexabenzotriphenylene (N1), m/z 528.1855 (M+, 100%).

Nanostructure N2

Figure S75: $^1$H NMR spectrum of naphtho[1,2,3,4-def]phenanthro[9,10-a]tetraphenyline (N2) (in C$_2$D$_2$Cl$_4$).
Figure S76: Expanded $^1$H NMR spectrum of naphtho[1,2,3,4-def]phenanthro[9,10-a]tetr phenylene (N2) (in $\text{C}_2\text{D}_2\text{Cl}_4$).

Figure S77: HPLC chromatogram of naphtho[1,2,3,4-def]phenanthro[9,10-a]tetraphenylene (N2) (PBr (anal.), 1.0 ml/min, 35°C, MeOH/DCM 6:4), $t_R = 17.26$ min, (inset) UV-vis spectrum.
Figure S78: LDI MS spectrum of naphtho[1,2,3,4-def]phenanthro[9,10-a]tetraphenylene (N2), m/z 528 (M+, 100).

Figure S79: HR MS (APPI) spectrum of naphtho[1,2,3,4-def]phenanthro[9,10-a]tetraphenylene (N2), m/z 528.1873 (M+, 100%).
Nanostructure N3

Figure S80: $^1$H NMR spectrum of naphtho[1,2,3,4-def]phenanthro[9,10-b]tetraphenylene (N3) (in C$_2$D$_2$Cl$_4$).

Figure S81: Expanded $^1$H NMR spectrum of naphtho[1,2,3,4-def]phenanthro[9,10-b]tetraphenylene (N3) (in C$_2$D$_2$Cl$_4$).
Figure S82: HPLC chromatogram of naphtho[1,2,3,4-def]phenanthro[9,10-b]tetraphenylene (N3) (PBr (analyt), 1.0 ml/min, 35 °C, MeOH/DCM 6:4), \( t_R = 16.70 \) min, (inset) UV/vis spectrum.

Figure S83: LDI MS spectrum of naphtho[1,2,3,4-def]phenanthro[9,10-b]tetraphenylene (N3), \( m/z 528 \) (M+, 100).
Figure S84: HR MS (APPI) spectrum of naphtho[1,2,3,4-def]phenanthro[9,10-b]tetraphenylene (N3), m/z 528.1870 (M⁺, 100 %).

Figure S85: HPLC chromatogram of the second reaction mixture (210 °C, 18 h) (PBr (anal.), 1.0 ml/min, 35 °C, MeOH/DCM 6:4).
Figure S86: $^1$H NMR spectrum of reaction mixture (in C$_2$D$_2$Cl$_4$).

Figure S87: First attempt: HPLC chromatogram of separation (PBr (semiprep), 5.0 ml/min, 40 °C, MeOH/DCM 6:4).
**Figure S88**: HPLC chromatogram of fraction F1 (PBr (anal.), 1.0 ml/min, 35 °C, MeOH/DCM 6:4).

**Figure S89**: HPLC chromatogram of pure fraction F2 (PBr (anal.), 1.0 ml/min, 35 °C, MeOH/DCM 6:4).
**Figure S90**: Second attempt: HPLC chromatogram of separation (Buckyprep (semiprep), 5.0 ml/min, 40 °C, MeOH/DCM 6:4).

**Figure S91**: HPLC chromatogram of pure fraction F1 (PBr (anal.), 1.0 ml/min, 35 °C, MeOH/DCM 6:4).
Figure S92: HPLC chromatogram of fraction F2 (PBr (anal.), 1.0 ml/min, 35 °C, MeOH/DCM 6:4).
3.4 Condensation of P2

Figure S93: HPLC chromatogram of the reaction mixture (PBr column (anal.), 1.0 mL/min, 35 °C, MeOH/DCM 9:1).

Figure S94: 'H NMR spectrum of the reaction mixture (in CD$_2$Cl$_2$).
Nanostructure N4

Figure S95: $^1$H NMR spectrum of tetraphenylene (N4) (in CD$_2$Cl$_2$).

Figure S96: $^{13}$C NMR spectrum of tetraphenylene (N4) (in CD$_2$Cl$_2$).
Figure S97: HPLC chromatogram of tetraphenylene (N4) (PBr column (anal.), 1.0 mL/min, 35 °C, MeOH/DCM 9:1), tR = 5.49 min, (inset) UV/vis spectrum.

Figure S98: HR MS (APPI) spectrum tetraphenylene (N4), m/z 304.1243 (M+, 100%).
Nanostructure N5

Figure S99: $^1$H NMR spectrum of 1-phenyltriphenylene (N5) (in CDCl$_3$).

Figure S100: Expanded $^1$H NMR spectrum of 1-phenyltriphenylene (N5) (in CDCl$_3$).
Figure S101: $^{13}$C NMR spectrum of 1-phenyltriphenylene (N5) (in CDCl$_3$).

Figure S102: HPLC chromatogram of 1-phenyltriphenylene (N5) (PBr column (anal.), 1.0 mL/min, 35 °C, MeOH/DCM 1:1), $t_R = 5.62$ min, (inset) UV/vis spectrum.
Figure S103: LDI MS spectrum of 1-phenyltriphenylene (N5), m/z 304 (M⁺, 100).

Nanostructure N6

Figure S104: ¹H NMR spectrum of 2-phenyltriphenylene (N6) (in CDCl₃).
Figure S105: Expanded $^1$H NMR spectrum of 2-phenyltriphenylene (N6) (in CDCl$_3$).

Figure S106: $^{13}$C NMR spectrum of 2-phenyltriphenylene (N6) (in CDCl$_3$).
Figure S107: HPLC chromatogram 2-phenyltriphenylene (N6) (PBr column (anal.), 1.0 mL/min, 35 °C, MeOH/DCM 1:1), $t_R = 7.22$ min, (inset) UV/vis spectrum.

Figure S108: LDI MS spectrum of 2-phenyltriphenylene (N6), $m/z$ 304 (M+, 100).
3.5 Condensation of P3

**Figure S109**: HPLC chromatogram of mixture after reaction (200 °C, 12 h) (PBr (semiprep), 1.0 ml/min, 40°C, MeOH/DCM 6:4). F1: tR = 6.69 min, F2: tR = 7.40 min, F3: tR = 9.58 min, F5: tR = 10.21 min, F6: tR = 11.28 min.

**Figure S110**: ¹H NMR spectrum of 2-(2'-fluoro-[1,1'-biphenyl]-2-yl)-1,4-diphenyltriphenylene (F1) (in C₂D₂Cl₄).
Figure S111: Expanded $^1$H NMR spectrum of 2-(2'-fluoro-[1,1'-biphenyl]-2-yl)-1,4-diphenyltriphenylene (F1) (in C$_2$D$_2$Cl$_4$).

Figure S112: $^{19}$F NMR spectrum of 2-(2'-fluoro-[1,1'-biphenyl]-2-yl)-1,4-diphenyltriphenylene (F1) (in C$_2$D$_2$Cl$_4$).
Figure S113: HPLC chromatogram of 2-(2'-fluoro-[1,1'-biphenyl]-2-yl)-1,4-diphenyltriphenylene (F1) (PBr (anal.), 1.0 ml/min, 35°C, MeOH/DCM 6:4), $t_R = 6.95$ min, (inset) UV/vis spectrum.

Figure S114: LDI MS spectrum of 2-(2'-fluoro-[1,1'-biphenyl]-2-yl)-1,4-diphenyltriphenylene (F1), $m/z$ 550 ($M^+$, 100).
Figure S115: HR MS (APPI) spectrum of 2-(2'-fluoro-[1,1'-biphenyl]-2-yl)-1,4-diphenyltriphenylene (F1), m/z 550.2095 (M⁺, 100 %).

Figure S116: HPLC chromatogram of the reaction mixture (210 °C, 18 h) (PBr (anal.), 1.0 ml/min, 35°C, MeOH/DCM 6:4).
Figure S117: HPLC chromatogram of the separation (210 °C, 18 h) (PBr (semiprep), 5.0 ml/min, 40°C, MeOH/DCM 6:4).

Nanostructure N7

Figure S118: $^1$H NMR spectrum of trans-tribenzo[3,4:5,6:7,8]cycloocta[1,2-b]tetraphenylene (N7) (in CD$_2$Cl$_2$).
Figure S119: Expanded $^1$H NMR spectrum of trans-tribenzo[3,4:5,6:7,8]cycloocta[1,2-b]tetraphenylene (N7) (in CD$_2$Cl$_2$).

Figure S120: HPLC chromatogram of trans-tribenzo[3,4:5,6:7,8]cycloocta[1,2-b]tetraphenylene (N7) (PB Br (anal.), 1.0 ml/min, 35°C, MeOH/DCM 6:4), $t_R = 6.62$ min, (inset) UV/vis spectrum.
Figure S121: LDI MS spectrum of trans-tribenzo[3,4:5,6:7,8]cycloocta[1,2-b]tetraphenylene (N7), m/z 530 (M⁺, 100).

Figure S122: HR MS (APPI) spectrum of trans-tribenzo[3,4:5,6:7,8]cycloocta[1,2-b]tetraphenylene (N7), m/z 530.2021 (M⁺, 100 %).
Figure S123: $^1$H NMR spectrum of cis-tribenzo[3,4:5,6:7,8]cycloocta[1,2-b]tetraphenylenes (N8) (in C$_2$D$_2$Cl$_4$).

Figure S124: Expanded $^1$H NMR spectrum of cis-tribenzo[3,4:5,6:7,8]cycloocta[1,2-b]tetraphenylenes (N8) (in C$_2$D$_2$Cl$_4$).
Figure S125: HPLC chromatogram of cis-tribenzo[3,4:5,6:7,8]cycloocta[1,2-b]tetraphenylenes (N8) (PBr (anal.), 1.0 ml/min, 35°C, MeOH/DCM 6:4), t_R = 6.91 min, (inset) UV/vis spectrum.

Figure S126: HR MS (APPI) spectrum of cis-tribenzo[3,4:5,6:7,8]cycloocta[1,2-b]tetraphenylene (N8), m/z 530.2030 (M+, 100%).
Nanostructure N9

Figure S127: $^1$H NMR spectrum of 5-phenylphenanthro[9,10-a]tetraphenylene (N9) (in C$_2$D$_2$Cl$_4$).

Figure S128: Expanded $^1$H NMR spectrum of 5-phenylphenanthro[9,10-a]tetraphenylene (N9) (in C$_2$D$_2$Cl$_4$).
Figure S129: $^{13}$C NMR spectrum of 5-phenylphenanthro[9,10-a]tetraphenylene (N9) (in C$_2$D$_2$Cl$_4$).

Figure S130: HPLC chromatogram of 5-phenylphenanthro[9,10-a]tetraphenylene (N9) (PBr (anal.), 1.0 ml/min, 35°C, MeOH/DCM 6:4), $t_R = 7.62$ min, (inset) UV/vis spectrum.
Figure S131: LDI MS spectrum of 5-phenylphenanthro[9,10-a]tetraphenylene (N9), m/z 530 (M+, 100).

Figure S132: HR MS (APPI) spectrum of 5-phenylphenanthro[9,10-a]tetraphenylene (N9), m/z 530.2031 (M+, 100%).
Nanostructure N10

**Figure S133:** $^1$H NMR spectrum of 6-phenylphenanthro[9,10-a]tetraphenylen (N10) (in C$_2$D$_2$Cl$_4$).

**Figure S134:** Expanded $^1$H NMR spectrum of 6-phenylphenanthro[9,10-a]tetraphenylen (N10) (in C$_2$D$_2$Cl$_4$).
Figure S135: HPLC chromatogram of 6-phenylphenanthro[9,10-a]tetraphenylene (N10) (PBr (anal.), 1.0 ml/min, 35°C, MeOH/DCM 6:4), t_R = 9.96 min, (inset) UV/vis spectrum.

Figure S136: LDI MS spectrum of 6-phenylphenanthro[9,10-a]tetraphenylene (N10), m/z 530 (M+, 100).
Figure S137: HR MS (APPI) spectrum of 6-phenylphenanthro[9,10-a]tetraphenylene (N10), m/z 530.2023 (M⁺, 100 %).

Figure S138: HPLC chromatogram of N11 + N12 after separation (PBr (anal.), 1.0 ml/min, 35°C, MeOH/DCM 6:4), t_R = 10.18 min, (inset) UV/vis spectrum.
Figure S139: $^1$H NMR spectrum (in CD$_2$Cl$_2$) of orange fraction; shows mixture of two products (N11 + N12).

Figure S140: Expanded $^1$H NMR spectrum (in CD$_2$Cl$_2$); shows mixture of two products (N11 + N12).
**Figure S141:** HPLC chromatogram of \( \text{N11} + \text{N12} \) (Buckyprep (anal.), 1.0 ml/min, 35°C, MeOH/DCM 7:3; \( \text{N11}: t_R = 10.90 \text{ min}, \text{N12}: t_R = 12.29 \text{ min} \)).

**Nanostructure N11**

**Figure S142:** \(^1\)H NMR spectrum of 9,18-diphenylphenanthro[9,10-b]triphenylene (\( \text{N11} \)) (in CD$_2$Cl$_2$).
Figure S143: Expanded $^1$H NMR spectrum of 9,18-diphenylphenanthro[9,10-b]triphenylene (N11) (in CD$_2$Cl$_2$).

Figure S144: $^{13}$C NMR spectrum of 9,18-diphenylphenanthro[9,10-b]triphenylene (N11) (in CD$_2$Cl$_2$).
Figure S145: HPLC chromatogram of 9,18-diphenylphenanthro[9,10-b]triphenylene (N11) (Buckyprep (anal.), 1.0 ml/min, 35°C, MeOH/DCM 7:3), $t_R = 10.91$ min, (inset) UV/vis spectrum.

Figure S146: LDI MS spectrum of 9,18-diphenylphenanthro[9,10-b]triphenylene (N11), m/z 530 (M+, 100).
Nanostructure N12

Figure S147: $^1$H NMR spectrum of 17,18-diphenyl dibenzof,jpicene (N12) (in CD$_2$Cl$_2$).

Figure S148: Expanded $^1$H NMR spectrum of 17,18-diphenyl dibenzof,jpicene (N12) (in CD$_2$Cl$_2$).
Figure S149: $^{13}$C NMR spectrum of 17,18-diphenyl[6,6]picene (N12) (in CD$_2$Cl$_2$).

Figure S150: HPLC chromatogram of 17,18-diphenyl[6,6]picene (N12) (Bucky prep (anal.), 1.0 ml/min, 35°C, MeOH/DCM 6:4), $t_R = 12.29$ min, (inset) UV/vis spectrum.
Figure S151: LDI MS spectrum of 17,18-diphenyldibenzo[f,j]picene (N12), m/z 530 (M+, 100).

Nanostructure N13

Figure S152: $^1$H NMR spectrum of 9-phenylphenanthro[9,10-b]tetraphenylen (N13) (in C$_2$D$_2$Cl$_4$).
Figure S153: Expanded $^1$H NMR spectrum of 9-phenylphenanthro[9,10-b]tetraphenylene (N13) (in C$_2$D$_2$Cl$_4$).

Figure S154: HPLC chromatogram of 9-phenylphenanthro[9,10-b]tetraphenylene (N13) (PBr (anal.), 1.0 ml/min, 35°C, MeOH/DCM 6:4), $t_R = 11.67$ min, (inset) UV/vis spectrum.
**Figure S155:** LDI MS spectrum of 9-phenylphenanthro[9,10-b]tetraphenylene (N13), *m/z* 530 (M⁺, 100).

**Figure S156:** HR MS (APPI) spectrum of 9-phenylphenanthro[9,10-b]tetraphenylene (N13), *m/z* 530.2032 (M⁺, 100%).
3.6 Condensation of P4

Figure S157: HPLC chromatogram of mixture after reaction (200 °C, 15 h) (PBr (semiprep), 1.0 ml/min, 35°C, DCM/MeOH 6:4).

Nanostructure N14

Figure S158: ¹H NMR spectrum of benzo[4,10]anthra[3,2,1,9-vwxa]naphtho[1,2,3,4-def]tetraphylene \( \text{(N14)} \) (in CD$_2$Cl$_2$).
Figure S159: Expanded $^1$H NMR spectrum of benzo[4,10]anthra[3,2,1,9-vwxa]naphtho[1,2,3,4-def]tetraphenylene (N14) (in CD$_2$Cl$_2$).

Figure S160: $^{13}$C NMR spectrum of benzo[4,10]anthra[3,2,1,9-vwxa]naphtho[1,2,3,4-def]tetraphenylene (N14) (in CD$_2$Cl$_2$).
Figure S161: COSY of benzo[4,10]anthra[3,2,1,9-\textit{vwxa}]naphtho[1,2,3,4-\textit{def}]tetraphenylene (N14) (in CD$_2$Cl$_2$).

Figure S162: HPLC chromatogram of benzo[4,10]anthra[3,2,1,9-\textit{vwxa}]naphtho[1,2,3,4-\textit{def}]tetraphenylene (N14) (PBr column (anal.), 1.0 ml/min, 35 °C, DCM/MeOH 6:4), $t_R = 8.43$ min, (inset) UV/vis spectrum.
Figure S163: LDI MS spectrum of benzo[4,10]anthra[3,2,1,9-vwx]naphtho[1,2,3,4-def]tetraphenylen (N14), m/z 526 (M⁺, 100).

Figure S164: HR MS (APPI) spectrum of benzo[4,10]anthra[3,2,1,9-vwx]naphtho[1,2,3,4-def]tetraphenylen (N14), m/z 526.1719 (M⁺, 100 %).
Nanostructure N15

Figure S165: $^1$H NMR spectrum of hexabenzo[a,cd,f,j,lm,o]perylene (N15) (in CD$_2$Cl$_2$).

Figure S166: $^1$H NMR spectrum of hexabenzo[a,cd,f,j,lm,o]perylene (N15) (in CD$_2$Cl$_2$).
Figure S167: HPLC chromatogram of hexabenzoc[ae, f, j, l, m, o]perylene (N15) (PBr column (anal.), 1.0 ml/min, 35 °C, DCM/MeOH 7:3), $t_R = 8.74$ min, (inset) UV/vis spectrum.

Figure S168: LDI MS spectrum of hexabenzoc[ae, f, j, l, m, o]perylene (N15), $m/z$ 526 (M+, 100).
Figure S169: HR MS (APPI) spectrum of hexabenzo[a,cd,f,j,lm,o]perylene (N15), m/z 526.1712 (M+, 100%).
4 Crystallographic Data

4.1 Oligophenylene P4

![Crystal structure of P4](image)

**Figure S170:** Crystal structure of P4.

**Table S1.** Crystal data, data collection and refinement details for P4 at 153 K.

| Identification code | P4 |
|--------------------|----|
| Formula, formula weight | C_{42}H_{26}F_{4}, 606.63 g/mol |
| Crystal system | monoclinic |
| Space group (no.), Z | P2_1/c, 2 |
| Lattice parameters /Å, /° | |
| a = 11.5749(2) | \(\alpha = 90\) |
| b = 7.43719(16) | \(\beta = 95.1020(18)\) |
| c = 17.7032(3) | \(\gamma = 90\) |
| V /Å³ | 1517.94(5) |
| \(\rho_{calc}\)/g/cm³ | 1.327 |
| \(\mu\)/mm⁻¹ | 0.762 |
| F(000) | 628.0 |
| Crystal size/mm³ | 0.206 × 0.097 × 0.034 |
| Radiation | CuKα (λ = 1.54184) |
| 2\(\theta\) range for data collection /° | 10.032 to 123.16 |
Index ranges

-12 ≤ h ≤ 12
-8 ≤ k ≤ 8
-19 ≤ l ≤ 20

Reflections collected

6708

Independent reflections

2330 \[ R_{int} = 0.0426, R_{sigma} = 0.0374 \]

Data/restraints/parameters

2330/0/208

Goodness-of-fit on F^2

1.059

Final R indexes \[ I>=2\sigma (I) \]

\[ R_1 = 0.0456, \ wR_2 = 0.1200 \]

Final R indexes [all data]

\[ R_1 = 0.0581, \ wR_2 = 0.1325 \]

Largest diff. peak/hole / e Å^-3

0.45/-0.24

Goniometer type:

Agilent SuperNova with Atlas detector

Structure solution:

SHELXS-2014

Structure refinement:

SHELXL-2014

Hydrogen treatment:

riding model

Disorder:

-

Comments:

0.5 molecules in asym. unit (symmetry)

CCDC-no.

1907573

Single-crystal X-ray diffraction

Crystals of the compounds N2, N3, N7-N10, which are suitable for single-crystal X-ray diffraction, were selected under high viscosity oil, and mounted with grease on a loop made of Kapton foil (Micromounts™, MiTeGen, Ithaca, NY). Diffraction data were collected at 298 K with a SMART APEXII CCD X-ray diffractometer (Bruker AXS, Karlsruhe, Germany), using graphite-monochromated Mo-Kα radiation. The reflection intensities were integrated with the SAINT subprogram in the Bruker Suite software,\(^1\) a multi-scan absorption correction was applied using SADABS,\(^2\) and the structures were solved by direct methods and refined by full-matrix least-square fitting with the SHELXTL software package.\(^3,^4\) Hydrogen atoms bonded to carbon were added to the structure model on calculated positions using a riding model. Crystal data and data collection details are given in Tables S2-S7.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication, CCDC-numbers see Tables S2-S7. Copies of the data can be obtained free of
charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax.: (internat.) + 44 1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

References

[S1] Bruker Suite, version 2015/9. Bruker AXS Inc., Madison, WI, 2015.

[S2] Sheldrick, G. M. SADABS — Bruker AXS area detector scaling and absorption, version 2014/5, University of Göttingen, Germany 2014.

[S3] Sheldrick, G. M. A Short History of SHELX. Acta Crystallogr., Sect. A: Found. Crystallogr. 2008, 64, 112-122.

[S4] Sheldrick, G. M. Crystal Structure Refinement with SHELXL. Acta Crystallogr., Sect. C: Struct. Chem. 2015, 71, 3-8.

4.2 Nanostructure N2

![Crystal structure of N2](image)

Figure S171: Crystal structure of N2.

Table S2. Crystal data, data collection and refinement details for N2 at 298 K.

| Identification code | N2        |
|--------------------|-----------|
| Formula, formula weight | C_{42}H_{24}, 528.61 |
| Space group (no.), Z     | P1̅(2), 2  |
| Lattice parameters /Å, /° | a = 9.311(3), α = 73.843(4)  
b = 11.204(4), β = 74.879(4) |
4.3 Nanostructure N3

![Crystal structure of N3](image)

**Figure S172:** Crystal structure of N3.

| Parameter | Value |
|-----------|-------|
| $c$ | 13.772(4) |
| $\gamma$ | 77.405(4) |
| $V$/Å$^3$ | 1315.7(7) |
| $\rho_{\text{x-ray}}$ g×cm$^3$ | 1.334 |
| Crystal size /mm$^3$ | 0.20 × 0.20 × 0.10 |
| Diffractometer | SMART APEX II, Bruker AXS |
| X-ray radiation, $\lambda$/Å | 0.71073 |
| Absorption correction | Multi-scan, SADABS |
| $2\theta$ range /° | $3.15 \leq 2\theta \leq 54.79$ |
| Index range | $-11 \leq h \leq 12,$  
$-14 \leq k \leq 14,$  
$-17 \leq l \leq 17$ |
| Reflection collected | 11084 |
| Data, $R_{\text{int}}$ | 5722, 0.042 |
| No. of parameters | 379 |
| Transmission: $t_{\text{min}}$, $t_{\text{max}}$ | 0.169, 0.260 |
| $R_1$ [$F^2 > 2\sigma(F^2)$] | 0.0595 |
| $wR(F^2)$ | 0.1696 |
| CCDC-no. | 1901181 |
Table S3. Crystal data, data collection and refinement details for N3 at 298 K.

| Identification code | N3                                      |
|---------------------|-----------------------------------------|
| Formula, formula weight | C_{42}H_{24}, 528.61                    |
| Space group (no.), Z   | P\bar{1}(2), 2                           |
| Lattice parameters /Å, /° | a = 9.792(4) \quad \alpha = 76.188(6) |
|                        | b = 11.159(5) \quad \beta = 79.094(5)  |
|                        | c = 16.034(7) \quad \gamma = 76.197(6) |
| V /Å³                | 1636(1)                                  |
| \rho_{\text{ray}} /g×cm³ | 1.073                                    |
| Crystal size /mm³     | 0.05 \times 0.04 \times 0.02            |
| Diffractometer        | SMART APEX II, Bruker AXS                |
| X-ray radiation, /Å    | 0.71073                                  |
| Absorption correction | Multi-scan, SADABS                      |
| 2\theta range /°      | 2.64 \leq 2\theta \leq 41.84            |
| Index range           | –9 \leq h \leq 9,                       |
|                        | –11 \leq k \leq 11,                     |
|                        | –15 \leq l \leq 16                      |
| Reflection collected  | 7960                                     |
| Data, R_{int}         | 3459, 0.049                              |
| No. of parameters     | 380                                      |
| Transmission: t_{min}, t_{max} | 0.406, 0.488                      |
| R_{1} [F^2 > 2s(F^2)] | 0.197                                    |
| wR(F^2)               | 0.481                                    |
| CCDC-no.              | 1901180                                  |
4.4 Nanostructure N7

![Figure S173: Crystal structure of N7.]

Table S4. Crystal data, data collection and refinement details for N7 at 298 K.

| Identification code | N7                                       |
|---------------------|------------------------------------------|
| Formula, formula weight | C_{42}H_{26}, 530.63                     |
| Space group (no.), Z  | P\text{\^{}} (2), 1                       |
| Lattice parameters /Å, /° | \(a = 8.809(8)\) \(\alpha = 87.02(1)\) |
|                      | \(b = 9.272(8)\) \(\beta = 77.49(1)\)  |
|                      | \(c = 9.338(8)\) \(\gamma = 71.30(1)\)  |
| \(V /\text{Å}^3\)     | 705(1)                                   |
| \(\rho_{\text{ray}} /\text{g}\times\text{cm}^3\) | 1.250                                    |
| Crystal size /mm³      | 0.08 × 0.06 × 0.05                       |
| Diffractometer         | SMART APEX II, Bruker AXS                |
| X-ray radiation, \(\lambda /\text{Å}\) | 0.71073                                  |
| Absorption correction  | Multi-scan, SADABS                       |
| \(2\theta\) range /°  | \(4.47 \leq 2\theta \leq 41.80\)        |
|                      | \(-8 \leq h \leq 8,\)                  |
|                      | \(-9 \leq k \leq 9,\)                  |
|                      | \(-9 \leq l \leq 9\)                   |
| Reflection collected   | 2359                                     |
| Data, \(R_{int}\)     | 1448, 0.019                             |
| No. of parameters      | 190                                      |
| Transmission: \(t_{\text{min}}, t_{\text{max}}\) | 0.205, 0.254                           |
| \(R_1 [F^2 > 2\sigma(F^2)]\) | 0.0953                                 |
4.5 Nanostructure N8

Figure S174: Crystal structure of N8.

Table S5. Crystal data, data collection and refinement details for N8 at 298 K.

| Identification code | N8 |
|---------------------|----|
| Formula, formula weight | C₆₀H₂₆ ⋅ C₆H₆, 608.73 |
| Space group (no.), Z | C2/c (15), 4 |
| Lattice parameters /Å, /° | a = 9.298(3)  α = 90 |
|  | b = 18.467(6)  β = 91.582(4) |
|  | c = 19.682(7)  γ = 90 |
| V /Å³ | 3378(2) |
| ρ_xray /g×cm³ | 1.197 |
| Crystal size /mm³ | 0.38 × 0.28 × 0.20 |
| Diffractometer | SMART APEX II, Bruker AXS |
| X-ray radiation, λ/Å | 0.71073 |
| Absorption correction | Multi-scan, SADABS |
| 2θ range /° | 4.14 ≤ 2θ ≤ 53.15 |
| Index range | −11 ≤ h ≤ 11, −23 ≤ k ≤ 23, −24 ≤ l ≤ 24 |
Reflection collected
Data, $R_{int}$
No. of parameters
Transmission: $t_{\text{min}}$, $t_{\text{max}}$
$R_1 [F^2 > 2\sigma(F^2)]$
$wR(F^2)$
CCDC-no.

| Reflection collected | 13620 |
|---------------------|-------|
| Data, $R_{int}$     | 3499, 0.054 |
| No. of parameters   | 218 |
| Transmission: $t_{\text{min}}$, $t_{\text{max}}$ | 0.196, 0.260 |
| $R_1 [F^2 > 2\sigma(F^2)]$ | 0.0488 |
| $wR(F^2)$           | 0.1348 |
| CCDC-no.            | 1901176 |

4.6 Nanostructure N9

Figure S175: Crystal structure of N9.

Table S6. Crystal data, data collection and refinement details for N9 at 298 K.

| Identification code | N9 |
|---------------------|----|
| Formula, formula weight | C$_{42}$H$_{26}$, 530.63 |
| Space group (no.), Z | P2(2), 2 |
| Lattice parameters /Å, /° | $a = 9.593(1)$, $\alpha = 92.650(1)$ |
|                       | $b = 9.941(1)$, $\beta = 98.989(1)$ |
|                       | $c = 14.999(1)$, $\gamma = 94.492(1)$ |
| $V$ /Å$^3$             | 1406.0(2) |
| $\rho_{\text{ray}}$ /g×cm$^3$ | 1.253 |
| Crystal size /mm$^3$   | 0.40 × 0.30 × 0.25 |
Table S7. Crystal data, data collection and refinement details for N10 at 298 K.

| Identification code | N10 |
|---------------------|-----|
| Formula, formula weight | C_{43}H_{26} \cdot \frac{1}{2}C_{6}H_{6}, 569.68 |
| Space group (no.), Z | P\overline{1}(2), 2 |
| Lattice parameters /Å, /° | \(a = 9.742(3)\) \(\alpha = 76.172(3)\) |
table

| Parameter                  | Value                  |
|----------------------------|------------------------|
| $b$                        | 10.922(3)              |
| $\beta$                    | 79.806(3)              |
| $c$                        | 15.404(4)              |
| $\gamma$                   | 76.041(3)              |
| $V / \text{Å}^3$           | 1532.1(7)              |
| $\rho_{\text{x-ray}} / g\times\text{cm}^3$ | 1.235                 |
| Crystal size /mm$^3$       | 0.40 $\times$ 0.30 $\times$ 0.10 |
| Diffractometer             | SMART APEX II, Bruker AXS |
| X-ray radiation, $\lambda$ /Å | 0.71073               |
| Absorption correction      | Multi-scan, SADABS     |
| $2\theta$ range /°         | 2.74 $\leq 2\theta \leq$ 52.85 |
| Index range                | $-12 \leq h \leq 12$, $-13 \leq k \leq 13$, $-18 \leq l \leq 19$ |
| Reflection collected       | 12669                  |
| Data, $R_{int}$            | 6236, 0.032            |
| No. of parameters          | 406                    |
| Transmission: $t_{\text{min}}$, $t_{\text{max}}$ | 0.214, 0.260          |
| $R_1$ [$F^2 > 2\sigma(F^2)$] | 0.0514                |
| $wR(F^2)$                  | 0.1510                 |
| CCDC-no.                   | 1901178                |

4.8 Nanostructure N11

Figure S177: Crystal structure of N11.
Table S8. Crystal data, data collection and refinement details for N11 at 153 K.

| Identification code | N11 |
|---------------------|-----|
| Formula, formula weight | C_{42.5}H_{27}Cl, 573.09 |
| Crystal system | triclinic |
| Space group (no.), Z | P\overline{1}, 4 |
| Lattice parameters / Å, ° | 
|  | \(a = 10.3511(5)\) | \(\alpha = 100.999(6)\) |
|  | \(b = 16.8593(8)\) | \(\beta = 96.353(6)\) |
|  | \(c = 17.2921(18)\) | \(\gamma = 94.379(4)\) |
| V /Å³ | 2929.3(4) |
| \(\rho_{calc} \)/g/cm³ | 1.299 |
| \(\mu \)/mm-1 | 1.376 |
| F(000) | 1196.0 |
| Crystal size /mm³ | 0.345 × 0.23 × 0.047 |
| Radiation | CuKα (\(\lambda = 1.54184\)) |
| 2θ range for data collection /° | 6.712 to 146.334 |
| Index ranges | -12 ≤ h ≤ 12, -20 ≤ k ≤ 20, -21 ≤ l ≤ 21 |
| Reflections collected | 16643 |
| Independent reflections | 16643 [\(R_{int} = N/A, R_{sigma} = 0.0817\)] |
| Data/restraints/parameters | 16643/3/789 |
| Goodness-of-fit on F² | 0.924 |
| Final R indexes [I>=2σ (I)] | \(R_1 = 0.0603, wR_2 = 0.1462\) |
| Final R indexes [all data] | \(R_1 = 0.1020, wR_2 = 0.1679\) |
| Largest diff. peak/hole / e Å⁻³ | 0.36/-0.73 |
| Goniometer type: | Agilent SuperNova with Atlas detector |
| Structure solution : | SHELXS-2014 |
| Structure refinement : | SHELXL-2014 |
| Hydrogen treatment: | riding model |
| Disorder: | DCM: Cl2 : Cl2a = 65:35% |
| Comments: | Crystal showed clear twinning! Twin spheres have been splitted and indexed; followed by a classical HKLF4/5 twin |
4.9 Nanostructure N14

Synchrotron X-ray data for a crystal of N14 (0.02 × 0.01 × 0.005 mm³) were collected at 100 K on BL14.3 at the BESSY storage ring (Berlin, Germany) using a MAR225 detector (\( \lambda = 0.8950 \) Å). The structure was solved and anisotropically refined using the SHELX package. Hydrogen atoms were placed in the calculated positions and refined in a riding mode.

Table S9. Crystal data, data collection and refinement details for N14 at 100 K.

| Identification code | N14 |
|---------------------|-----|
| Formula, formula weight | C₄₂H₂₂, 526.59 |
| Crystal system | triclinic |
| Space group (no.), Z | P\( \bar{1} \), 2 |
| Lattice parameters /Å, /° | \( a = 8.699(1) \), \( \alpha = 113.193(10) \) |
| | \( b = 12.357(1) \), \( \beta = 96.574(10) \) |
| | \( c = 13.324(1) \), \( \gamma = 97.330(10) \) |
| V /Å³ | 1284.2(2) |
| Property                   | Value                  |
|----------------------------|------------------------|
| $\rho_{\text{ray}}$ /g\cdot\text{cm}^3 | 1.362                  |
| Crystal size /mm$^3$       | $0.02 \times 0.01 \times 0.005$ |
| $\mu$/mm$^{-1}$           | 0.127                  |
| $F(000)$                   | 548.0                  |
| $2\theta_{\text{max}}$ /° | 36.918                 |
| $h,k,l_{\text{max}}$      | 10,15,15               |
| No. of reflections         | 5011                   |
| No. of parameters          | 379                    |
| Transmission: $t_{\text{min}}$, $t_{\text{max}}$ | 0.998, 0.999          |
| $R_1(F)$                   | 0.109                  |
| $wR_2(F^2)$                | 0.297                  |
| CCDC-no.                   | 1901217                |
5 Quantum Chemical Calculations

5.1 Optimisation of N1-N15, NMR

All quantum chemical calculations were performed with Gaussian 09 Revision D.01. Prior to the calculation of NMR, the geometry of each structure drawn was optimized using B3LYP (noncharged singlet without solvation). Minima character of optimised structures was proven by vibrational analysis. NMR calculations were performed with same method and basis set, GIAO approach and continuum (PCM model) dichloromethane solvent. Shieldings of TMS calculated in the same manner was taken as a reference.

Size of bars indicates number of protons:

![Size of bars indicating number of protons](image)

Presentation: top: experimental NMR, bottom: calculated NMR

Nanostructure N1

![Nanostructure N1](image)

**Figure S179:** Experimental (top) and calculated (bottom) $^1$H NMR spectra of nanostructure N1.
Nanostructure N2

![Nanostructure N2](image1)

Figure S180: Experimental (top) and calculated (bottom) $^1$H NMR spectra of nanostructure N2.

Nanostructure N3

![Nanostructure N3](image2)

Figure S181: Experimental (top) and calculated (bottom) $^1$H NMR spectra of nanostructure N3.

Nanostructure N7

![Nanostructure N7](image3)

Figure S182: Experimental (top) and calculated (bottom) $^1$H NMR spectra of nanostructure N7.
Nanostructure N8

Figure S183: Experimental (top) and calculated (bottom) $^1$H NMR spectra of nanostructure N8.

Nanostructure N9

Figure S184: Experimental (top) and calculated (bottom) $^1$H NMR spectra of nanostructure N9.

Nanostructure N10

Figure S185: Experimental (top) and calculated (bottom) $^1$H NMR spectra of nanostructure N10.
Nanostructure N11

Figure S186: Experimental (top) and calculated (bottom) $^1$H NMR spectra of nanostructure N11.

Nanostructure N12

Figure S187: Experimental (top) and calculated (bottom) $^1$H NMR spectra of nanostructure N12.

Nanostructure N13

Figure S188: Experimental (top) and calculated (bottom) $^1$H NMR spectra of nanostructure N13.
Nanostructure N14

![Nanostructure N14](image)

**Figure S189:** Experimental (top) and calculated (bottom) $^1$H NMR spectra of nanostructure N14.

Nanostructure N15

![Nanostructure N15](image)

**Figure S190:** Experimental (top) and calculated (bottom) $^1$H NMR spectra of nanostructure N15.
5.2 Nuclear-Independent Chemical Shift (NICS)

For calculation of NICS\textsuperscript{28} values so called ghost atoms (Bq) were placed in the center of every ring and NMR was calculated in the same way as discussed above but without solvent.

Benzene (for six-membered rings), triphenylene and tetraphenylene (N4, for eight-membered rings) were used as reference compounds. The NMR chemical shifts obtained for each ghost atom (Bq) were inverted to get the respective NICS values.
5.3 Calculation of Mechanism for CDHF of P4
Calculation of Mechanism for CDHF of P4 was performed with B3LYP/def2-SVP\textsuperscript{29} and Grimme’s D3BJ dispersion correction\textsuperscript{30-32}.

| Structure | Total energy (Hartree) | Relative energy (kcal/mol) |
|-----------|-----------------------|---------------------------|
| E         | -1614.43894           | -6.1                      |
| TS1       | -1614.38999           | 24.6                      |
| A         | -1614.41068           | 11.6                      |
| TS2       | -1614.38835           | 25.6                      |
| Spiro     | -1614.42922           | 0.0                       |
| TS3       | -1614.39090           | 24.0                      |
| B         | -1614.41491           | 9.0                       |
| TS4       | -1614.39462           | 21.7                      |
| P         | -1614.44909           | -12.5                     |
5.4 HOMO-LUMO, TD and Singlet-Triplet gap.

HOMO-LUMO gap was taken from final structures optimised on B3LYP/6-311G as discussed above. As expected, HOMO-LUMO gap is significantly larger than optical gap (over 1 eV) and might be closer to electrochemical gap. Even in this case trend is described correctly. Singlet-Triplet gap was calculated as difference between B3LYP/6-311G energy of optimised closed-shell singlet and energy of triplet state in the same geometry (vertical excitation). Despite such direct excitation is forbidden, these results are very close to measured gap for all compounds except N15. Interestingly, in TD-B3LYP calculations for triplet excited states only second excitation has appropriate energy, while the first triplet excitation was found to be too low. Reason of this artefact wasn’t located.

TD-B3LYP calculations for singlet excited states was found to overestimate the gap on 0.3-0.7 eV, whenever trend is described correctly. Increasing the basis set to cc-pVTZ had almost no effect on the computed values despite significant increase in computation time. Also no effect was seen from changing B3LYP to PBE0 functional, despite these calculations shows excellent agreement for low-gap PAH. Finally, the most reliable are TD-PBE/6-311G calculations with MAE of 0.06 eV and maximal error of 0.16 eV.

Table S10. Optical gap, TD, singlet-triplet and HOMO-LUMO gap.

|     | Opt. Gap | TD-PBE/6-311 | TD-B3LYP/6-311G | S-T gap | H-L gap |
|-----|----------|--------------|-----------------|---------|---------|
| N1  | 2.53     | 2.55         | 2.89            | 2.48    | 3.68    |
| N2  | 2.99     | 3.07         | 3.45            | 2.91    | 4.11    |
| N3  | 2.88     | 2.97         | 3.33            | 2.67    | 3.95    |
| N7  | 4.07     | 4.11         | 4.71            | 3.88    | 5.32    |
| N8  | 3.94     | 4.10         | 4.70            | 3.89    | 5.31    |
| N9  | 3.26     | 3.36         | 3.74            | 3.21    | 4.45    |
| N10 | 3.31     | 3.44         | 3.83            | 3.35    | 4.59    |
| N11 | 2.92     | 2.87         | 3.22            | 2.85    | 3.96    |
| N12 | 2.88     | 2.90         | 3.26            | 2.64    | 3.89    |
| N13 | 3.40     | 3.46         | 3.85            | 3.39    | 4.64    |
| N14 | 2.92     | 2.92         | 3.29            | 2.92    | 4.04    |
| N15 | 2.43     | 2.43         | 2.69            | 1.91    | 3.01    |

*All values are in eV.
Figure S191: Linear correlation between experimentally obtained optical gap and HOMO-LUMO gap.
5.5 XYZ Coordinates of Optimized Structures

Nanostructure N1

66
symmetry d3

C  -0.703403000  1.233800000  0.063056000
C  -1.420203000 -0.007735000 -0.063056000
C  -0.716800000 -1.226065000  0.063056000
C  -0.716800000 -1.226065000 -0.063056000
C  -1.420203000 -0.007735000  0.063056000
C  -0.703403000  1.233800000 -0.063056000
C  -1.337887000  2.492681000  0.493961000
C  -1.489781000 -2.409885000  0.493961000
C  -0.644005000  3.724444000 -0.344288000
C  -1.207387000  4.903847000  0.879277000
C  -0.886287000 -3.450085000  1.235632000
C  -3.547465000 -1.304497000  0.344288000
C  -4.850549000 -1.406296000  0.879277000
C  -1.337887000 -2.492681000  0.957495000
C  -3.547465000  1.235632000  0.879277000
C  -2.827699000 -0.087696000 -0.493961000
H  -2.873775000  1.860595000 -1.425039000
H  -3.048210000  1.558465000 -1.425039000
C  -0.174435000 -3.419060000 -1.425039000
C  -2.873775000  1.860595000  1.425039000
H  -0.174435000 -3.419060000  1.425039000
H  -3.048210000  1.558465000  1.425039000
C  -4.719774000 -3.499918000  0.787369000
Nanostructure N2

66
symmetry c1

C -1.025255000 0.569238000 -0.049885000
C 0.057323000 -0.269540000 0.302390000
C 1.390894000 0.133128000 0.035584000
C 1.630733000 1.485442000 -0.321691000
C 0.552681000 2.372976000 -0.405041000
C -0.767429000 1.949392000 -0.255926000
C -1.846317000 2.914729000 0.302390000
C -1.919106000 -2.076027000 -1.315014000
C -1.011055000 -2.889815000 -0.622073000
C -0.327982000 -3.907644000 -1.301079000
C -0.502906000 -4.076778000 -2.671923000
C -1.361808000 -3.230494000 -3.373350000
C -2.075104000 -2.243165000 -2.698734000
C -1.634247000 4.297010000 -0.268088000
C -2.609658000 5.216939000 0.091485000
C -3.822613000 4.772143000 0.625418000
C -4.073074000 3.411956000 0.730957000
C -3.116127000 2.465216000 0.321648000
C -2.412614000 0.125198000 -0.122296000
C 2.987239000 1.996112000 -0.443844000
C -3.431784000 1.049240000 0.229044000
C -4.761029000 0.609703000 0.343549000
C -5.108365000 -0.691664000 0.012441000
C -4.141410000 -1.546601000 -0.509576000
C -2.804207000 -1.141035000 -0.607748000
C 3.242469000 3.307322000 -0.894346000
C 4.520423000 3.842358000 -0.855604000
C 5.825660000 3.073800000 -0.368360000
C 5.362008000 1.761876000 0.020070000
C 4.077029000 1.188504000 -0.050255000
C 0.024828000 -1.191938000 2.568322000
C 3.855167000 -0.225388000 0.189881000
Nanostructure N3

66
symmetry c1

C  0.855344000  -0.886260000  -0.674592000
C  0.696656000  0.471540000  -0.256508000
C  -0.609183000  1.013733000  -0.222167000
C  -1.717493000  0.112400000  -0.019516000
C  -1.555125000  -1.242450000  -0.394815000
C  -0.271314000  -1.679178000  -0.801684000
C  3.016312000  -0.377641000  1.549598000
C  -0.747583000  2.425748000  -0.628160000
C  0.413698000  3.242746000  -0.752451000
C  0.292772000  4.522959000  -1.336273000
C  -0.924459000  5.001026000  -1.793717000
C  -2.064459000  4.189613000  -1.699057000
C  -1.970515000  2.926709000  -1.137959000
C  2.961172000  -0.277685000  2.952028000
C  3.097868000  -1.401356000  3.766470000

C  4.944936000  -1.100652000  0.366454000
C  4.765077000  -2.473518000  0.424999000
C  3.482405000  -3.005128000  0.271854000
C  2.398224000  -2.155070000  0.118495000
C  2.542251000  -0.755330000  0.366454000
C  0.252222000  -2.181874000  3.506799000
C  -0.777979000  -3.406812000  3.097038000
C  -1.026582000  -3.635614000  1.746509000
C  -0.759577000  -2.641227000  0.796997000
C  0.224620000  -1.405753000  1.201330000
C  0.754866000  -3.445223000  -0.542108000
C  0.753178000  -2.542251000  -0.743941000
H  0.754866000  -3.445223000  -0.542108000
H  0.753178000  -2.542251000  -0.743941000
Nanostructure N7

Symmetry c2h

C   2.527270000  3.182858000  3.122407000
C   2.047335000  2.145546000  2.323180000
C   0.918558000  2.316374000  1.504032000
C   0.256181000  3.564081000  1.501417000
C   0.747224000  4.597612000  2.316963000
C   1.873869000  4.416362000  3.118683000
C   0.424151000  1.154648000  0.705068000
C   0.424151000  1.154648000 -0.705068000
C   0.000000000  0.000000000 -1.376900000
C  -0.424151000 -1.154648000 -0.705068000
C  -0.424151000 -1.154648000  0.705068000
C   0.000000000  0.000000000  1.376900000
C  -0.918558000 -2.316374000 -1.504032000
C  -0.256181000 -3.564081000 -1.501417000
C  -0.747224000 -4.597612000 -2.316963000
C  -1.873869000 -4.416362000 -3.118683000
C  -2.527270000 -3.182858000 -3.122407000
C  -2.047335000 -2.145546000 -2.323180000
C  -0.918558000 -3.564081000  1.504032000
C  -0.256181000 -4.597612000  2.316963000
C  -0.747224000 -4.416362000  3.118683000
C  -2.183400000 -4.085226000  1.387407000
C  -1.873869000 -3.182858000 -3.122407000
C  -0.918558000 -2.316374000  1.504032000
C  -0.256181000 -4.597612000  2.316963000
C  -0.747224000 -4.416362000  3.118683000
C  -2.183400000 -4.085226000  1.387407000
C   0.987440000 -3.800977000  0.706293000
C  -0.918558000 -2.316374000  1.504032000
C   0.256181000 -3.564081000 -1.376900000
C  -0.424151000  1.154648000 -0.705068000
C   0.747224000  4.597612000  2.316963000
C   1.873869000  4.416362000  3.118683000
C   2.527270000  3.182858000  3.122407000
C   2.047335000  2.145546000  2.323180000
C  -0.256181000 -3.564081000  1.504117000
C  -0.747224000 -4.597612000  2.316963000
C  -1.873869000 -4.416362000  3.118683000
C  -2.527270000 -3.182858000  3.122407000
C  -2.047335000 -2.145546000  2.323180000
H   3.402960000  3.029187000  3.739005000
H   2.550945000  1.187955000  2.321476000
H   0.237124000  5.551864000  2.311234000
H   2.237197000  5.230133000  3.732262000
H   0.000000000  0.000000000 -2.458846000
H  -0.237124000 -5.551864000 -2.311234000
H  -2.237197000 -5.230133000 -3.732262000
H  -3.402960000 -3.029187000 -3.739005000
H  -2.550945000 -1.187955000 -2.321476000
H  -2.178370000  4.084550000 -2.469447000
Nanostructure N8

68
symmetry c1

C -3.868199000 -3.115855000 -2.183606000
C -2.726787000 -2.319947000 -2.091697000
C -2.491922000 -1.503595000 -0.972150000
C -3.432012000 -1.500827000 0.082089000
C -4.573599000 -2.313623000 -0.021222000
C -4.797656000 -3.112189000 -1.142291000
C -1.230183000 0.705128000 -0.912804000
C -1.230223000 0.705062000 -0.912826000
C 0.000041000 1.376862000 -0.919871000
C 1.230184000 0.705135000 -0.912802000
C 1.230223000 0.705055000 -0.912828000
C 0.000041000 1.376855000 -0.919874000
C 2.491923000 1.503602000 -0.912800000
C 3.432013000 1.500825000 0.082094000
C 4.573601000 2.313619000 -0.021214000
C 4.797659000 3.112192000 -1.142277000
C 3.868202000 3.115867000 -2.183592000
C 2.726788000 2.319960000 -2.091687000
C -3.223853000 -0.706139000 1.331012000
C -3.223853000 0.706139000 1.331014000
C -3.223918000 0.706270000 1.330948000
C -3.078964000 1.387519000 2.551422000
C -2.928170000 0.698024000 3.754081000
C -2.928097000 -0.697645000 3.754145000
C -3.078825000 -1.387267000 2.551549000
C -3.223919000 -0.706276000 1.330945000
C -3.078966000 -1.387530000 2.551417000
C -2.928171000 -0.698038000 3.754079000
C -2.928096000 0.697631000 3.754146000
C -3.078824000 1.387257000 2.551553000
C -2.492007000 1.503459000 -0.972288000
C 2.492007000 -1.503454000 -0.972294000
C -3.432107000 1.500800000 0.081940000
C  -4.573724000  2.313537000  -0.021493000
C  -4.797803000  3.111934000  -1.142691000
C  -3.868341000  3.115483000  -2.184003000
C  -2.726896000  2.319636000  -2.091957000
C  -2.726894000  2.319624000  -2.091968000
H  -4.029863000  -3.729939000  -3.059668000
H  -2.045920000  -2.318169000  -2.897464000
H  -5.291116000  -2.307392000  0.788641000
H  -5.686899000  -3.723260000  -1.201535000
H  -0.000740000  2.458768000  -0.921065000
H   0.000750000  -2.458762000  -0.921072000
H   5.291120000  2.307382000  0.788648000
H   5.686814000  3.723261000  -1.201519000
H   4.029866000  3.729956000  -3.059650000
H   2.004593000  2.318189000  -2.897454000
H  -3.078159000  2.469538000  2.546530000
H  -2.809025000  -1.245132000  4.679762000
H  -3.077919000  -2.469287000  2.546783000
H  -3.078163000  -2.469549000  2.546545000
H   2.809159000  -1.245624000  4.679644000
H   3.077917000  2.469276000  2.546790000
H  -5.291250000  2.307390000  0.788363000
H  -5.686878000  3.722964000  -1.202018000
H  -4.030025000  3.729433000  -3.060142000
H  -2.004692000  2.317773000  -2.897715000
H   5.291247000  -2.307402000  0.788355000
H   5.687700000  -3.722968000  -1.202032000
H   4.030020000  -3.729421000  -3.060158000
H   2.004691000  -2.317755000  -2.897727000
H  -2.809158000  1.245607000  4.679649000
H   2.809023000  1.245114000  4.679765000
Nanostructure N9

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | 1.602102000 | -1.398552000 | -0.077421000 |
| C    | 0.329532000 | -1.924649000 | -0.268943000 |
| C    | -0.782130000 | -1.120544000 | -0.564992000 |
| C    | -0.654174000 | 0.274555000 | -0.497665000 |
| C    | 0.624326000 | 0.851238000 | -0.197320000 |
| C    | 1.783682000 | 0.013583000 | -0.187320000 |
| C    | 3.103011000 | 0.638291000 | -0.403787000 |
| C    | -2.044290000 | -1.819665000 | -0.964868000 |
| C    | -1.829269000 | 1.109321000 | -0.916342000 |
| C    | 2.671325000 | -2.357191000 | 0.337420000 |
| C    | 2.904790000 | -3.540820000 | -0.384311000 |
| C    | 3.856046000 | -4.231495000 | 1.215509000 |
| C    | 4.586468000 | -3.028920000 | 1.948189000 |
| C    | 4.355666000 | 1.851238000 | -0.187320000 |
| C    | 3.407988000 | 2.705136000 | -1.815857000 |
| C    | 2.778106000 | 2.659092000 | -2.544200000 |
| C    | 1.722185000 | 1.869360000 | -2.093008000 |
| C    | 3.252231000 | 2.045149000 | 0.174399000 |
| C    | 4.491989000 | 2.640756000 | -0.597179000 |
| C    | 5.564560000 | 1.887035000 | -1.043798000 |
| C    | 5.413696000 | 0.502856000 | -1.203461000 |
| C    | 4.204688000 | 0.016490000 | 0.898121000 |
| C    | 3.372020000 | -1.810461000 | 1.101922000 |
| C    | 2.284243000 | 4.171384000 | 0.628660000 |
| C    | 1.215978000 | 4.933318000 | 1.071072000 |
| C    | -0.065474000 | 4.368686000 | 1.092035000 |
| C    | 0.255878000 | 3.066312000 | 0.657772000 |
| C    | 0.808979000 | 2.273735000 | 0.167211000 |
| C    | 3.146727000 | -3.339402000 | 1.089300800 |
| C    | 3.252231000 | 2.045149000 | 0.174399000 |
| H    | 0.187475000 | 2.992996000 | 0.182478000 |
| H    | 2.350373000 | -3.723966000 | 1.295507000 |
| H    | 4.026556000 | -5.369509000 | 0.521920000 |
| H    | 5.238741000 | -4.948393000 | 1.552078000 |
| H    | 4.910083000 | -2.876334000 | 2.858547000 |
| H    | 3.229724000 | -1.237104000 | 2.089190000 |
| H    | -0.014661000 | 1.976224000 | 0.084563000 |
| H    | -4.794436000 | 3.316270000 | -2.164920000 |
| H    | 2.761192000 | 3.234278000 | 3.545270000 |
| H    | -0.794503000 | 1.840399000 | 2.648231000 |
Nanostructure N10

68
symmetry c1
C  1.774584000  1.422431000  0.086569000
C  1.556111000  0.027052000 -0.093044000
C  0.228264000 -0.408028000 -0.429989000
C  -0.856714000  0.485862000 -0.393052000
C  -0.641740000  1.841429000 -0.021068000
C  0.661518000  2.277654000  0.165098000
C  -1.750932000  2.826951000  0.150543000
C  -0.028509000 -1.777471000 -0.993454000
C  0.536793000 -2.106038000 -2.236255000
C  0.357671000 -3.369790000 -2.802324000
C  -0.391840000 -4.330120000 -2.124071000
C  -0.970979000 -4.013440000 -0.895348000
C  -0.812738000 -2.740948000 -0.321517000
C  -1.730116000  4.050952000 -0.540497000
C  -2.739149000  4.998116000 -0.351994000
C  -3.785990000  4.740105000  0.535752000
C  -3.815051000  3.529104000  1.233423000
C  -2.808648000  2.581901000  1.042391000
C  3.137462000  1.971435000  0.129307000
C  -2.224559000  0.071480000 -0.854015000
C  3.376475000  3.366378000  0.151235000
C  4.657829000  3.887594000  0.087730000
C  5.756290000  3.021987000 -0.016901000
C  5.549601000  1.653075000 -0.029960000
C  4.252406000  1.096416000  0.061059000
C  -2.745923000  0.662988000 -2.016770000
C  -4.035381000  0.378566000 -2.461909000
C  -4.839182000 -0.501416000 -1.735099000
C  -4.334281000 -1.102185000 -0.582993000
C  -3.028824000 -0.838556000 -0.134721000
C  4.031822000 -0.350242000  0.138448000
C  -2.529549000 -1.536792000  1.085416000
C  -3.167104000 -1.349091000  2.321908000

H  4.601821000  3.712747000 -0.529604000
H  6.500874000  2.368846000 -1.292193000
H  6.229510000 -0.095166000 -1.586527000
H  4.101985000 -1.158183000 -1.072074000
H  -5.204144000 -2.564816000  0.057541000
H  -5.161786000 -3.912583000 -2.017814000
H  -3.116659000 -3.918829000 -3.439933000
H  -1.141820000 -2.599023000 -2.749740000
H  3.276209000  4.596242000  0.665175000
H  1.376914000  5.944786000  1.419685000
H  -0.907181000  4.936499000  1.465623000
H  -1.241474000  2.646068000  0.726893000
H  -3.332331000  2.167844000  2.283004000
H  -3.695534000  0.976421000  4.419294000
H  -3.808954000 -1.510193000  4.442198000
H  -3.561763000 -2.768550000  2.324696000
Nanostructure N11

68
symmetry c2

C  
-2.750339000  -2.039772000  3.460995000
C  -1.690912000  -2.944127000  3.372785000
C  -1.058379000  -3.151791000  2.145957000
C  -1.458806000  -2.454375000  0.995668000
C  5.118473000  -1.235141000  0.328168000
C  4.933454000  -2.594688000  0.508843000
C  3.631675000  -3.109863000  0.536409000
C  2.707528000  -0.880084000  0.096495000
H  0.805288000  3.319257000  0.404624000
H  1.132505000  -1.363594000  -2.749851000
H  0.802436000  -3.596161000  -3.761578000
H  -0.533209000  -5.314300000  -0.536409000
H  -1.568835000  -4.749429000  -0.373523000
H  -0.929022000  -4.250366000  -1.240607000
H  -2.709282000  5.931092000  0.899715000
H  -4.568835000  5.472329000  0.682881000
H  -4.618833000  3.324270000  1.928517000
H  -2.829353000  1.653327000  1.595046000
H  2.547998000  4.055816000  0.198215000
H  4.805985000  4.959079000  0.102690000
H  6.759988000  3.418854000  -0.090249000
H  6.406937000  1.004035000  -0.122300000
H  -2.129468000  1.359691000  -2.568235000
H  -4.410459000  0.845425000  -3.362930000
H  -5.844934000  -0.724889000  -2.065620000
H  -4.944937000  -1.800719000  -0.025990000
H  -3.996581000  -0.656497000  2.383433000
H  -3.249238000  -1.873662000  4.406576000
H  -1.359798000  -3.484869000  4.249374000
H  -0.243727000  -3.860413000  2.073808000
H  6.123248000  -0.843953000  0.370657000
H  5.785986000  -3.243962000  0.657493000
H  3.462509000  -4.161990000  0.722920000
H  1.564584000  -2.685143000  0.397067000

Nanostructure N11

68
symmetry c2

C  0.698246000  1.212826000  0.156364000
C  -0.698167000  1.212897000  -0.156963000
C  -1.417964000  0.000410000  -0.000350000
C  -0.698246000  -1.212826000  0.156364000
C  0.698167000  -1.212897000  -0.156963000
C  1.417964000  0.000410000  -0.000350000
C  2.914965000  -0.000151000  -0.000256000
C  -2.914965000  0.000151000  -0.000256000
C  -3.834066000  -0.809525000  -0.896134000
C  -5.029656000  -0.807302000  -0.898348000
C  -5.733136000  0.000511000  -0.000158000
C  -5.029406000  0.808154000  0.897949000
C  -3.633791000  0.810040000  0.895632000
C  3.634066000  0.809525000  -0.896134000
## Nanostructure N12

| 68 | symmetry c1 |
|---|---|
| C | -1.425401000 | -0.116826000 | -0.072313000 |
| C | -0.647595000 | -1.285128000 | 0.114307000 |
| C | 0.765197000 | 1.214059000 | 0.066970000 |
| C | 1.434255000 | 0.013489000 | 0.065911000 |
| C | 0.647616000 | 1.285128000 | 0.114307000 |
| C | 0.765197000 | 1.221084000 | 0.071961000 |
| C | 1.434255000 | 0.013489000 | 0.065911000 |
| C | -1.525708000 | 2.437952000 | -0.085423000 |
| C | 1.298207000 | 2.568197000 | 0.085785000 |
| C | 1.239200000 | 3.455697000 | 1.159778000 |
| C | 0.725920000 | 4.715356000 | 1.149961000 |
| C | 2.507280000 | 5.113047000 | 0.061711000 |
| C | 2.624040000 | 4.241099000 | -1.016069000 |
| C | 2.083940000 | 1.214059000 | 0.066970000 |
| C | 2.355193000 | 2.763300000 | 0.999832000 |
| C | -3.073727000 | 3.960001000 | 1.017570000 |
| C | -2.976029000 | 4.853415000 | -0.052378000 |
| C | -2.150893000 | 4.542485000 | -1.136723000 |
| C | -1.429622000 | 3.347301000 | -1.151040000 |
| C | -2.872227000 | -0.309629000 | -0.326520000 |
| C | 2.893187000 | -0.047223000 | 0.317956000 |
| C | -3.650998000 | 0.627166000 | -1.048129000 |
| C | -4.982577000 | 0.393357000 | -1.356640000 |
| C | -5.596415000 | -0.802495000 | -0.963879000 |
| C | -4.850981000 | -1.755534000 | -0.290122000 |
| C | -3.492976000 | -1.542012000 | 0.032741000 |
| C | 3.586264000 | 0.959546000 | 1.032834000 |
| C | 4.933510000 | 0.847174000 | 1.341530000 |
| C | 5.651070000 | -0.291828000 | 0.955971000 |
| C | 4.993201000 | -1.311041000 | 0.287968000 |
| C | 3.621701000 | -1.221078000 | -0.035704000 |
| C | -2.707303000 | -2.572652000 | 0.708845000 |
| C | 2.932030000 | -2.320952000 | -0.707310000 |
| C | 3.630832000 | -3.345110000 | -1.385921000 |
| C | 2.961268000 | -4.372388000 | -2.029989000 |
| C | 1.557499000 | -4.389492000 | -2.035286000 |
| C | 0.852430000 | -3.391696000 | -1.384553000 |
| C | 1.513781000 | -2.352723000 | -0.683879000 |
| C | -3.315930000 | -3.651520000 | 1.393289000 |
| C | -2.552585000 | -4.611923000 | 2.041368000 |
| C | -1.152849000 | -4.504187000 | 2.044348000 |
| C | -0.539911000 | -3.450906000 | 1.387652000 |
| C | -1.291779000 | -2.477926000 | 0.683719000 |
| H | 0.517454000 | 3.155410000 | 2.002933000 |
| H | 1.580631000 | 5.385241000 | 1.987397000 |
| H | 2.971382000 | 6.090390000 | 0.052830000 |
| H | 3.284307000 | 4.540672000 | -1.864113000 |
| H | 2.228122000 | 2.305011000 | -1.836005000 |
| H | 2.439452000 | 2.070662000 | 1.826797000 |
| H | -3.708394000 | 4.192665000 | 1.862703000 |
| H | -3.533462000 | 5.780679000 | -0.040639000 |
Nanostructure N13

68

symmetry c1

C  1.691393000  -1.346126000  -0.193388000
C  1.709798000   0.069943000  -0.044315000
C  0.505533000   0.796501000  -0.334744000
C  -0.710496000  0.114694000  -0.544331000
C  -0.741012000  3.147133000   0.280253000
C  0.515041000  -2.001817000  -0.656643000
C  0.231980000   3.147133000  -0.544331000
C  -0.227942000   4.525038000   0.545750000
C  0.515563000   5.064108000  -0.997810000
C  1.255655000   4.214268000  -1.824037000
C  1.256287000   2.837404000  -1.594382000
C  -3.052651000  -0.211308000   0.285520000
C  -4.171702000  -2.845451000  -0.124094000
C  -2.692730000  -3.731786000  -0.948360000
C  -3.235142000  -3.800271000  -1.882960000
C  -2.112828000  -2.986856000  -1.729867000
C  2.944937000  -2.113070000  -0.223620000
C  -1.966771000   0.847222000  -0.919353000
C  2.964162000  -3.493333000  -0.535415000
C  4.151594000  -4.193667000  -0.668341000
C  5.374404000  -3.526080000  -0.507429000
C  5.381891000  -2.178244000  -0.189930000
C  4.182370000  -1.448459000  -0.020545000
C  -2.066659000   1.449321000  -2.183492000
C  -3.210263000   2.150077000  -2.562693000
C  -4.280332000   2.263779000  -1.672941000
C  -4.199948000   1.660708000  -0.418511000
C  -3.058445000   0.940082000  -0.029685000
C  4.179012000  -0.048253000   0.412550000
| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| C    | -3.022270 | 0.305037  | 1.322160  |
| C    | -3.064899 | 1.110882  | 2.471630  |
| C    | -3.068530 | 0.550659  | 3.749649  |
| C    | -3.038042 | -0.837074 | 1.469801  |
| C    | -3.012296 | -1.650342 | 3.895370  |
| C    | -3.002564 | -1.100290 | 1.479801  |
| H    | 0.411902  | -3.068546 | 0.400181  |
| H    | 0.805069  | 2.735059  | 1.099298  |
| H    | 0.805852  | 5.175322  | 0.699535  |
| H    | 0.516374  | 6.131702  | 0.848040  |
| H    | 1.832381  | 4.621793  | 2.644118  |
| H    | -4.973543 | -2.785076 | 0.848040  |

**Nanostructure N14**

64

symmetry c1

| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| C    | -0.076062 | -0.495652 | -0.090432 |
| C    | 0.899981  | 0.561940  | 0.027009  |
| C    | 0.420126  | 1.890648  | 0.247107  |
| C    | 0.894194  | 2.082261  | 0.692815  |
| C    | 1.844426  | 1.074188  | 0.612004  |
| C    | -1.458430 | -0.157124 | 0.015763  |
| C    | -2.482514 | -0.932267 | -0.657451 |
| C    | 1.207101  | 3.056222  | -0.190204 |
| C    | 2.324164  | 2.843112  | -1.038888 |
| C    | 2.902309  | 3.952663  | -1.692694 |
| C    | 2.450670  | 5.243670  | -1.464462 |
| C    | 1.410310  | 5.463487  | -0.550933 |
**Nanostructure N15**

64
symmetry d2

| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| C    | -0.168557000 | 1.223160000 | -0.692995000 |
| C    | 0.168557000  | 1.223160000 | 0.692995000  |
| C    | 0.000000000  | 0.000000000 | 1.402129000  |
| C    | -0.168557000 | -1.223160000 | 0.692995000  |
| C    | 0.168557000  | -1.223160000 | -0.692995000 |
| C    | 0.000000000  | 0.000000000 | -1.402129000 |
| C    | 0.000000000  | 0.000000000 | -2.850729000 |
| C    | 0.357825000  | 1.182468000 | 3.566037000  |
| C    | 0.329564000  | 1.159638000 | 4.969947000  |
| C    | 0.000000000  | 0.000000000 | 5.662240000  |
| C    | -0.168557000 | -1.223160000 | -0.692995000 |
| C    | 0.168557000  | -1.223160000 | 2.850729000  |
| C    | 0.000000000  | 0.000000000 | -2.850729000 |
| C    | 0.357825000  | 1.182468000 | -3.566037000 |
| C    | 0.329564000  | 1.159638000 | -4.969947000 |
| C    | 0.000000000  | 0.000000000 | -5.662240000 |
| C    | -0.168557000 | 1.223160000 | -4.969947000 |
| C    | 0.168557000  | 1.223160000 | -5.662240000 |
| C    | -0.329564000 | -1.159638000 | 0.700940000  |
| C    | -0.357825000 | -1.182468000 | 1.402618000  |
| C    | -0.329564000 | -1.159638000 | -2.850729000 |
| C    | -0.357825000 | -1.182468000 | -3.566037000 |
| C    | 0.329564000  | 1.159638000 | -4.969947000 |
| C    | 0.357825000  | 1.182468000 | -3.566037000 |
| C    | 0.000000000  | 0.000000000 | -5.662240000 |
| C    | -0.329564000 | 1.159638000 | -4.969947000 |
| C    | -0.357825000 | 1.182468000 | -3.566037000 |
| C    | -0.738473000 | 2.369827000 | -1.402618000 |
| C    | -0.738473000 | -2.369827000 | 1.402618000  |
| C    | -0.818874000 | 2.358387000 | 2.822219000  |
| C    | -1.414615000 | 3.463130000 | -3.475929000 |
| C    | -1.949563000 | 4.525431000 | 2.767852000  |
| C    | -1.936132000 | 4.501613000 | -1.363844000 |
| C    | -1.349195000 | 3.439335000 | -0.700940000 |
| C    | -0.818874000 | -2.358387000 | 2.822219000  |
| C    | -1.414615000 | -3.463130000 | 3.475929000  |
| C    | -1.949563000 | -4.525431000 | 2.767852000  |
| C    | -1.936132000 | -4.501613000 | -1.363844000 |
| C    | -1.349195000 | -3.439335000 | -0.700940000 |
| C    | -1.936132000 | -4.501613000 | -1.363844000 |
| C    | -1.949563000 | -4.525431000 | -2.767852000 |
| C    | 1.414615000  | -3.463130000 | -3.475929000 |
| C    | 0.818874000  | -2.358387000 | -2.822219000 |
| C    | 0.738473000  | -2.369827000 | -1.402618000 |
| C    | 1.936132000  | 4.501613000 | 1.363844000  |
| C    | 1.949563000  | 4.525431000 | 2.767852000  |
| C    | 1.414615000  | 3.463130000 | 3.475929000  |
| C    | 0.818874000  | 2.358387000 | 2.822219000  |
| C    | 0.738473000  | 2.369827000 | 1.402618000  |
| H    | -1.370077000 | 3.414601000 | 0.376659000  |
| H    | 1.370077000  | -3.414601000 | 0.376659000  |
| H    | -1.370077000 | -3.414601000 | -0.376659000 |
| H    | 1.370077000  | 3.414601000 | -0.376659000 |
| H    | 0.573132000  | 2.047851000 | 5.532191000  |
| H    | 0.000000000  | 0.000000000 | 6.744074000  |
| H    | -0.573132000 | -2.047851000 | 5.532191000  |
| H    | 0.573132000  | -2.047851000 | -5.532191000 |
| H    | 0.000000000  | 0.000000000 | -6.744074000 |
|   | X         | Y         | Z         |
|---|-----------|-----------|-----------|
| H | -0.573132 | 2.047851  | -5.532191 |
| H | -1.488067 | 3.473197  | -4.552790 |
| H | -2.404501 | 5.352931  | -3.295685 |
| H | -2.398232 | 5.300682  | -0.799900 |
| H | -1.488067 | 3.473197  | 4.552790  |
| H | -2.404501 | 5.352931  | 3.295685  |
| H | -2.398232 | 5.300682  | 0.799900  |
| H | -1.488067 | 3.473197  | -4.552790 |
| H | 2.404501  | 5.352931  | 3.295685  |
| H | 2.398232  | 5.300682  | 0.799900  |

**E**

67 symmetry c1

|   | X         | Y         | Z         |
|---|-----------|-----------|-----------|
| C | 0.937225  | 0.985096  | -0.033080 |
| C | -0.476357 | 1.392615  | 0.241875  |
| C | -1.484484 | -0.923242 | 0.169736  |
| C | -1.114660 | -0.440768 | -0.055025 |
| C | 0.212378  | -1.383896 | -0.198039 |
| C | 1.268591  | -0.473799 | -0.095096 |
| C | 0.454300  | -2.729380 | -0.704309 |
| C | 1.791150  | -3.199236 | -0.776185 |
| C | 2.025203  | -4.486370 | -1.318661 |
| C | 0.989952  | -5.265506 | -1.803420 |
| C | 2.884434  | -2.331897 | -0.349079 |
| C | 2.641906  | -0.941483 | -0.072459 |
| C | 3.771089  | -0.106849 | 0.245592  |
| C | 5.048766  | -0.655307 | 0.278721  |
| C | 5.267457  | -2.017328 | 0.035356  |
| C | 4.197935  | -2.837840 | -0.266822 |
| H | 1.244143  | 1.412366  | 0.938340  |
| H | 1.591136  | 1.506673  | -0.742743 |
| H | 3.041157  | -4.869240 | -1.395524 |
| H | 1.201968  | -6.249960 | -2.225211 |
| H | 5.889097  | -0.005198 | 0.528805  |
| H | 6.277451  | -2.428267 | 0.091980  |
| H | 4.382183  | -3.896041 | -0.440106 |
| C | -0.583700 | -3.522377 | 1.252698  |
| C | -0.325288 | -4.769508 | -1.790454 |
| H | -1.602079 | -3.139244 | 1.277272  |
| H | -1.139661 | -5.357577 | -2.218251 |
| C | 3.703538  | 1.343855  | 0.604211  |
| C | 4.018749  | 2.324562  | -0.347412 |
| C | 3.379321  | 1.742929  | 1.910308  |
| C | 3.978000  | 3.681453  | -0.008707 |
| C | 3.333738  | 3.098590  | 2.247397  |
| C | 3.626579  | 4.071973  | 1.286364  |
|  | X          | Y          | Z          |
|---|------------|------------|------------|
| H | 4.293923000| 2.020564000| -1.360211000|
| H | 3.160086000| 0.982888000| 2.664387000 |
| H | 4.229408000| 3.137418000| -0.671907000|
| H | 3.160086000| 0.982888000| 2.664387000 |
| C | -0.803139000| 3.760426000| -0.508782000|
| C | 0.210255000| 3.752011000| -0.627591000|
| C | 2.175867000| 3.137418000| -0.671907000|
| C | 0.108272000| 5.060771000| -0.924416000|
| C | -2.463318000| 4.483322000| -0.989182000|
| C | -1.455919000| 5.425247000| -1.116152000|
| H | 1.255789000| 3.487849000| -0.477301000|
| H | 0.680886000| 5.809933000| -1.011349000|
| H | 3.494849000| 4.802938000| -1.127608000|
| H | 1.711361000| 6.458936000| -1.358804000|
| C | 2.873213000| 0.821623000| -0.092584000|
| C | 3.225782000| 2.146255000| -0.471968000|
| C | 3.879060000| -0.134192000| 0.218597000|
| C | -4.591935000| 2.455171000| -0.626413000|
| C | -5.225173000| 0.223062000| 0.049565000|
| C | -5.741911000| 1.501337000| -0.385283000|
| H | -4.897297000| 3.450418000| -0.945616000|
| H | -6.016266000| -0.497028000| 0.255027000|
| H | -6.625844000| 1.758722000| -0.523436000|
| C | -2.089705000| -1.789323000| 0.786118000|
| C | -3.472008000| -1.420224000| 0.778445000|
| C | -1.691731000| -2.972116000| 1.467292000|
| C | -4.401159000| -2.304698000| 1.365616000|
| C | -2.621430000| -3.797239000| 2.065311000|
| C | -3.989590000| -3.473183000| 1.987955000|
| H | -0.633097000| -3.215017000| 1.535941000|
| H | 0.900965000| -1.128686000| -0.293508000|
| H | 1.369612000| 0.239278000| -0.419762000|
| H | 1.832595000| -2.166732000| -0.730827000|
| C | 3.214904000| -1.854377000| -0.869628000|
| C | 4.073197000| -2.822888000| -1.427186000|
| C | 3.597595000| -4.058248000| -1.845359000|
| C | 3.719140000| -0.544022000| -0.433597000|
| C | 2.806365000| 0.512290000| -0.174810000|
| C | 3.274687000| 1.755218000| 0.333748000|
| C | 4.653507000| 1.949990000| 0.466037000|
| C | 5.558737000| 0.930686000| 0.160895000|

**TS1**

67

symmetry c1

|  | X          | Y          | Z          |
|---|------------|------------|------------|
| C | 0.383535000| 1.289049000| -0.564536000|
| C | -1.000292000| 1.023800000| -0.514737000|
| C | -1.413634000| -0.285846000| -0.148636000|
| C | -0.443621000| -1.322211000| 0.104553000|
| C | 0.900965000| -1.128686000| -0.293508000|
| C | 1.369612000| 0.239278000| -0.419762000|
| C | 1.832595000| -2.166732000| -0.730827000|
| C | 3.214904000| -1.854377000| -0.869628000|
| C | 4.073197000| -2.822888000| -1.427186000|
| C | 3.597595000| -4.058248000| -1.845359000|
| C | 3.719140000| -0.544022000| -0.433597000|
| C | 2.806365000| 0.512290000| -0.174810000|
| C | 3.274687000| 1.755218000| 0.333748000|
| C | 4.653507000| 1.949990000| 0.466037000|
| C | 5.558737000| 0.930686000| 0.160895000|
| 67  | symmetry c1  |
|-----|-------------|
| C   | 0.299525000 | -1.332962000 | -0.903732000 |
| C   | 1.338024000 | -0.470325000 | -0.671329000 |
| C   | 1.035868000 | 0.874431000  | -0.229080000 |
| C   | -0.327900000| 1.298767000  | -0.003378000 |
| C   | -1.357790000| 0.521776000  | -0.531838000 |
| C   | -1.104157000| -0.896610000 | -0.900591000 |
| C   | -2.703301000| 0.964596000  | -0.886749000 |
| C   | -3.755630000| 0.004933000  | -0.884205000 |
| C   | -5.016947000| 0.393452000  | -1.361036000 |
| C   | -5.241809000| 1.685655000  | -1.832224000 |
| C   | -2.161269000| -1.786568000 | -0.204749000 |
| H   | 0.488961000 | -2.347743000 | -1.239505000 |
| H   | -1.377394000| -0.981249000 | -1.978774000 |
| C   | -5.834226000| -0.327950000 | -1.380355000 |
| H   | -6.230590000| 1.959635000  | -2.206198000 |
| H   | -2.718703000| -4.736670000 | 1.396643000  |
| H   | -5.079287000| -4.026521000 | 1.068950000  |
| H   | -5.570945000| -1.811367000 | 0.075542000  |
| C   | -2.945344000| 2.265298000  | -1.375050000 |
| C   | -4.201961000| 2.624707000  | -1.844174000 |
| H   | -2.126501000| 2.983613000  | -1.412275000 |
| H   | -4.371079000| 3.629509000  | -2.235710000 |
| C   | -0.495840000| -3.435981000 | 0.811973000  |
| C   | -0.003812000| -4.689503000 | 0.411405000  |
| C   | -0.311669000| -2.617635000 | 1.623249000  |
| C   | -1.269614000| -5.108731000 | 0.802973000  |
| C   | -1.587028000| -3.036983000 | 2.010268000  |
| C   | -2.067527000| -4.283270000 | 1.602739000  |
| C   | -0.624751000| -5.334867000 | -0.214194000 |
| H   | -0.078393000| -1.658557000 | 1.971382000  |
| H   | 1.639959000 | -6.085885000 | 0.484936000  |
| H   | 2.201791000 | -2.392535000 | 2.642130000  |
| H   | 3.062487000 | -4.612941000 | 1.908924000  |
| H   | 2.733001000 | -0.899103000 | -0.827409000 |
| C   | 3.065708000 | -2.248160000 | -1.057386000 |
| C   | 3.769699000 | 0.061683000  | -0.735509000 |
| C   | 4.385600000 | -2.646445000 | -1.207778000 |
| C   | 5.106851000 | -0.365552000 | -0.890747000 |
| C   | 5.414310000 | -1.696586000 | -1.126842000 |
| H   | 2.288597000 | -3.009953000 | -1.094078000 |
| H   | 4.619653000 | -3.693620000 | -1.376652000 |
| H   | 5.923012000 | 0.350000000  | -0.805307000 |
| H   | 6.456441000 | -2.002865000 | -1.236757000 |
| C   | 2.092509000 | 1.826648000  | -0.101453000 |
| C   | 3.437028000 | 1.459740000  | -0.455041000 |
| C   | 1.799771000 | 3.177137000  | 0.295079000  |
| C   | 4.409402000 | 2.465522000  | -0.512498000 |

A
C 2.812429000 4.138703000 0.211107000  
C 4.094868000 3.787171000 -0.204235000  
H 5.426320000 2.228381000 -0.818710000  
H 2.605551000 5.177277000 0.463460000  
H 4.867334000 4.555573000 -0.278456000  
C -0.563768000 2.547277000 0.729559000  
C 0.480278000 3.498775000 0.835385000  
C -1.777902000 2.782922000 1.409519000  
C 0.236920000 4.701198000 1.535509000  
C -1.990357000 3.962480000 2.105389000  
C -0.983421000 4.939672000 2.148380000  
H -2.555510000 2.021081000 1.402699000  
H 1.028078000 5.442780000 1.636466000  
H -2.934019000 4.121778000 2.630819000  
H -1.145071000 5.871549000 2.693868000  

TS2

67  
symmetry c1  
C 0.354984000 -1.647497000 -1.381307000  
C 1.274150000 -0.666135000 -1.085666000  
C 0.809610000 0.598147000 -0.532903000  
C -0.567701000 0.820508000 -0.293663000  
C -1.518524000 -0.116235000 -0.825831000  
C -1.058311000 -1.407729000 -1.290491000  
C -2.895613000 0.208671000 -1.299051000  
C -3.863626000 -0.740142000 -0.916192000  
C -5.174925000 -0.626557000 -1.389612000  
C -5.503510000 0.433264000 -2.239540000  
C -3.316562000 -1.713366000 0.031996000  
C -1.893791000 -1.685165000 0.148385000  
C -1.237599000 -2.329060000 1.228207000  
C -2.021520000 -3.133318000 2.065987000  
C -3.403159000 -3.254533000 1.886897000  
C -4.055736000 -2.526454000 0.889660000  
H 0.669608000 -2.604157000 -1.789238000  
H -1.665498000 -1.917337000 -2.043998000  
H -5.936597000 -1.352406000 -1.098175000  
H -6.525541000 0.531752000 -2.610848000  
H -1.528030000 -3.656982000 2.886769000  
H -3.980858000 -3.888190000 2.563014000  
H -5.143531000 -2.556523000 0.807617000  
C -3.217018000 1.260536000 -2.151981000  
C -4.534219000 1.370906000 -2.615317000  
H -2.459797000 1.990615000 -2.442849000  
H -4.806028000 2.199106000 -3.272875000  
C 0.216657000 -2.205047000 1.497419000  
C 1.092378000 -3.264976000 1.212281000  
C 0.723675000 -1.026436000 2.062060000  
C 2.462649000 -3.127330000 1.446844000  
C 2.092078000 -0.893820000 2.299789000  
C 2.964928000 -1.939209000 1.982131000  
H 0.696476000 -4.193360000 0.793869000
Spiro

67

symmetry c1

C  -0.445288000  -2.498790000  0.398471000
C  -1.404910000  -1.447807000  0.562418000
C   -0.962553000  -0.081071000  0.608391000
C   0.415364000   0.235228000  0.524079000
C   1.438718000  -0.857629000  0.302348000
C   0.867584000  -2.232911000  0.245210000
C   2.554714000  -0.986402000  1.362318000
C   3.807912000  -1.121161000  0.724398000
C   4.957082000  -1.322519000  1.494434000
C   4.834492000  -1.384423000  2.886382000
C   3.632741000  -0.943333000  -0.721999000
C   2.268333000  -0.709033000  -0.995130000
C   1.799385000  -0.430658000  -2.280318000
C   2.754197000  -0.377996000  -3.310912000
C   4.109867000  -0.621624000  -3.056176000
C   4.563178000  -0.905567000  -1.764224000
162
|Atom| Coordinates| Coordinates| Coordinates|
|---|---|---|---|
|H| -0.336569000 -0.713954000 -2.535197000 | H| -0.148600000 -5.378280000 -0.820696000 | H| 1.667446000 -0.148600000 5.378280000 |
|H| 1.778405000 -2.441825000 -2.100764000 | C| 2.767590000 2.371569000 -0.251334000 |
|C| 2.990674000 3.743156000 -0.477915000 |
|C| 3.880310000 1.507562000 -0.104142000 |
|C| 4.424800000 5.378280000 -0.820696000 |
|C| 5.179649000 2.051315000 -0.197411000 |
|C| 5.379528000 3.404149000 -0.427908000 |
|C| 2.767590000 -0.251334000 0.481894000 |
|C| 3.664180000 0.083329000 0.164894000 |
|C| 2.155674000 -1.763949000 0.886562000 |
|C| 4.715797000 -0.837115000 0.132667000 |
|C| 3.246039000 -1.763949000 0.886562000 |
|C| 2.345910000 -0.397045000 0.481895000 |
|C| 4.715797000 -0.837115000 0.132667000 |
|C| 4.501829000 -2.182215000 0.438391000 |
|C| 5.179649000 -0.251334000 0.481894000 |
|C| 3.664180000 0.083329000 0.164894000 |
|C| 2.155674000 -1.763949000 0.886562000 |
|C| 1.778405000 -0.251334000 0.481894000 |
|C| 3.664180000 0.083329000 0.164894000 |
|C| 2.155674000 -1.763949000 0.886562000 |
|C| 2.345910000 -0.397045000 0.481895000 |
|C| 4.715797000 -0.837115000 0.132667000 |
|C| 3.246039000 -1.763949000 0.886562000 |
|C| 4.501829000 -2.182215000 0.438391000 |
|C| 5.179649000 -0.251334000 0.481894000 |
|C| 3.664180000 0.083329000 0.164894000 |
|C| 2.155674000 -1.763949000 0.886562000 |
|C| 4.715797000 -0.837115000 0.132667000 |
|C| 3.246039000 -1.763949000 0.886562000 |
|C| 2.345910000 -0.397045000 0.481895000 |
|C| 4.715797000 -0.837115000 0.132667000 |
|C| 3.246039000 -1.763949000 0.886562000 |
|C| 2.345910000 -0.397045000 0.481895000 |
|C| 4.715797000 -0.837115000 0.132667000 |
|C| 3.246039000 -1.763949000 0.886562000 |

**TS4**

67

symmetry c1

|Atom| Coordinates| Coordinates| Coordinates|
|---|---|---|---|
|C| -0.137614000 2.574707000 0.021791000 | C| 1.128962000 1.956575000 0.082563000 |
|C| 1.168373000 0.573422000 0.411478000 |
|C| 0.048284000 -0.179549000 0.569573000 |
|C| 1.257210000 0.352091000 0.065856000 |
|C| -1.363091000 1.795312000 -0.004211000 |
|C| -2.696944000 2.405472000 0.193942000 |
|C| -3.837940000 1.566899000 0.131990000 |
|C| -5.091766000 2.133213000 0.437806000 |
|C| -5.221834000 3.479382000 0.754340000 |
|C| -3.686400000 0.169120000 -0.305392000 |
|C| -2.404406000 -0.421139000 -0.404761000 |
|C| -2.259335000 -1.701168000 -1.026535000 |
|C| -3.409620000 -2.413763000 -1.371568000 |
|C| -4.684440000 -1.877045000 -1.171121000 |
|C| -4.824447000 -0.587666000 -0.677810000 |
| Attrib | X         | Y         | Z         |
|-------|-----------|-----------|-----------|
| C     | 2.545088000 | -1.429434000 | 0.809546000 |
| C     | 4.842266000 | -0.007316000 | 0.018608000 |
| C     | 3.787680000 | -2.068815000 | 0.707730000 |
| C     | 4.921454000 | -1.365896000 | 0.298340000 |
| H     | 5.747933000 | 0.519206000  | -0.278090000 |
| H     | 3.880571000 | -3.128510000 | 0.942059000 |
| C     | 0.082381000 | -1.468668000 | 1.233947000 |
| C     | 1.360318000 | -2.101981000 | 1.332968000 |
| C     | -1.047067000 | -2.083005000 | 1.836275000 |
| C     | 1.434826000 | -3.357865000 | 1.966913000 |
| C     | -0.936038000 | -3.301725000 | 2.475080000 |
| C     | 0.311061000 | -3.951978000 | 2.521053000 |
| H     | -2.006643000 | -1.570878000 | 1.817832000 |
| H     | 2.394236000  | -3.865075000 | 2.055788000 |
| H     | -1.808527000 | -3.751765000 | 2.952047000 |
| H     | 0.402533000  | -4.919810000 | 3.018804000 |
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