Electronic Suprimentary Information

for

Torsional chirality generation based on cyclic oligomers constructed from an odd number of pyrenes

Ryo Kurosaki, Mitsuharu Suzuki, Hironobu Hayashi, Michiya Fujiki, Naoki Aratani* and

Hiroko Yamada*

Contents

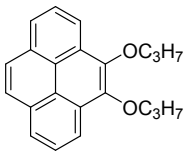
1. Instrumentation and Materials

^{1}H NMR (500 MHz) and ^{13}C NMR (100 MHz, 126 MHz, and 150 MHz) spectra were recorded with JEOL JNM-ECX400 spectrometer, JEOL JNM-ECX500 spectrometer, and JEOL JNM-ECX600 spectrometer at ambient temperature by using tetramethylsilane as an internal standard. The high-resolution MS were measured by a JEOL JMS-700 MStation (EI magnetic sector (70 eV)) and a BRUKER Autoflex II (MALDI-spiral TOF MS). X-ray crystallographic data were recorded at 90 K with a BRUKER-APEXII X-Ray diffractometer using Mo-Kα radiation equipped with a large area CCD detector.

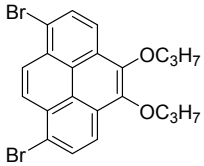
UV/Vis absorption spectra were measured with a JASCO UV/Vis/NIR spectrophotometer V-570, and fluorescence spectra were measured with a JASCO PL spectrofluorometer FP-6600. Fluorescence quantum yields were measured on a HAMAMATSU Absolute PL Quantum Yield Measurement System C9920-02G. Optical separations were performed through a SUMICHIRAL OA-3100 chiral column with a diode array detector SPD-M10A. CD spectra were recorded using a JASCO J-820 spectropolarimeter. CPL and PL spectra were collected using a JASCO CPL-200 spectrofluoropolarimeter.

TLC, PLC and gravity column chromatography were performed on Art. 5554 (Merck KGaA) plates, Art. 13792 (Merck KGaA) plates and silica gel 60N (Kanto Chemical), respectively. All solvents and chemicals were reagent-grade quality, obtained commercially, and used without further purification. For spectral measurements, spectral-grade CH_2Cl_2 was purchased from Nacalai Tesque.

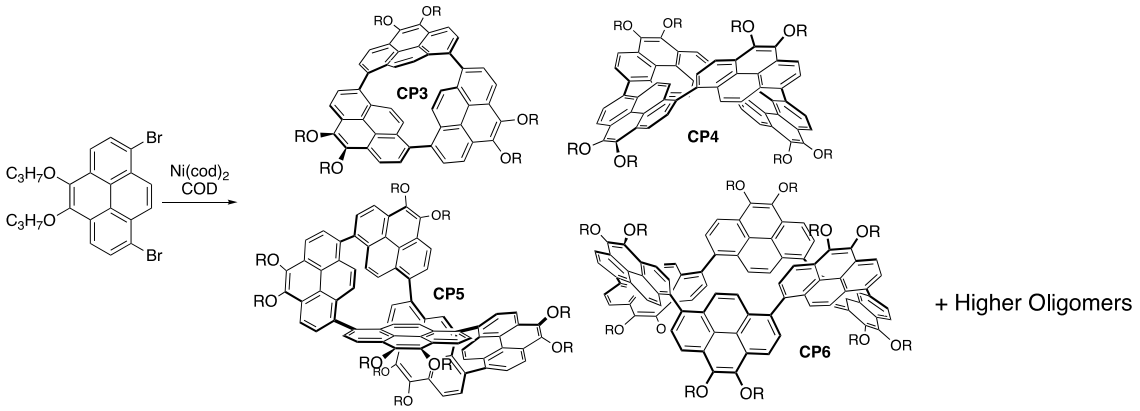
2. Experimental Section



4,5-Dipropoxypyrene (P1)[S1]: To a solution of pyrene-4,5-dione (1.16 g, 5.00 mmol) in THF (20 mL) and H_2O (20 mL) were added tetra-*n*-butylammonium bromide (TBAB) (484 mg, 1.50 mmol) and $Na_2S_2O_4$ (2.61 g, 15.0 mmol). After 5 min, a solution of KOH (2.28 g, 40.0 mmol) in H_2O (20 mL) was added to the reaction mixture followed by 1-bromopropane (2.27 mL, 25.0 mmol). The red colored reaction mixture was stirred at 100°C for 12 h. The reaction mixture was cooled and extracted with AcOEt. The layers were separated and the aqueous phase was extracted with AcOEt. The combined organic extracts were washed with water followed by brine and dried over Na_2SO_4. The solvent was removed under reduced pressure. The crude products were subjected to silica gel column chromatography (R_f = 0.35 with CH_2Cl_2/hexanes = 1:5) to give 4,5-dipropoxypyrene (**P1**) (1.52 g, 94%) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.50 (d, J = 7.5 Hz, 2H), 8.14 (d, J = 7.5 Hz, 2H), 8.06 (s, 2H), 8.02 (t, J = 7.5 Hz, 2H), 4.31 (t, J = 7.0 Hz, 4H), 2.01 (m, 4H) and 1.18 (t, J = 7.5 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.03, 131.05, 128.89, 127.30, 125.93, 124.28, 122.83, 119.40, 75.29, 23.84 and 10.84 ppm; HR-MS (EI): *m/z*: calcd for $C_{22}H_{22}O_2$, 318.1620 $[M]^+$; found: 318.1626; UV-vis (CH_2Cl_2): λ_{max} (ε [$M^{-1}cm^{-1}$]) = 281 (31214), 332 (20658) and 346 (25308) nm; Fl (CH_2Cl_2, λ_{ex} = 346 nm): λ_{max} = 381 and 401 nm, Φ_F = 0.08; Fl (solid, λ_{ex} = 346 nm): λ_{max} = 420 nm, Φ_F = 0.12.



1,8-Dibromo-4,5-dipropoxypyrene[S1]**:** Bromine (0.34 mL, 6.60 mmol) was added dropwise to a solution of 4,5-dipropoxypyrene (955 mg, 3.00 mmol) in CH_2Cl_2 (25 mL) over 5 min at room temperature. After complete addition of bromine, stirring was continued at room temperature for 5 min. The reaction mixture was poured into sodium thiosulfate solution and the layers were separated. The organic phase was washed with water followed by brine and dried over Na_2SO_4. The solvent was removed under reduced pressure. The crude products were subjected to silica gel column chromatography (R_f = 0.20 with CH_2Cl_2/hexanes = 1:10) to give 1,8-dibromo-4,5-dipropoxypyrene (1.37 g, 96%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.53 (s, 2H), 8.38 (d, J = 8.5 Hz, 2H), 8.28 (d, J = 8.5 Hz, 2H), 4.29 (t, J = 7.0 Hz, 4H), 1.98 (m, 4H) and 1.17 (t, J = 7.5 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.70, 130.71, 129.39, 128.65, 127.44, 123.44, 120.81, 119.91, 75.37, 23.76 and 10.80 ppm; HR-MS (EI): *m/z*: calcd for $C_{22}H_{20}Br_2O_2$, 473.9830 $[M]^+$; found: 473.9820, 475.9807, 477.9792.



1,8-Linked cyclic pyrene oligomers CP*n*[S2]: A mixture of 2,2'-bipyridine (300 mg, 1.92 mmol), 1,5-cyclooctadiene (0.24 mL, 1.92 mmol), $Ni(cod)_2$ (528 mg, 1.92 mmol) in toluene (1.76 mL) and DMF (1.76 mL) was heated at 80°C for 30 min under Ar. A solution of 1,8-dibromo-4,5-dipropoxypyrene (382 mg, 0.80 mmol) in toluene (7.0 mL) was added to the solution, and the whole was refluxed for 18 h under Ar. After cooling to room temperature, the reaction mixture was quenched with 10% HCl for 1 h. The solid was collected by filtration and rinsed with toluene. The filtrate was treated with water, and the organic materials were extracted with toluene. The combined organic solution was washed with brine and dried over Na_2SO_4, and evaporated to give crude products. The crude products were separated by silica gel column chromatography and gel permeation chromatography ($CHCl_3$ eluent) to give **CP3** (8.9 mg, 3.5%) as a red solid, **CP4** (8.8 mg, 3.5%), **CP5** (7.8 mg, 3.1%), **CP6** (5.1 mg, 2.1%), **CP7** (0.7 mg, 0.3%) and **CP8** (1.3 mg, 0.5%) as yellow solids. **CP3:** ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.67 (d, J = 8.0 Hz, 6H), 8.60 (d, J = 8.0 Hz, 6H), 6.99 (s, 6H), 4.39 (t, J = 7.0 Hz, 12H), 2.06 (m, 12H) and 1.22 (t, J = 7.5 Hz, 18H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.03, 134.75, 129.51, 128.33, 127.89, 125.52, 123.41, 118.94, 75.58, 23.88 and 10.88 ppm; HR-MS (Spiral MALDI): *m/z*: calcd for $C_{66}H_{60}O_6$, 948.4384 $[M]^+$; found: 948.4383; UV-vis (CH_2Cl_2): λ_{max} (ε [10^3 M^{-1} cm^{-1}]) = 298 (16.9), 395 (16.1) and 505 (4.34) nm; Fl (CH_2Cl_2, λ_{ex} = 395 nm): λ_{max} = 599 nm, Φ_F = 0.34; Fl (solid, λ_{ex} = 395 nm): λ_{max} = 635 nm, Φ_F = 0.04. **CP4**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.67 (d, J = 8.5 Hz, 8H), 8.18 (d, J = 8.5 Hz, 8H), 7.34 (s, 8H), 4.41 (t, J = 7.0 Hz, 16H), 2.06 (m, 16H) and 1.22 (t, J = 7.5 Hz, 24H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 144.00, 135.73, 129.64, 128.86, 126.10, 122.67, 119.52, 75.41, 23.88 and 10.87 ppm; HR-MS (Spiral MALDI): *m/z*: calcd for $C_{88}H_{80}O_8$, 1264.5848 $[M]^+$; found: 1264.5851; UV-vis (CH_2Cl_2): λ_{max} (ε [10^3 M^{-1} cm^{-1}]) = 288 (46.7), and 363 (37.2) nm; Fl (CH_2Cl_2, λ_{ex} = 363 nm): λ_{max} = 465 nm, Φ_F = 60%; Fl (solid, λ_{ex} = 363 nm): λ_{max} = 498 nm, Φ_F = 12%. **CP5**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.66 (d, J = 8.5 Hz, 2H), 8.60 (d, J = 8.0 Hz, 2H), 8.55 (d, J = 8.0 Hz, 2H), 8.51 (d, J = 8.0 Hz, 2H), 8.49 (d, J = 8.0 Hz, 2H), 8.42 (d, J = 8.0 Hz, 2H), 8.27 (s, 2H), 8.20 (d, J = 9.5 Hz, 2H), 8.01 (d, J = 8.0 Hz, 2H), 7.91 (d, J = 8.0 Hz, 2H), 7.76 (d, J = 8.5 Hz, 2H), 7.73 (d, J = 9.5 Hz, 2H), 7.70 (d, J = 8.0 Hz, 2H), 6.49 (d, J = 10.0 Hz, 2H), 5.72 (d, J = 10.0 Hz, 2H), 4.37 (m, 20H), 2.03 (m, 20H), and 1.19 (m, 30H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 144.12, 143.95, 143.76, 143.57, 143.44, 136.98, 136.72, 135.98, 135.59, 135.25, 133.42, 133.33, 131.34, 130.36, 129.79, 128.81, 128.74, 128.57, 128.51, 128.47, 127.45, 126.22, 126.01, 125.67, 125.55, 125.43, 124.86, 122.97, 122.79, 122.63, 122.56, 122.46, 119.58, 119.51, 118.77, 118.57, 118.47, 75.38, 75.27, 75.23, 58.51, 23.87, 23.83, 18.45, 10.85 and 10.81 ppm; HR-MS (Spiral MALDI): *m/z*:

calcd for $C_{110}H_{100}O_{10}$, 1580.7311 $[M]^+$; found: 1581.7313; UV-vis (CH_2Cl_2): λ_{max} (ε [10^3 M^{-1} cm^{-1}]) = 290 (96.6), and 367 (77.7) nm; Fl (CH_2Cl_2, λ_{ex} = 367 nm): λ_{max} = 455 nm, Φ_F = 64%; Fl (solid, λ_{ex} = 367 nm): λ_{max} = 483 nm, Φ_F = 14%. **CP6**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.57 (d, J = 8.0 Hz, 12H), 8.00 (d, J = 8.0 Hz, 12H), 7.36 (s, 12H), 4.37 (m, 24H), 2.03 (m, 24H) and 1.19 (t, J = 7.0 Hz, 36H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 144.09, 135.50, 130.02, 129.21, 128.68, 125.54, 123.20, 118.66, 75.46, 23.87 and 10.84 ppm; HR-MS (Spiral MALDI): *m/z*: calcd for $C_{132}H_{120}O_{12}$, 1896.8774 $[M]^+$; found: 1897.8768; UV-vis (CH_2Cl_2): λ_{max} (ε [10^4 M^{-1} cm^{-1}]) = 293 (14.3), and 375 (11.8) nm; Fl (CH_2Cl_2, λ_{ex} = 375 nm): λ_{max} = 456 nm, Φ_F = 68%; Fl (solid, λ_{ex} = 375 nm): λ_{max} = 487 nm, Φ_F = 28%. **CP7**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.63 (d, J = 8.5 Hz, 2H), 8.61-8.56 (m, 8H), 8.53 (d, J = 8.0 Hz, 2H), 8.51 (d, J = 8.0 Hz, 2H), 8.44 (d, J = 8.0 Hz, 2H), 8.38 (d, J = 9.5 Hz, 2H), 8.26 (d, J = 8.0 Hz, 2H), 8.14 (d, J = 10.0 Hz, 2H), 8.08 (s, 2H), 8.00-8.97 (m, 4H), 7.91 (d, J = 8.0 Hz, 2H), 7.85 (d, J = 8.0 Hz, 4H), 7.82 (d, J = 8.0 Hz, 2H), 7.78 (d, J = 9.0 Hz, 2H), 7.14-7.10 (m, 4H), 4.45-4.25 (m, 28H), 2.08-1.96 (m, 28H), and 1.24-1.14 (m, 42H) ppm; HR-MS (Spiral MALDI): *m/z*: calcd for $C_{154}H_{140}O_{14}$, 2213.0238 $[M]^+$; found: 2213.0238; UV-vis (CH_2Cl_2): λ_{max} (ε [10^4 M^{-1} cm^{-1}]) = 295 (18.2), and 388 (13.3) nm; Fl (CH_2Cl_2, λ_{ex} = 388 nm): λ_{max} = 484 nm, Φ_F = 43%; Fl (solid, λ_{ex} = 388 nm): λ_{max} = 506 nm, Φ_F = 2%. **CP8**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.62 (d, J = 8.0 Hz, 16H), 8.16 (d, J = 9.0 Hz, 16H), 7.94 (s, 16H), 4.39-4.37 (m, 32H), 2.07-2.04 (m, 32H) and 1.21 (t, J = 7.5 Hz, 48H) ppm; HR-MS (Spiral MALDI): *m/z*: calcd for $C_{176}H_{160}O_{16}$, 2529.1701 $[M]^+$; found: 2529.1689; UV-vis (CH_2Cl_2): λ_{max} (ε [10^4 M^{-1} cm^{-1}]) = 295 (23.2), and 403 (18.3) nm; Fl (CH_2Cl_2, λ_{ex} = 403 nm): λ_{max} = 466 nm, Φ_F = 55%; Fl (solid, λ_{ex} = 403 nm): λ_{max} = 500 nm, Φ_F = 4%.

Table S1. Photophysical Data of **P1** and **CP4–CP8**

compound	$\lambda_{abs,\ solution}$ [nm] (logε)	λ_{ex} [nm]	$\lambda_{ems,\ solution\ /\ solid}$ [nm]	$\Phi_{f,\ solution\ /\ solid}$ [%]
P1	281 (4.49) / 332 (4.32) / 346 (4.40)	346	381, 401 / 420	8 / 12
CP4	288 (4.67) / 363 (4.57)	363	465 / 498	60 / 12
CP5	290 (4.98) / 367 (4.89)	367	455 / 483	64 / 14
CP6	293 (5.15) / 375 (5.07)	375	456 / 487	68 / 28
CP7	295 (5.26) / 388 (5.12)	388	484 / 506	43 / 2
CP8	295 (5.37) / 403 (5.26)	403	466 / 500	55 / 4

3. NMR Spectra

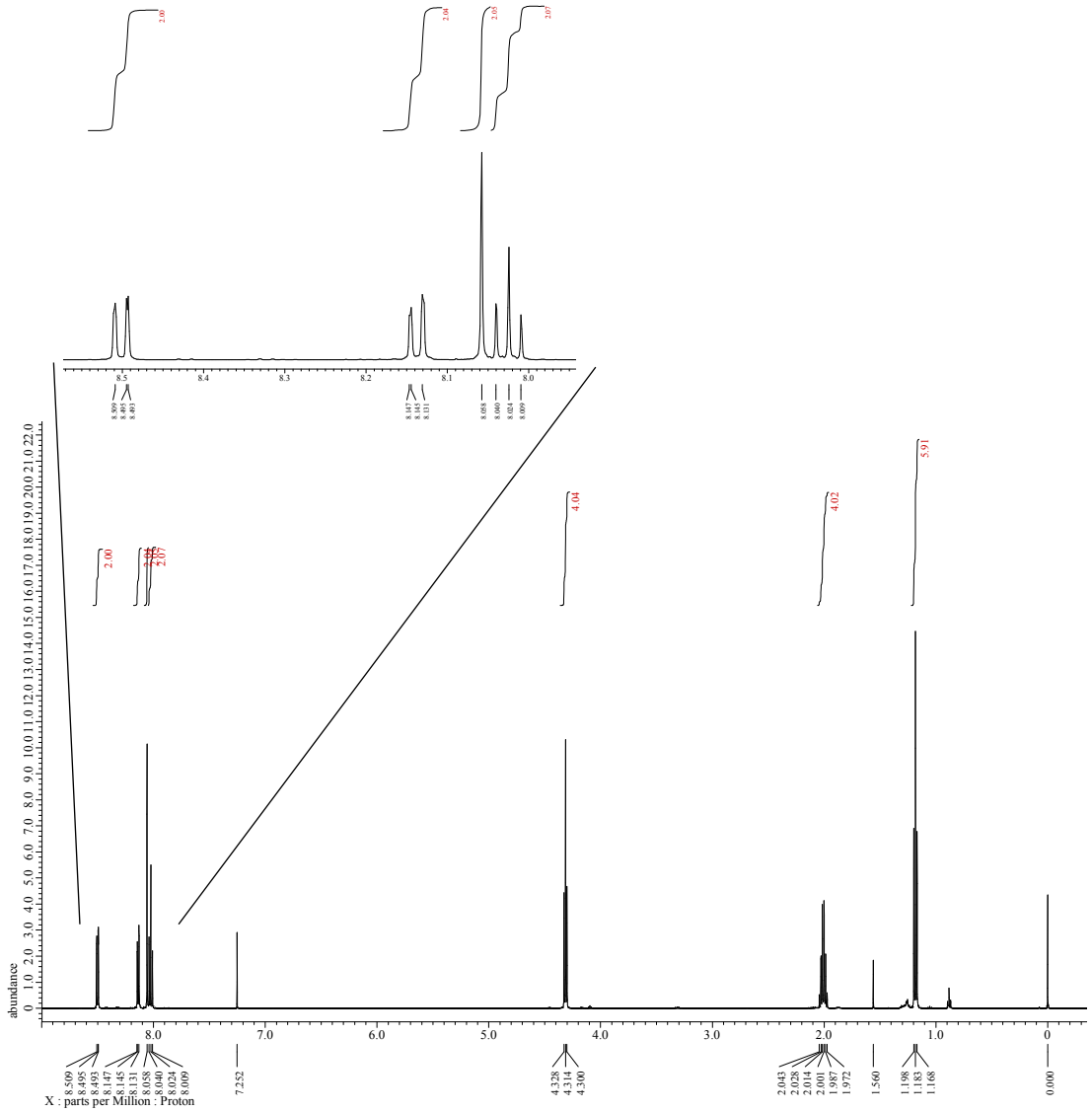


Figure S1. ^{1}H NMR spectrum of 4,5-dipropoxypyrene (**P1**) in $CDCl_3$ at room temperature.

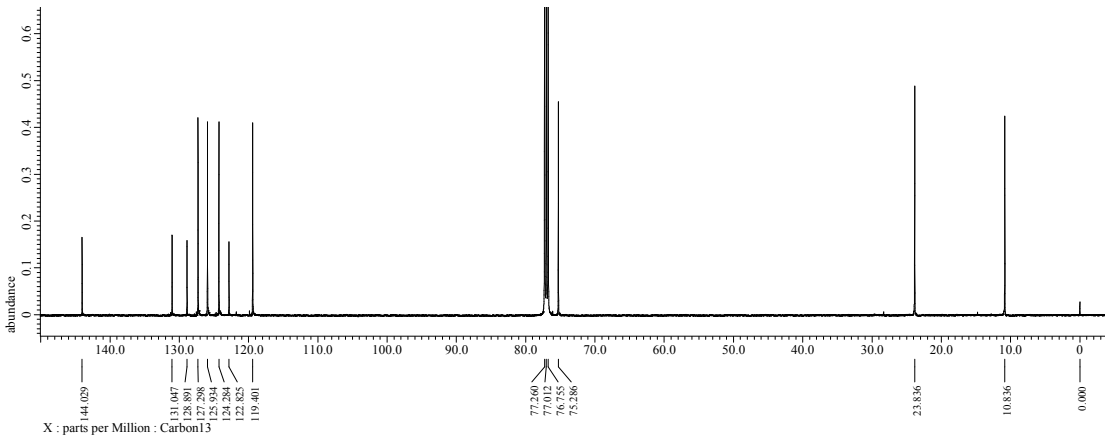


Figure S2. ^{13}C NMR spectrum of 4,5-dipropoxypyrene (**P1**) in $CDCl_3$ at room temperature.

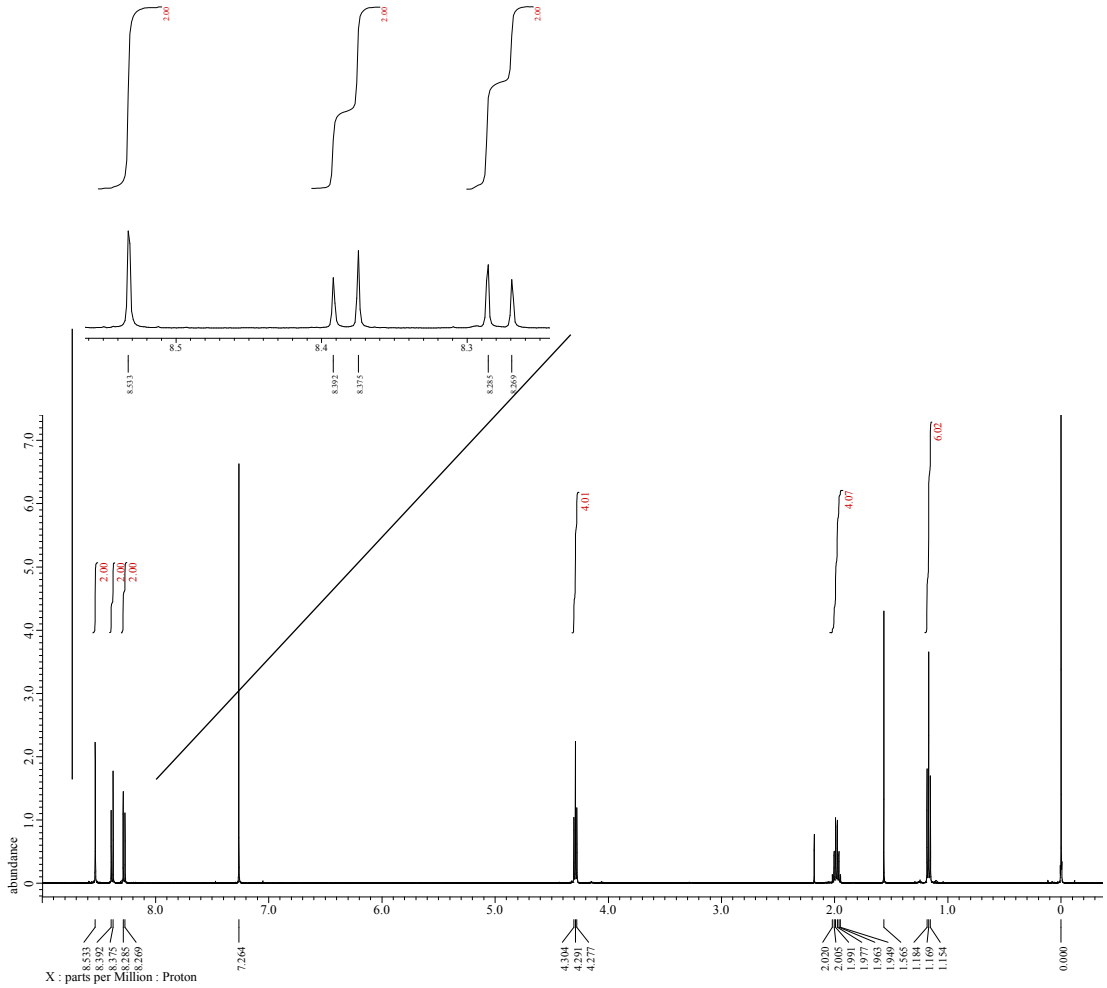


Figure S3. ^{1}H NMR spectrum of 1,8-dibromo-4,5-dipropoxypyrene in $CDCl_3$ at room temperature.

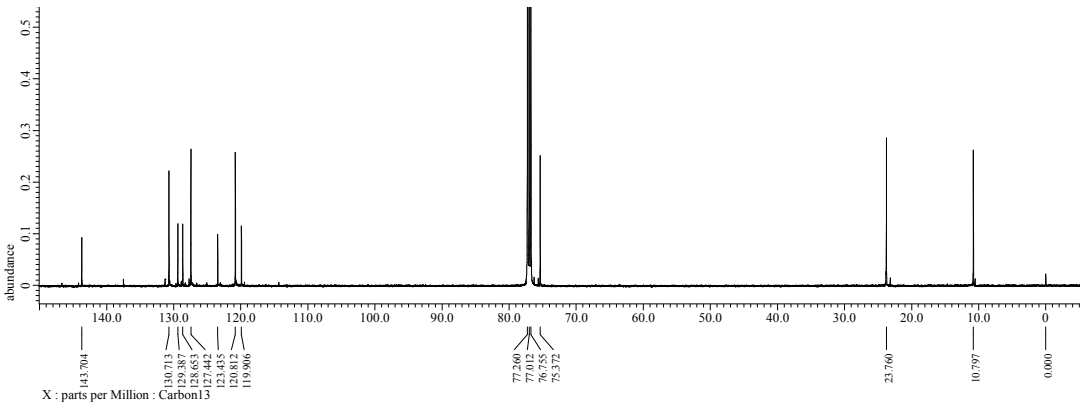


Figure S4. ^{13}C NMR spectrum of 1,8-dibromo-4,5-dipropoxypyrene in $CDCl_3$ at room temperature.

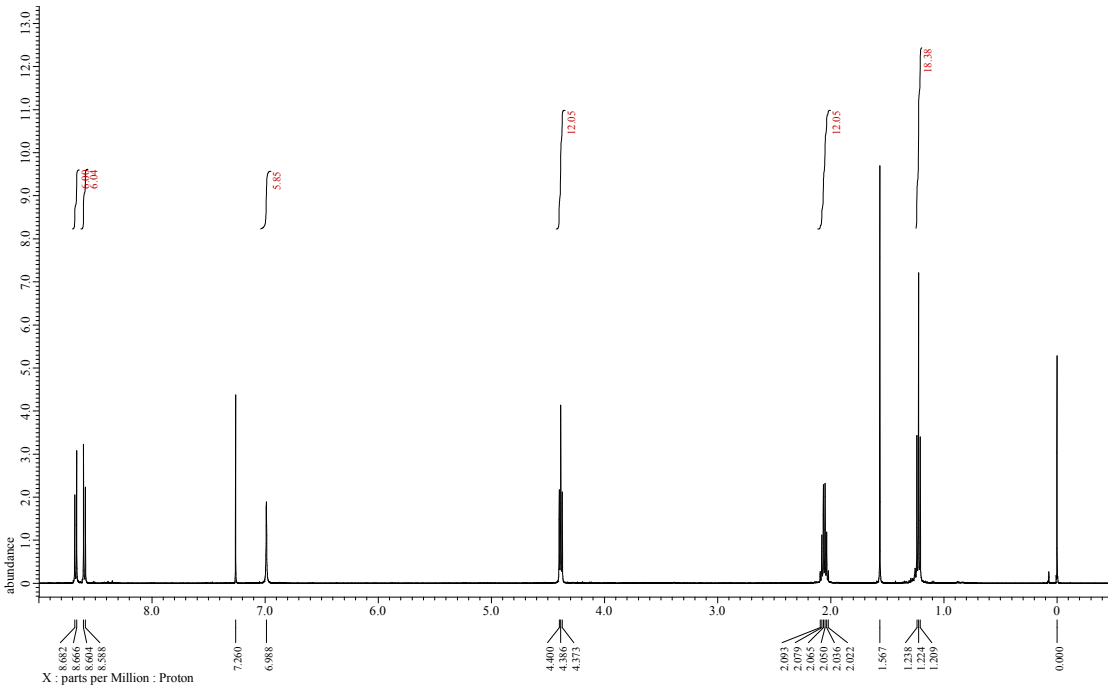


Figure S5. ^{1}H NMR spectrum of **CP3** in $CDCl_3$ at room temperature.

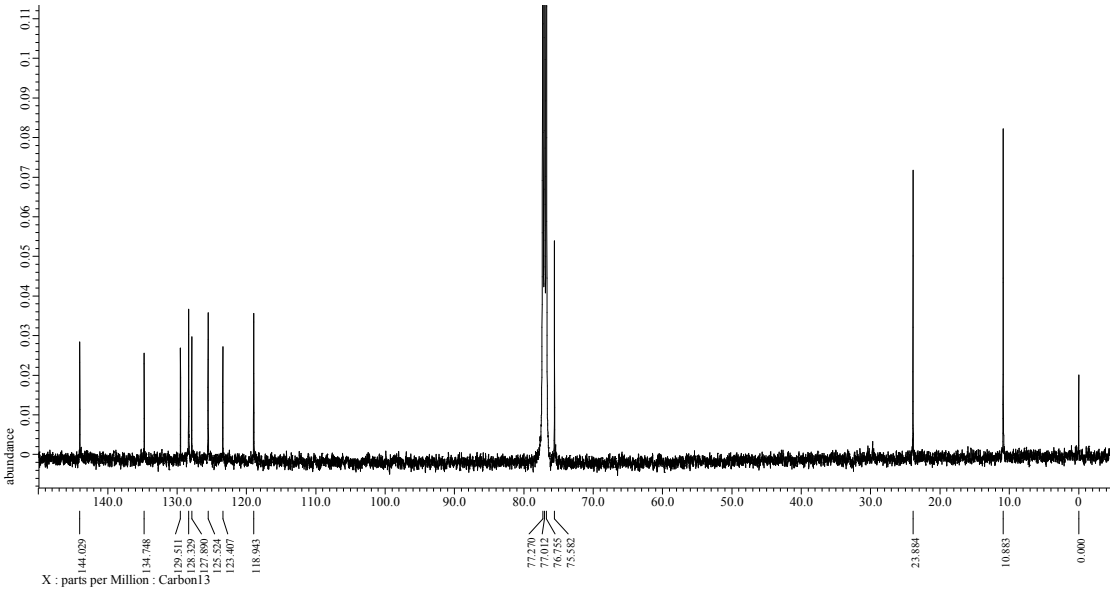


Figure S6. ^{13}C NMR spectrum of **CP3** in $CDCl_3$ at room temperature.

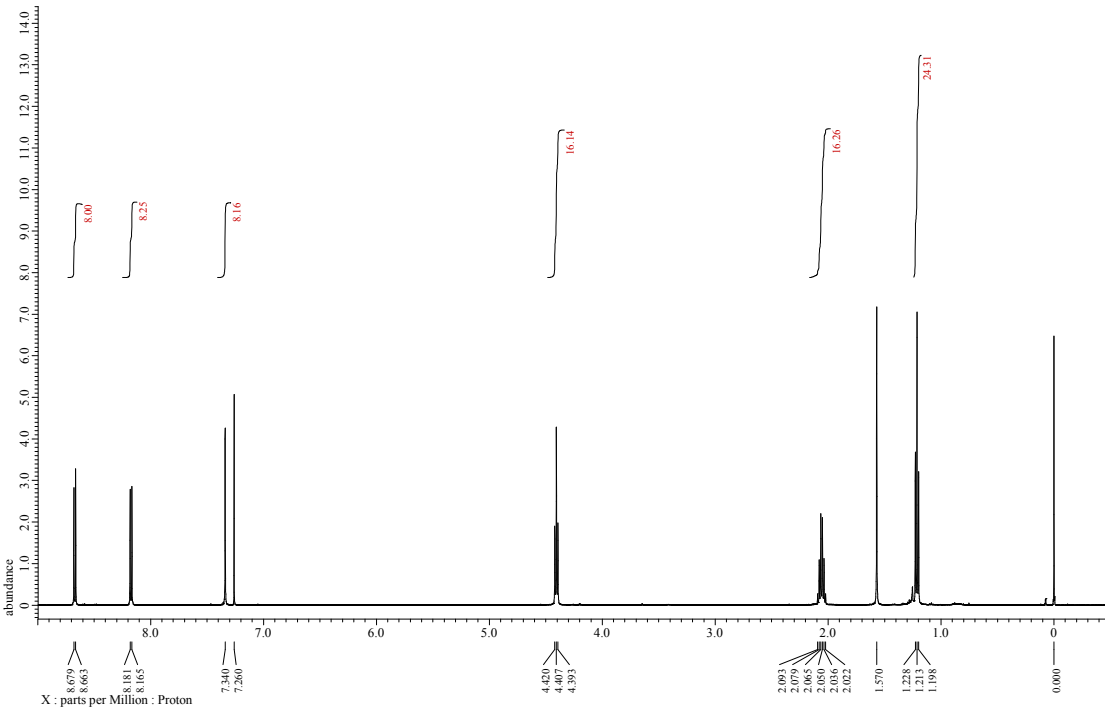


Figure S7. ^{1}H NMR spectrum of **CP4** in $CDCl_3$ at room temperature.

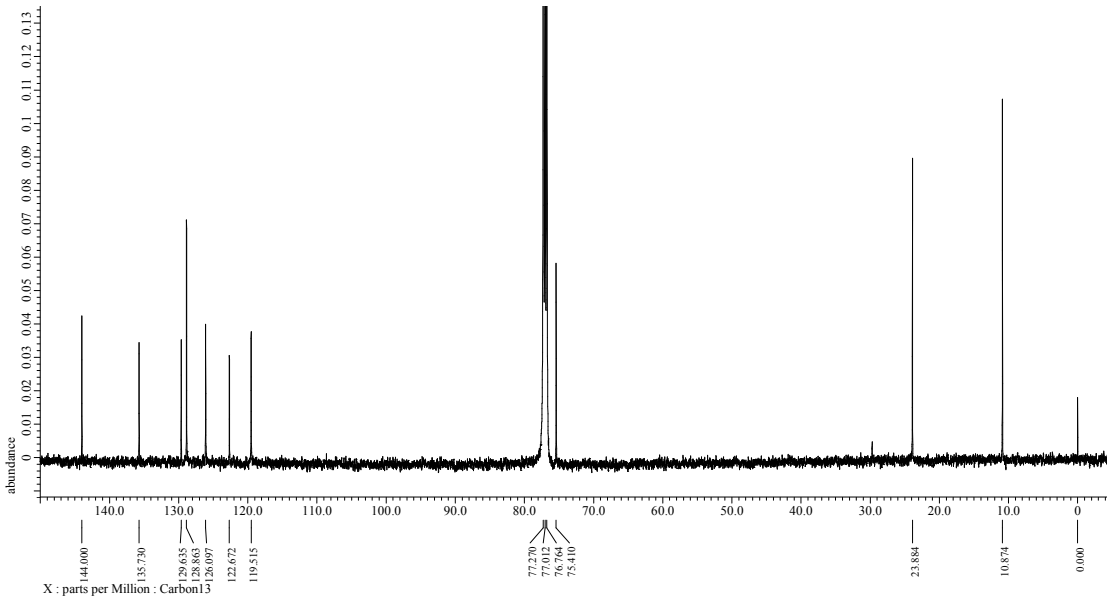


Figure S8. ^{13}C NMR spectrum of **CP4** in $CDCl_3$ at room temperature.

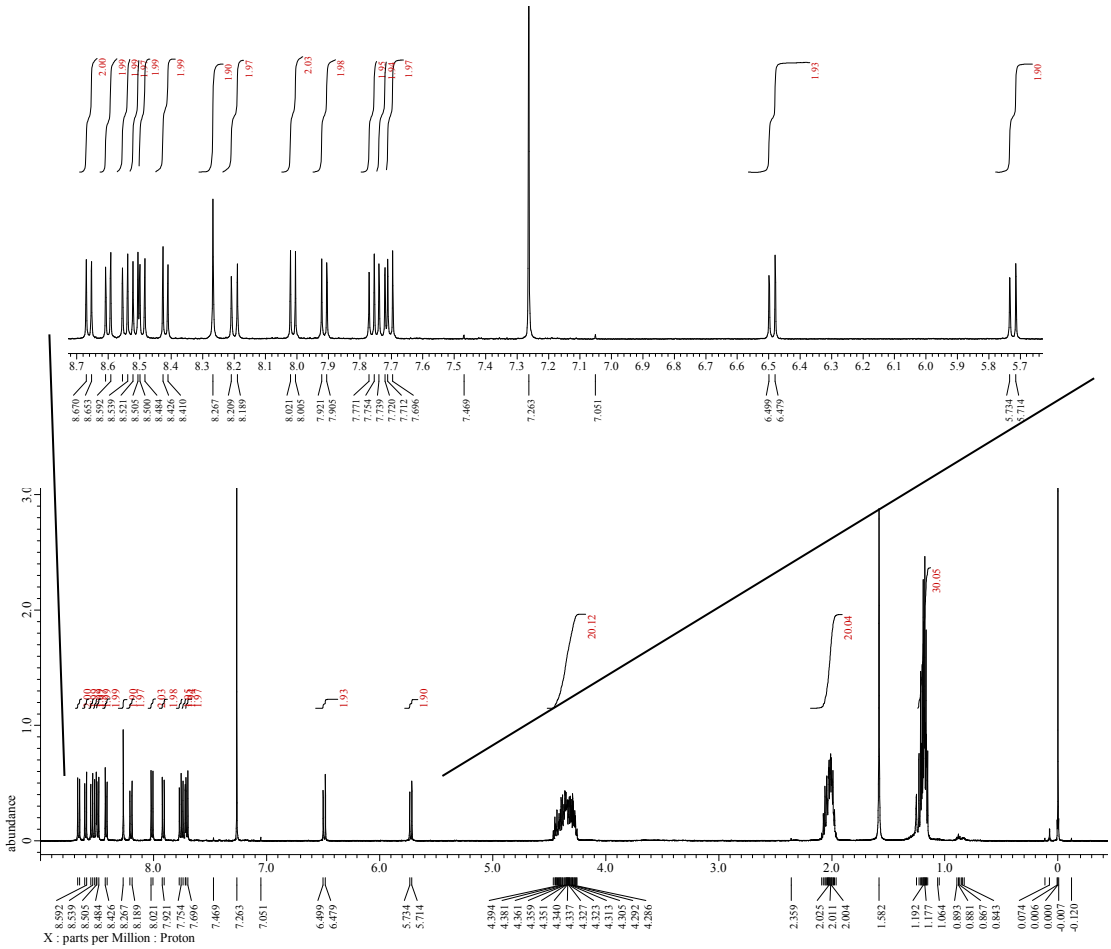


Figure S9. ^{1}H NMR spectrum of **CP5** in $CDCl_3$ at room temperature.

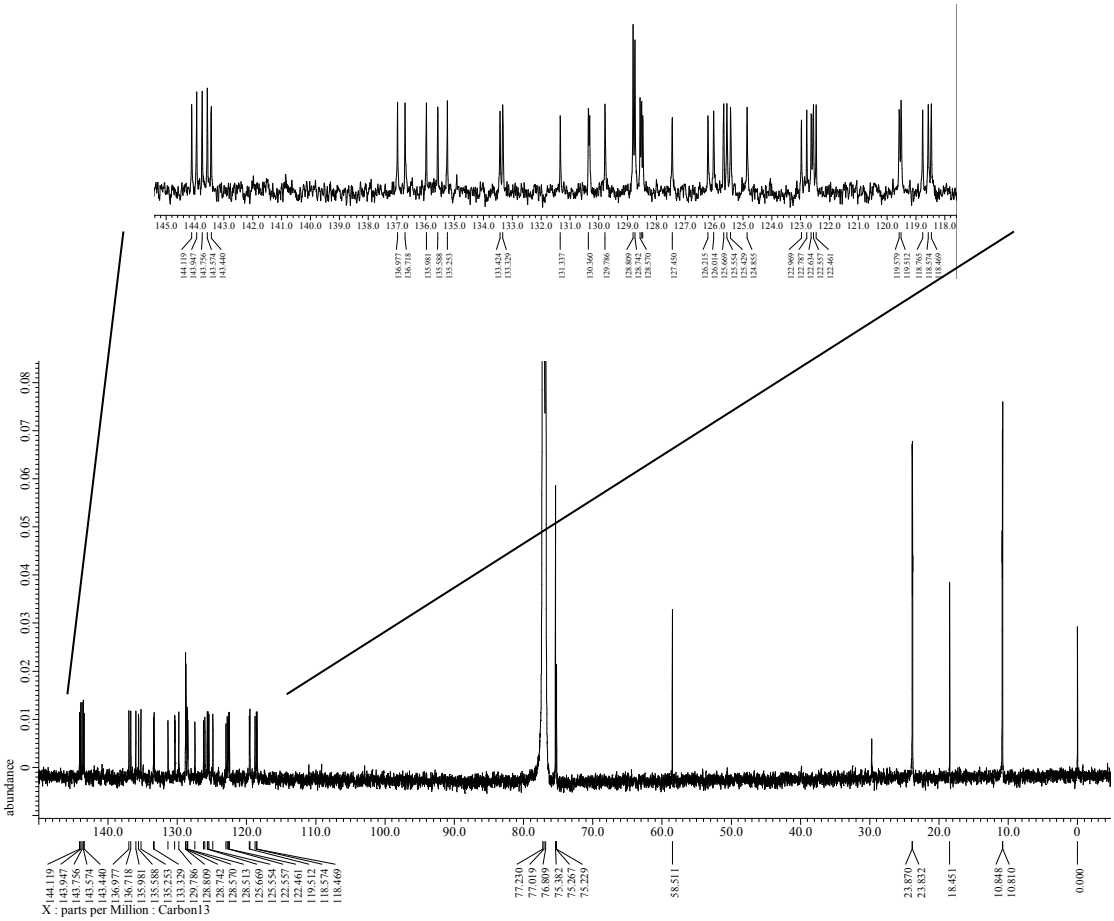


Figure S10. ^{13}C NMR spectrum of **CP5** in $CDCl_3$ at room temperature.

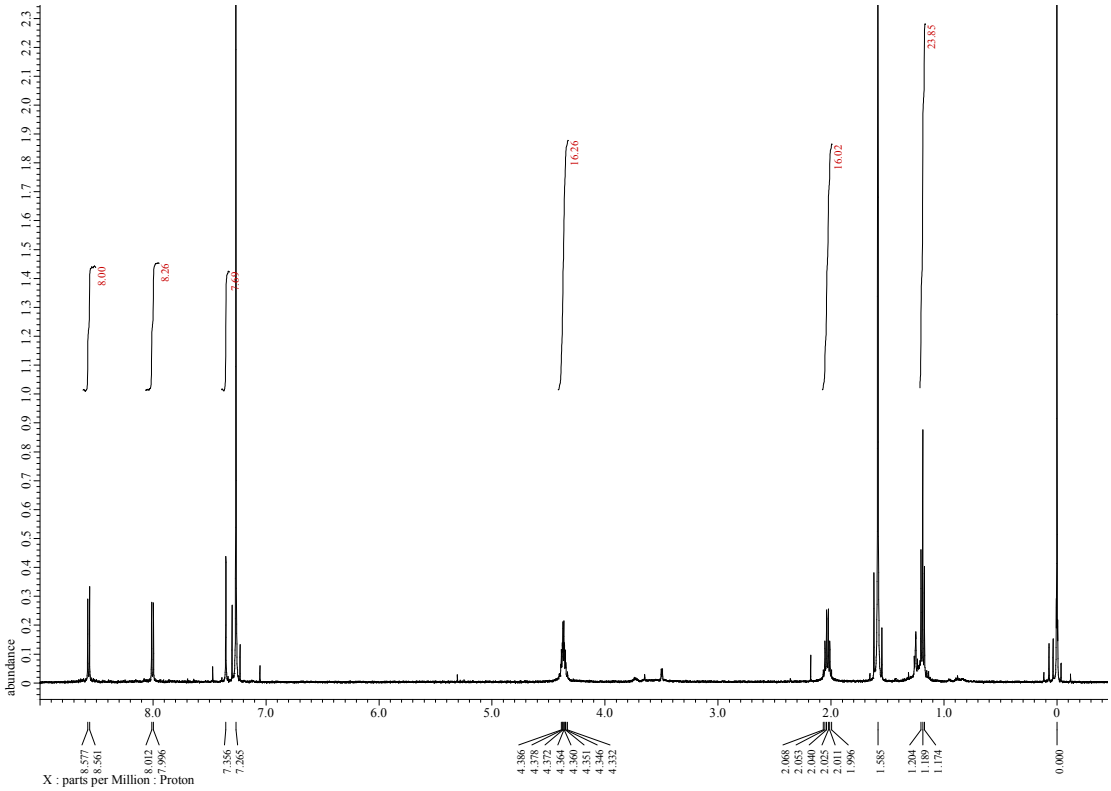


Figure S11. ^{1}H NMR spectrum of **CP6** in $CDCl_3$ at room temperature.

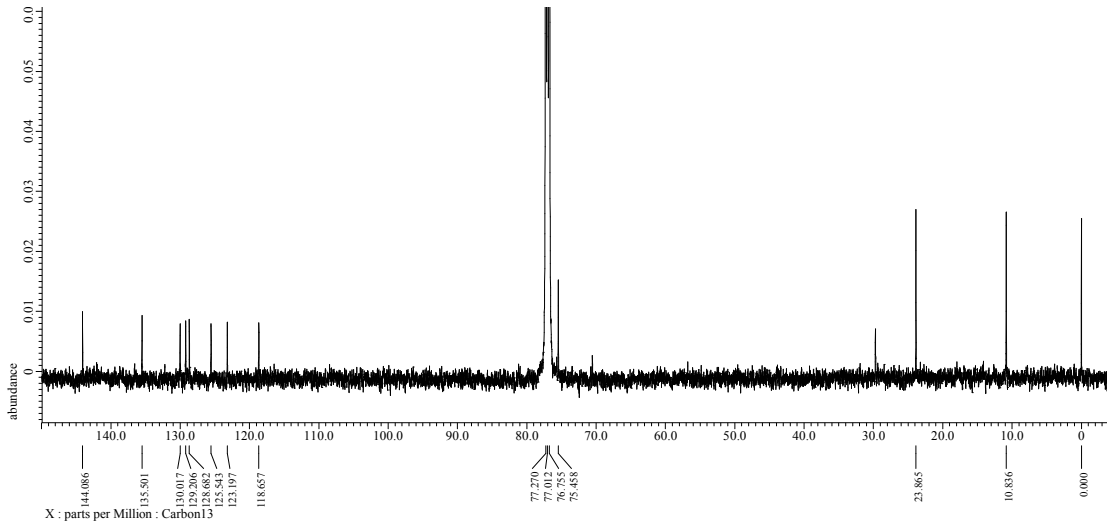


Figure S12. ^{13}C NMR spectrum of **CP6** in $CDCl_3$ at room temperature.

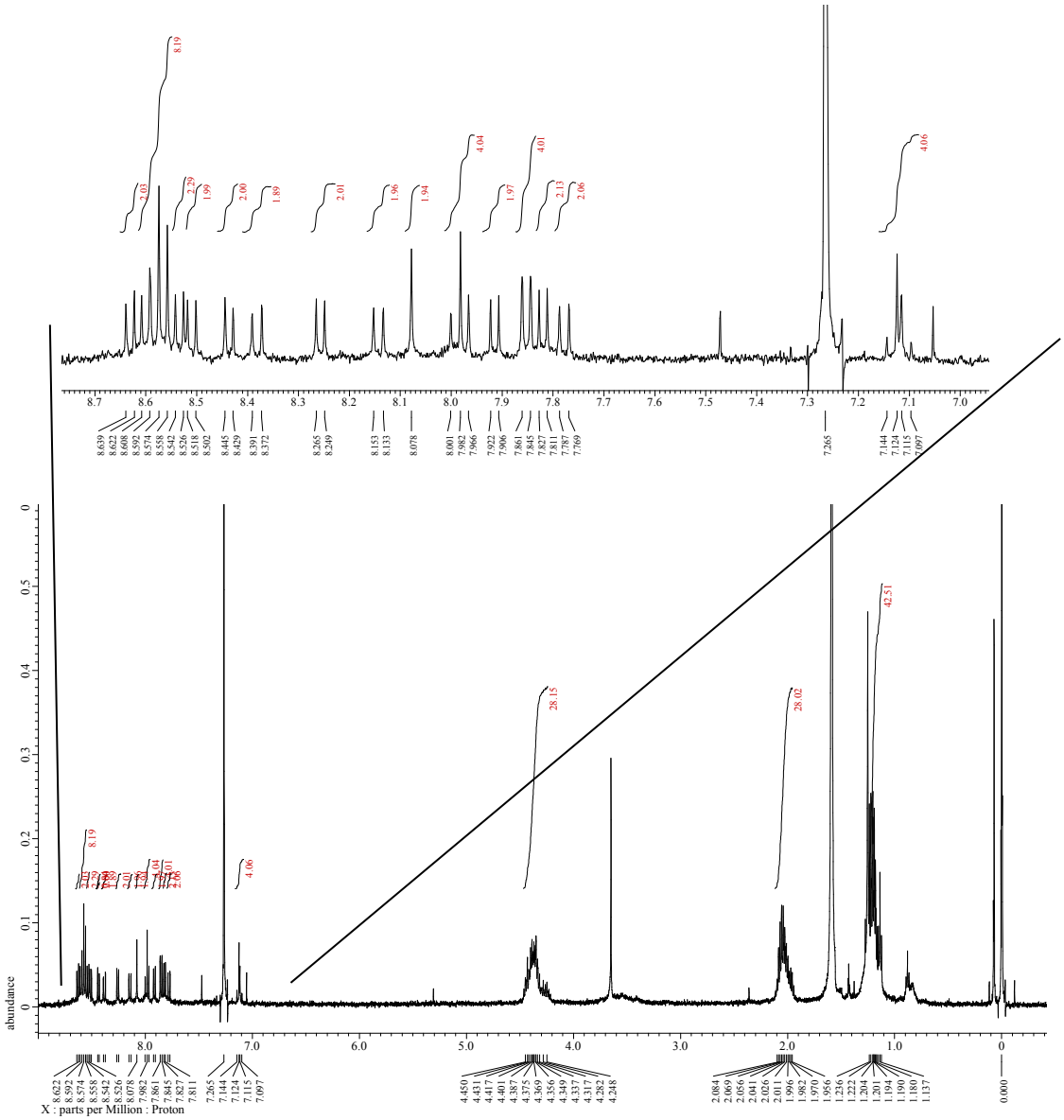


Figure S13. ^{1}H NMR spectrum of **CP7** in $CDCl_3$ at room temperature.

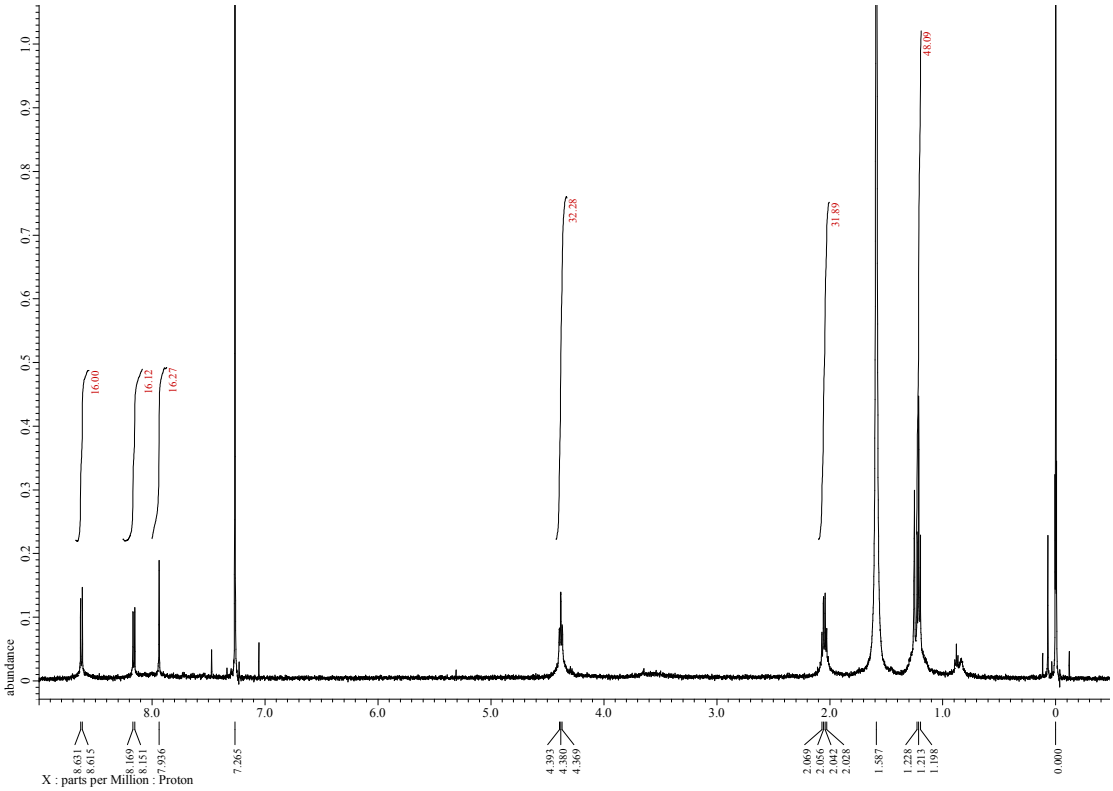


Figure S14. ^{1}H NMR spectrum of **CP8** in $CDCl_3$ at room temperature.

4. HR-MS

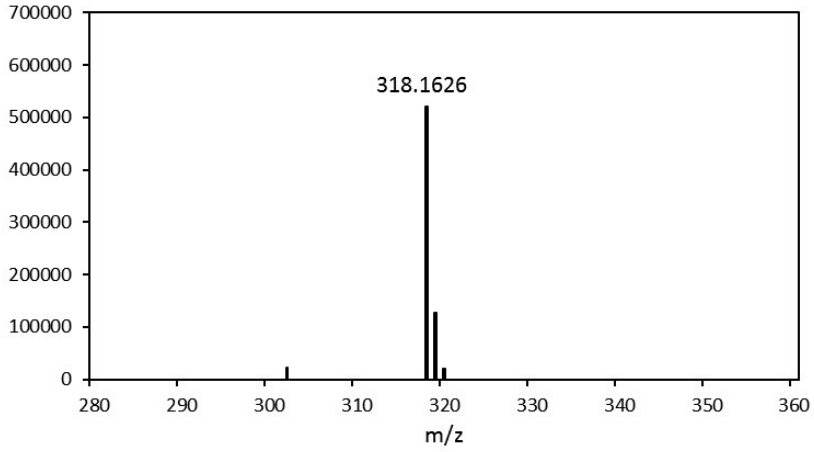


Figure S15. HR-EI mass spectrum of **P1**.

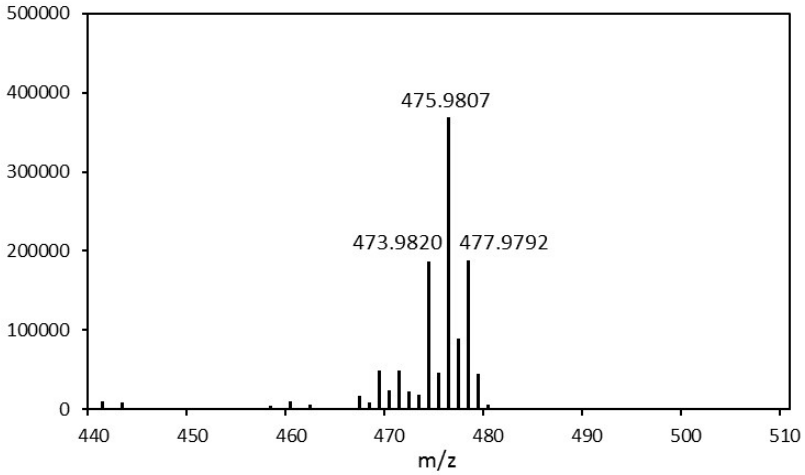


Figure S16. HR-EI mass spectrum of 1,8-dibromo-4,5-dipropoxypyrene.

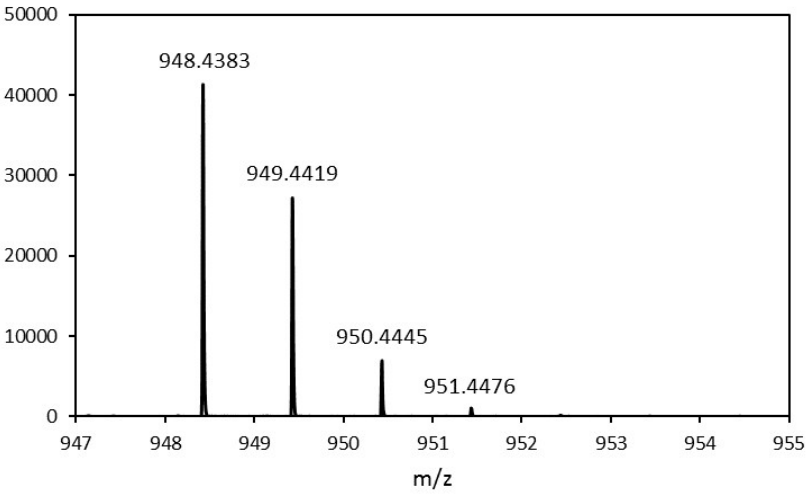


Figure S17. HR-Spiral-MALDI-TOF mass spectrum of **CP3**.

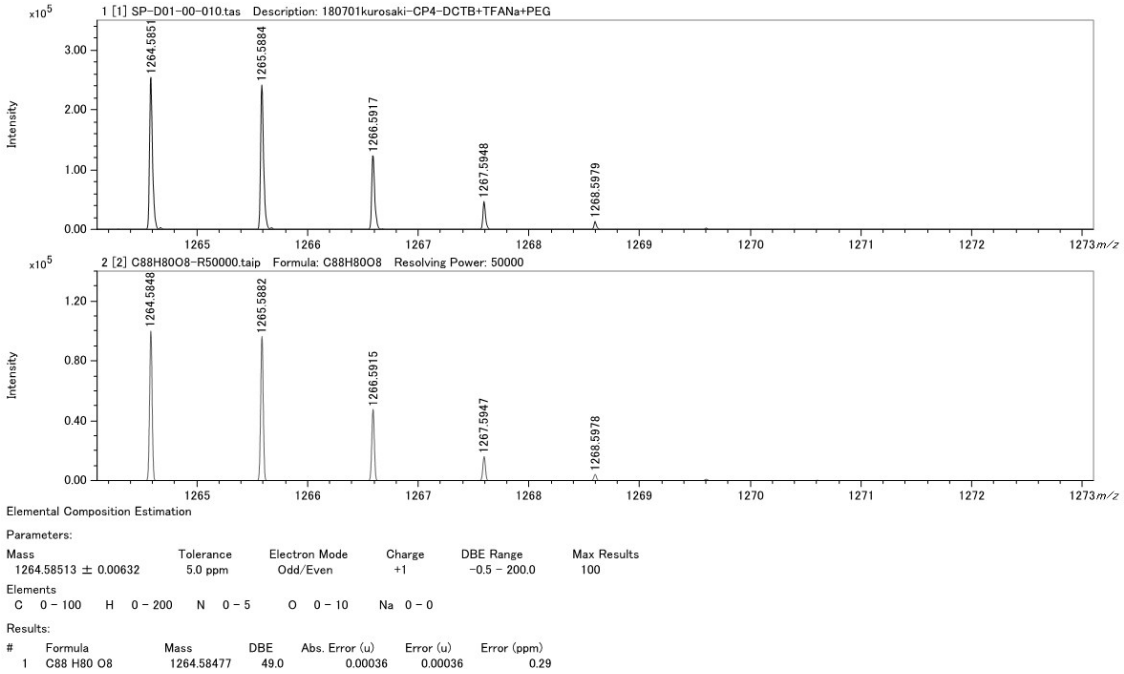


Figure S18. HR-Spiral-MALDI-TOF mass spectrum of **CP4**.

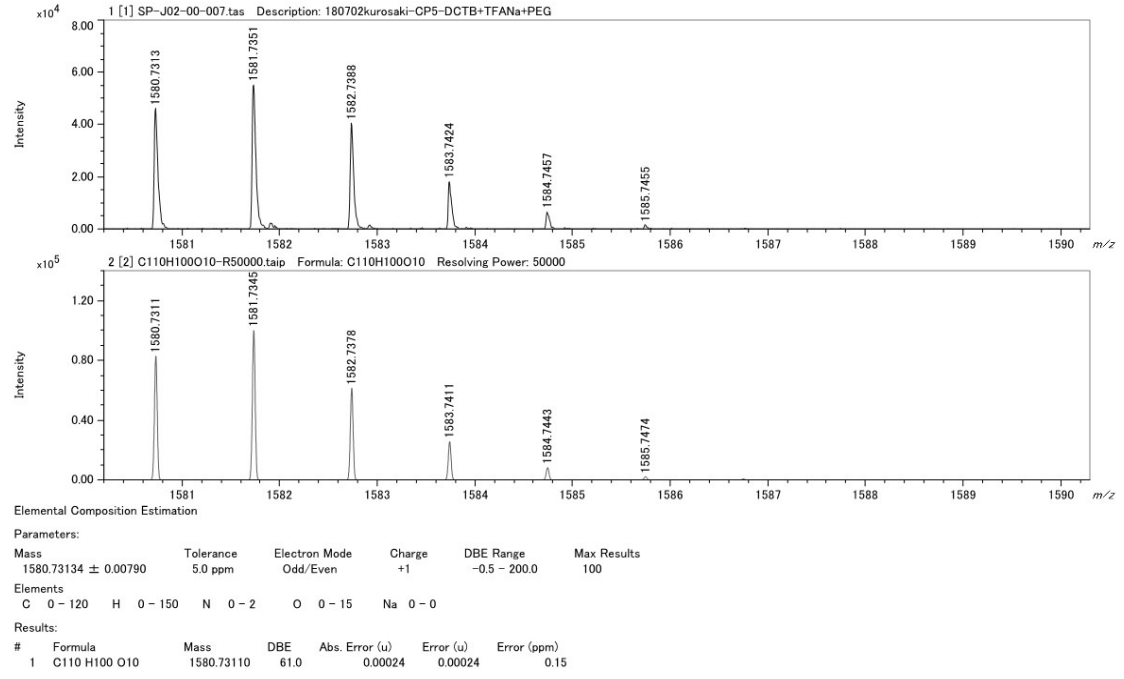


Figure S19. HR-Spiral-MALDI-TOF mass spectrum of **CP5**.

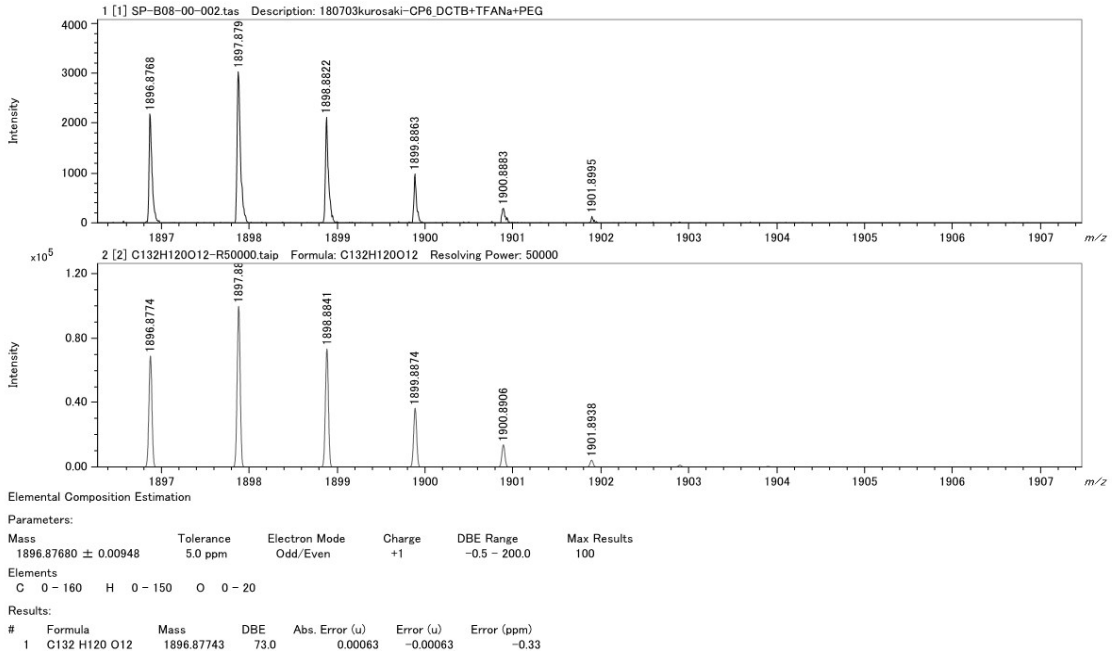


Figure S20. HR-Spiral-MALDI-TOF mass spectrum of **CP6**.

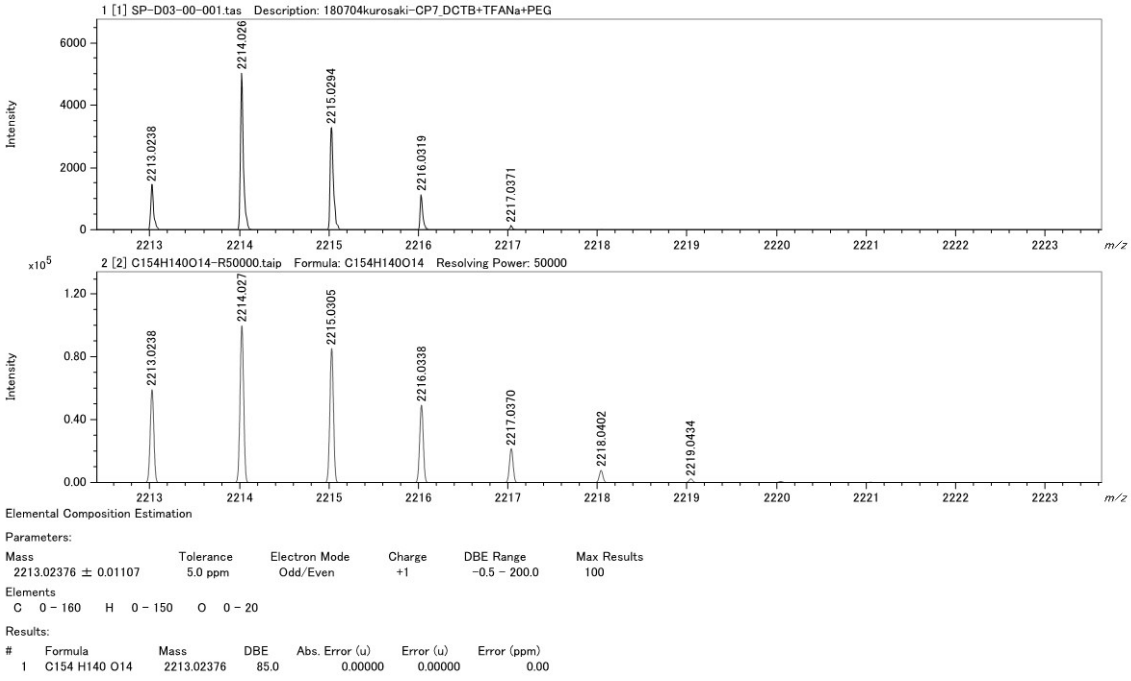
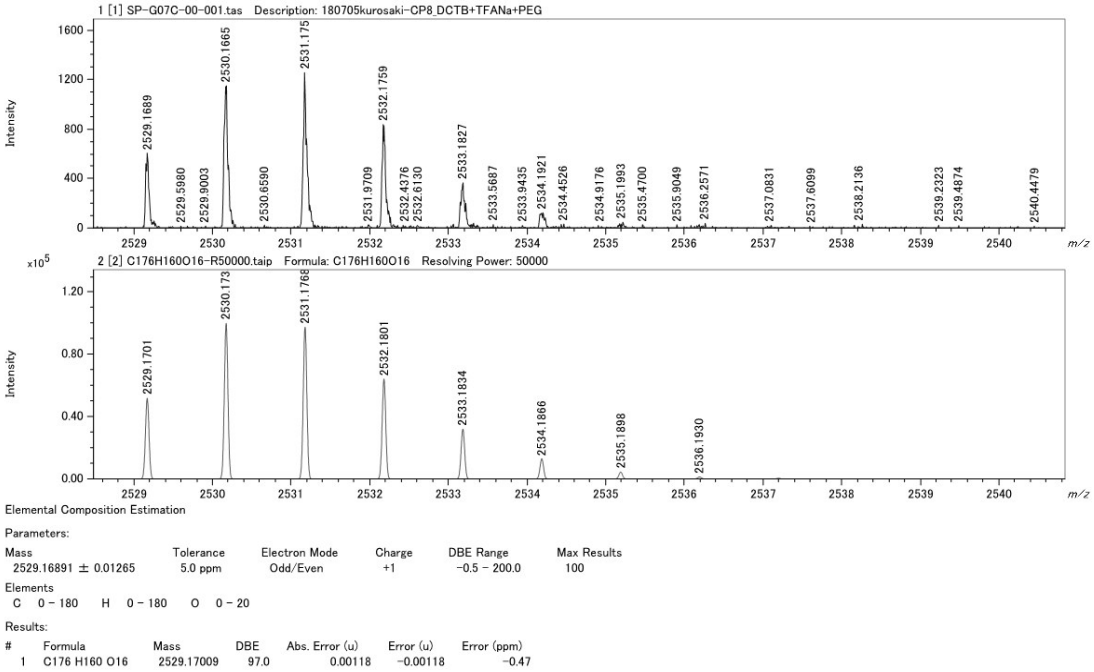


Figure S21. HR-Spiral-MALDI-TOF mass spectrum of **CP7**.



Elemental Composition Estimation

Parameters:

Mass	Tolerance	Electron Mode	Charge	DBE Range	Max Results
2529.16891 ± 0.01265	5.0 ppm	Odd/Even	+1	−0.5 – 200.0	100

Elements

C 0 – 180 H 0 – 180 O 0 – 20

Results:

#	Formula	Mass	DBE	Abs. Error (u)	Error (u)	Error (ppm)
1	C176 H160 O16	2529.17009	97.0	0.00118	−0.00118	−0.47

Figure S22. HR-Spiral-MALDI-TOF mass spectrum of **CP8**.

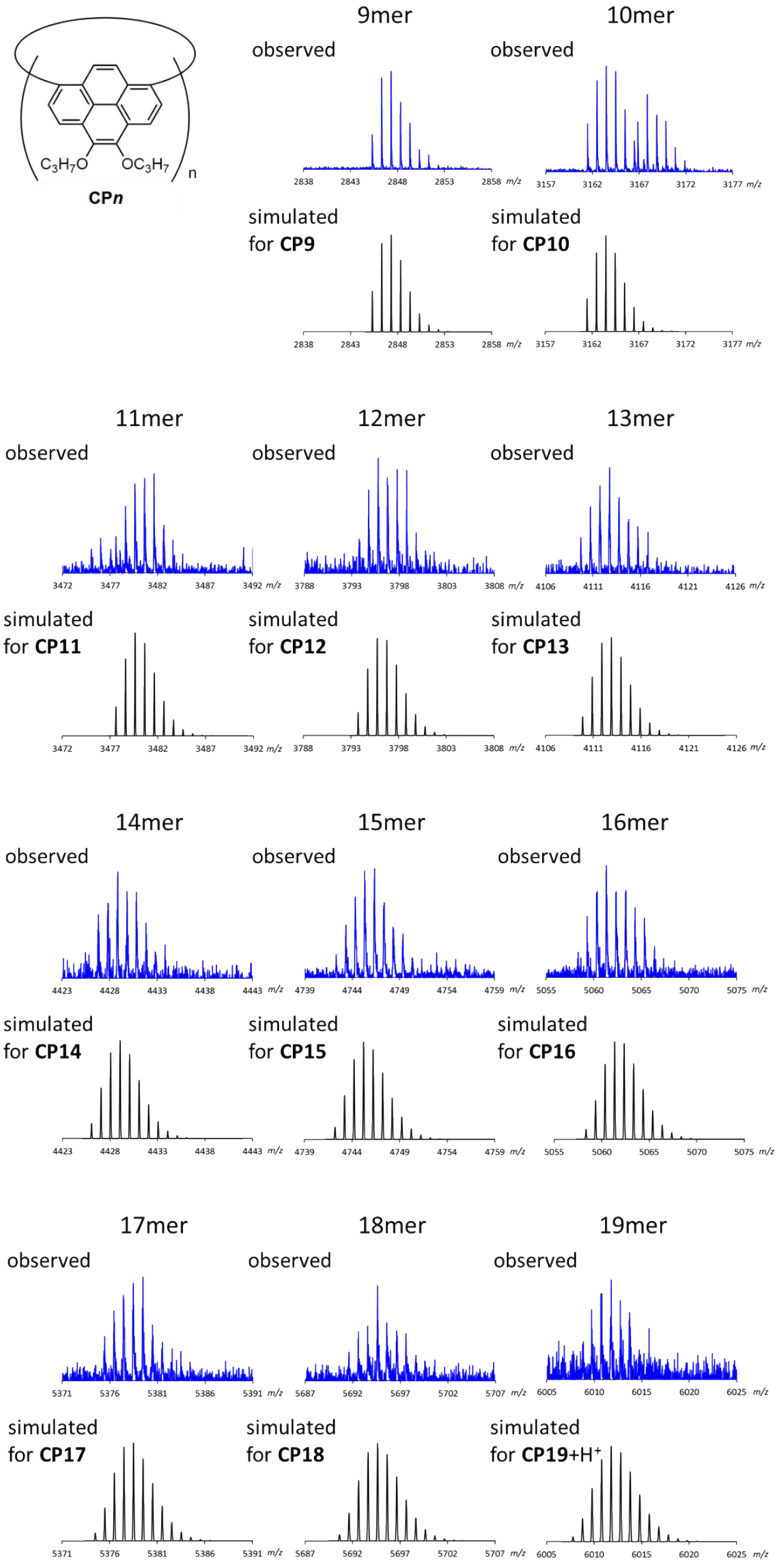


Figure S23. HR-Spiral-MALDI-TOF mass spectra showing the enlarged details of each peak (matrix: TCNQ, ionization mode: linear positive). Simulated peaks at the bottom are calculated for cyclic oligomers.

5. UV–vis Absorption and Fluorescence Spectra

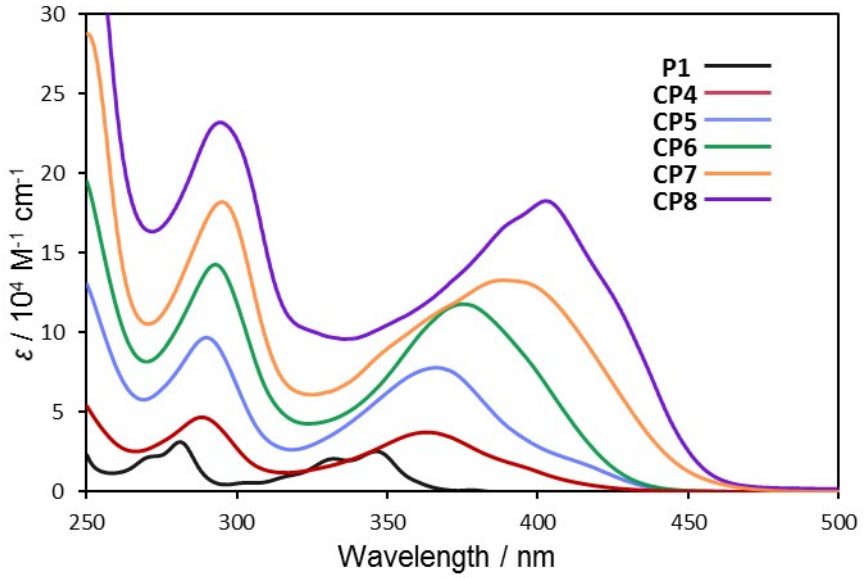


Figure S24. UV–visible absorption spectra of **P1**, **CP4**, **CP5**, **CP6**, **CP7** and **CP8** in CH_2Cl_2.

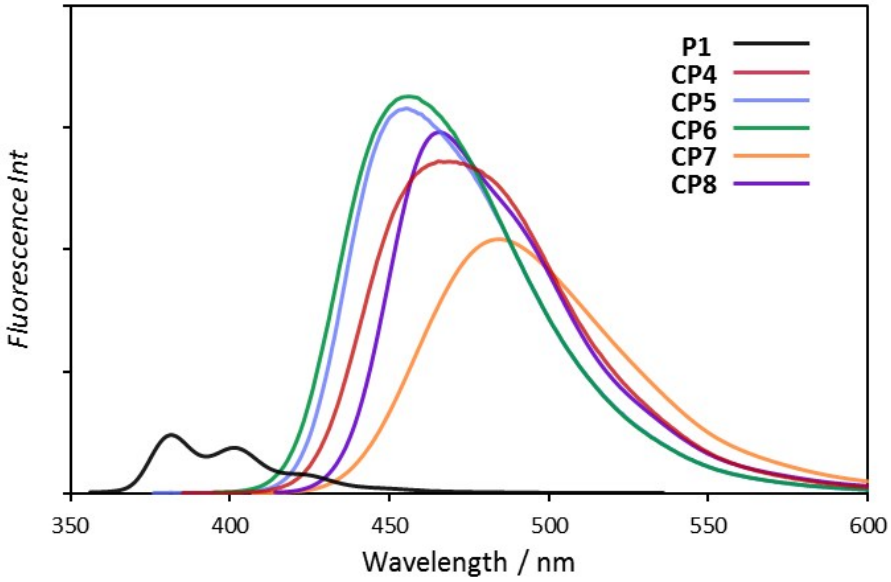


Figure S25. Fluorescence spectra of **P1**, **CP4**, **CP5**, **CP6**, **CP7** and **CP8** in CH_2Cl_2. Excitation wavelengths are the longest absorption maximum of each compound. Fluorescence intensity reflects the absolute fluorescence quantum yields.

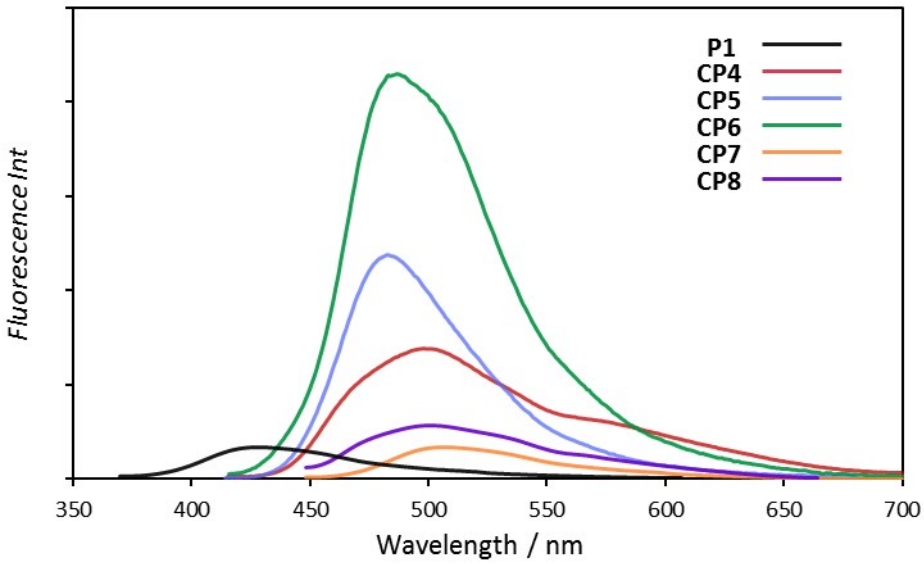


Figure S26. Fluorescence spectra of **P1**, **CP4**, **CP5**, **CP6**, **CP7** and **CP8** in solid. Excitation wavelengths are the longest absorption maximum of each compound. Fluorescence intensity reflects the absolute fluorescence quantum yields.

6. VT-NMR Spectra of CP5

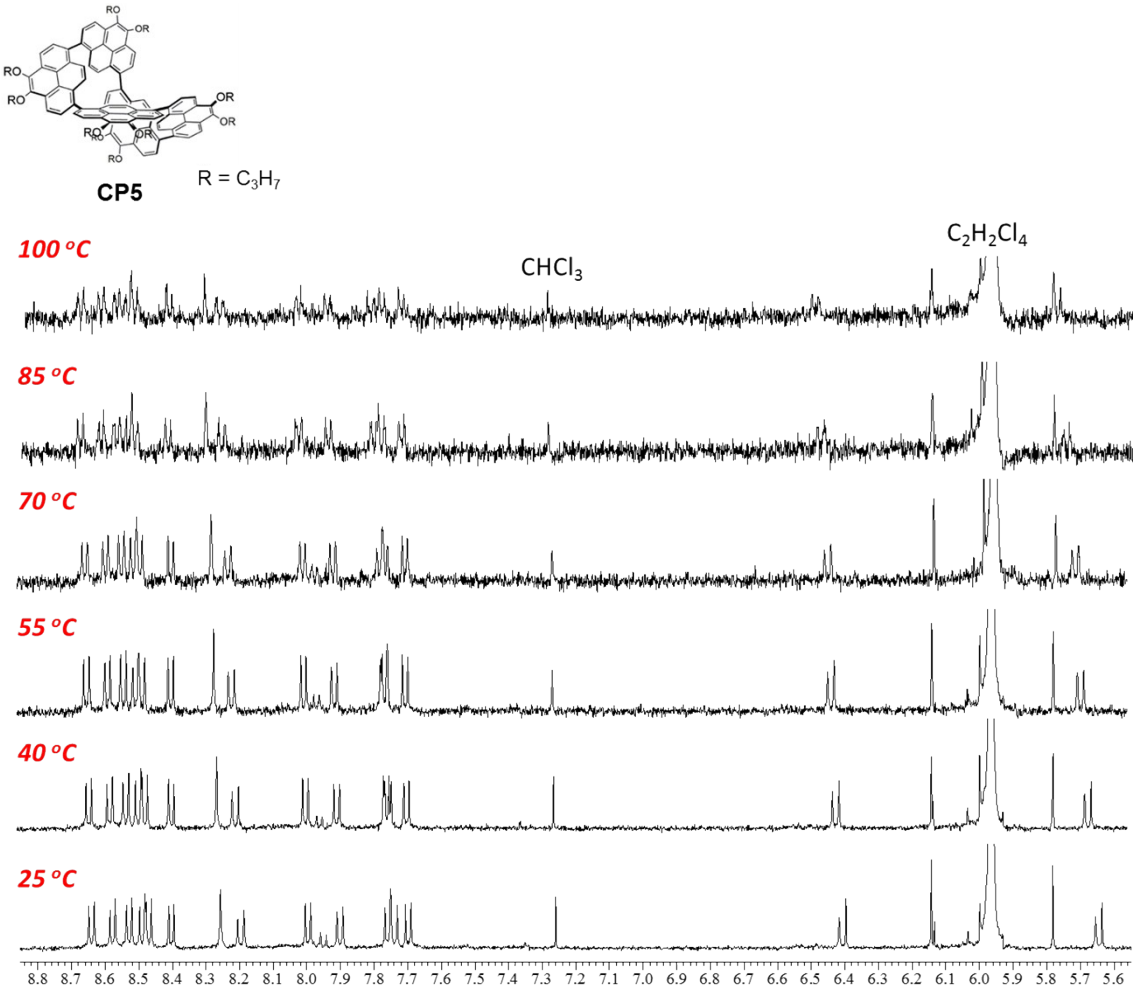


Figure S27. VT-NMR spectra of **CP5** in tetrachloroethane-d_2.

7. CD Spectral Change of CP5

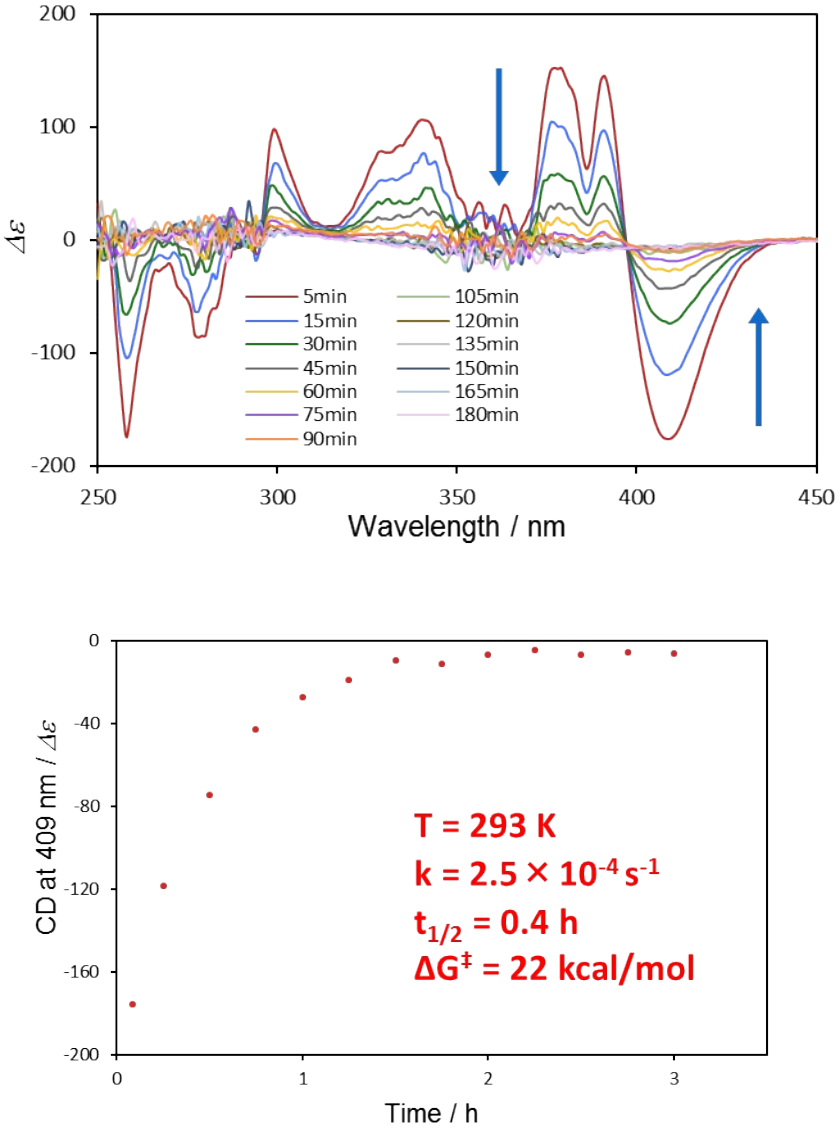


Figure S28. (Top) CD spectral change of (*R*,*S*,*R*,*S*,*R*)-**CP5** in hexane at 20°C and (bottom) time profile at 409 nm.

8. DFT Calculations

8.1. Computational Details

We focused on the model structures in which all the propyl groups were replaced by methyl groups. All the local minima and transition states were optimized (without any restrictions) at the B3LYP/6-31G(d) level.[S3,S4] All the geometry optimization and TD-DFT calculations were carried out using the Gaussian09 program.

8.2. Calculation results

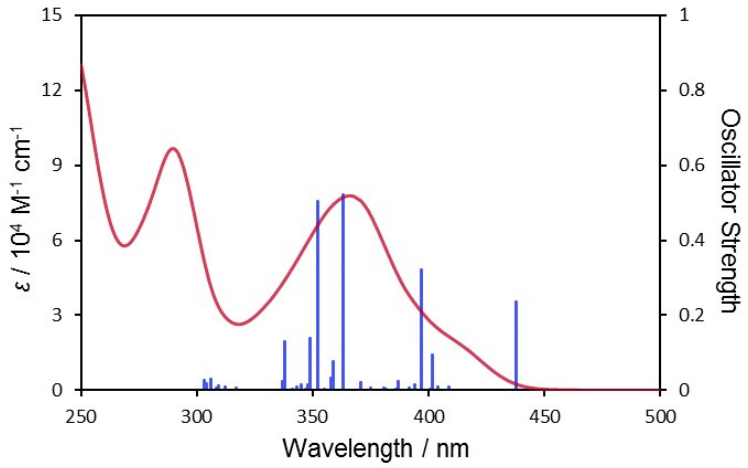


Figure S29. The excitation energies and the oscillator strengths of **CP5** calculated by the TD-DFT method (in blue) and the experimental UV-vis absorption spectrum (in red). One of the reasons of a slight mismatch between experimental and calculated spectra is probably because of the large molecular size of **CP5** and relatively low calculation level (B3LYP/6-31G(d)). It is also known that the B3LYP overestimates the charge delocalization so that the intensified π-conjugation between pyrene units in calculation would be another reason.

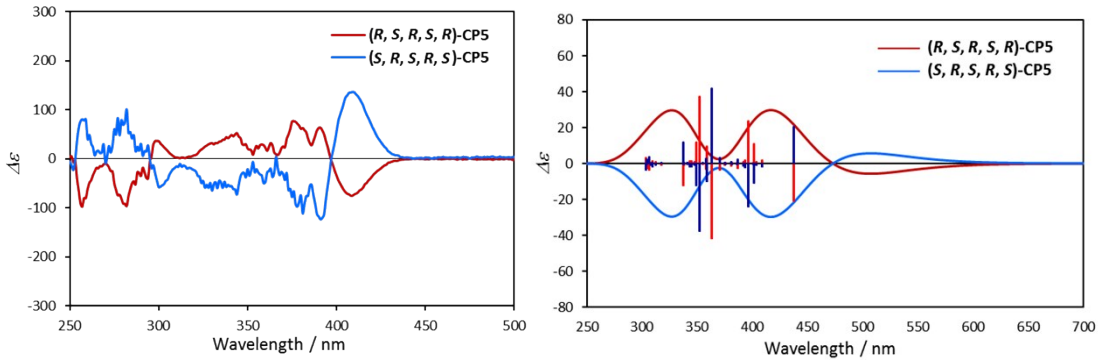


Figure S30. The CD spectra of **CP5** (left) in hexane and the calculated spectra by the by the TD-DFT method (right).

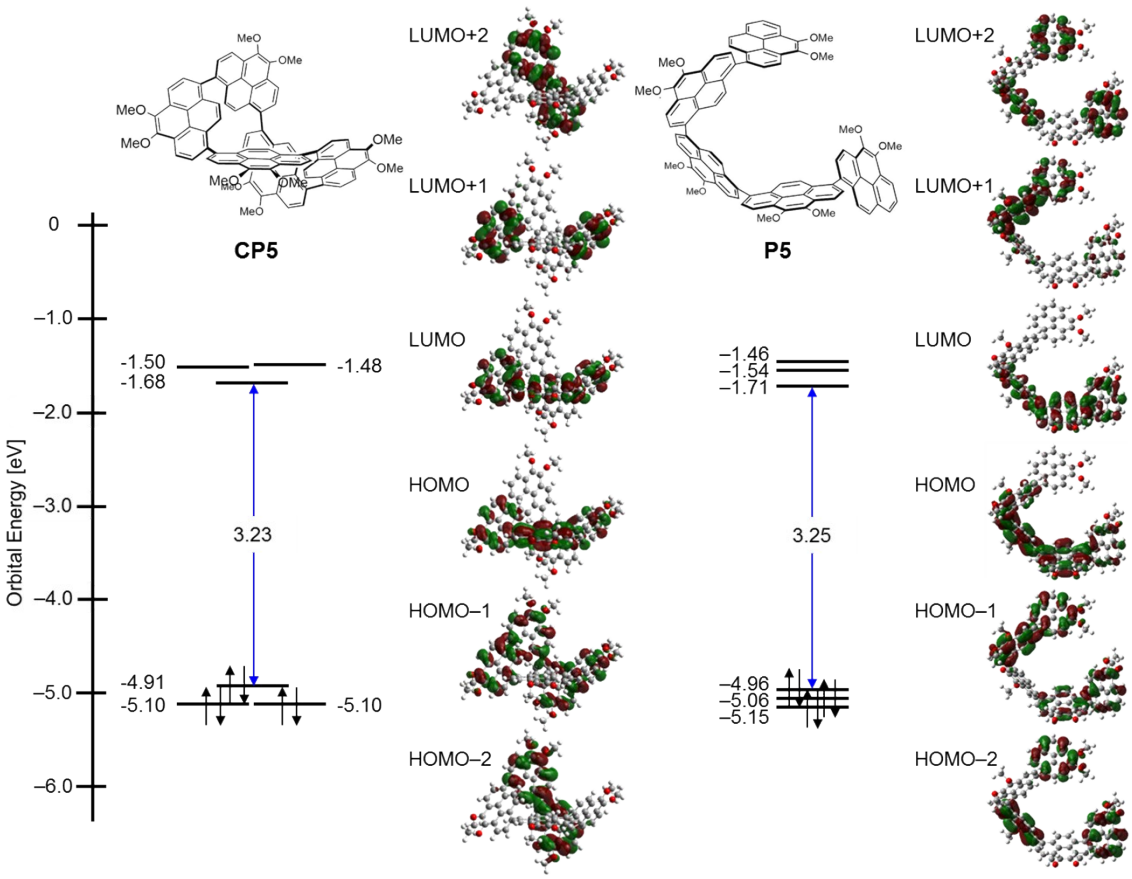


Figure S31. MO diagrams of **CP5** and linear pyrenylene 5-mer calculated at the B3LYP/6-31G(d) level. The propyl groups were replaced by methyl groups.

8.3. Calculation results for CP7

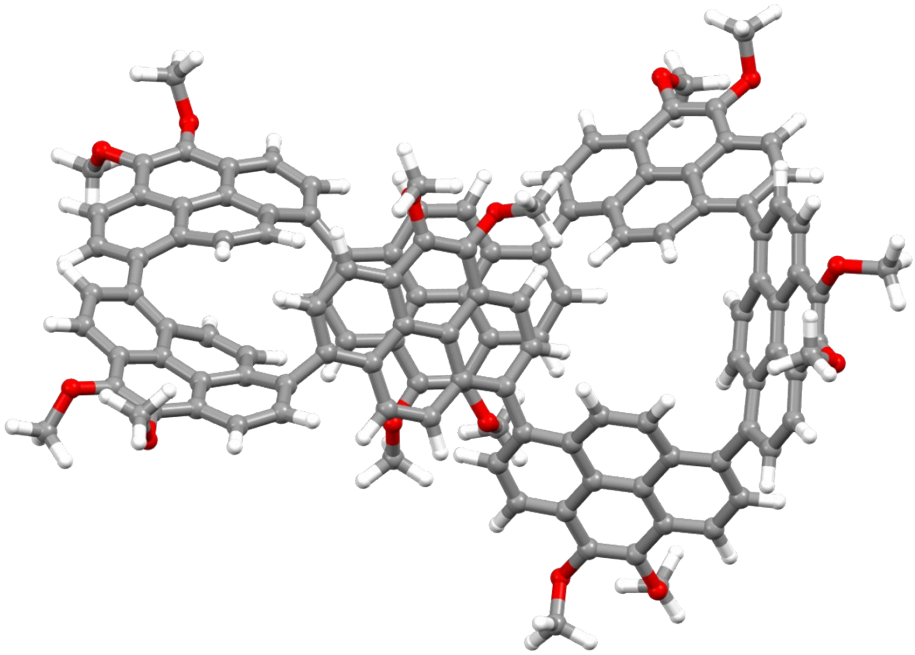


Figure S32. Optimized structure of **CP7** calculated at B3LYP/6-31G(d) level. The calculations were performed for methoxy substituted models

9. X-ray Crystal Structures

Table S2. Crystal data and structure refinement for **CP4**.

Empirical formula	$C_{80}H_{80}O_8$·(dichloromethane)$_{1.6}$·(water)$_{0.4}$
Formula weight	1407.39
Temperature	90(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 21.774(4) Å
	b = 45.367(8) Å β = 92.690(3)°
	c = 36.900(6) Å
Volume	36411(11) Å^3
Z	20
Density (calculated)	1.284 g/cm^3
Absorption coefficient	0.194 mm^{-1}
F(000)	14840
Crystal size	0.20 x 0.15 x 0.10 mm^3
Theta range for data collection	1.193 to 21.00°
Index ranges	$-21 \le h \le 16$, $-43 \le k \le 45$, $-37 \le l \le 37$
Reflections collected	131659
Independent reflections	38869 [R(int) = 0.2403]
Completeness to theta = 21.0°	99.4%
Max. and min. transmission	0.981 and 0.797
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	38869 / 183 / 4560
Goodness-of-fit on F^2	1.060
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.1233
R indices (all data)	wR_2 = 0.4012
Largest diff. peak and hole	0936 and –0.846 e.Å^{-3}

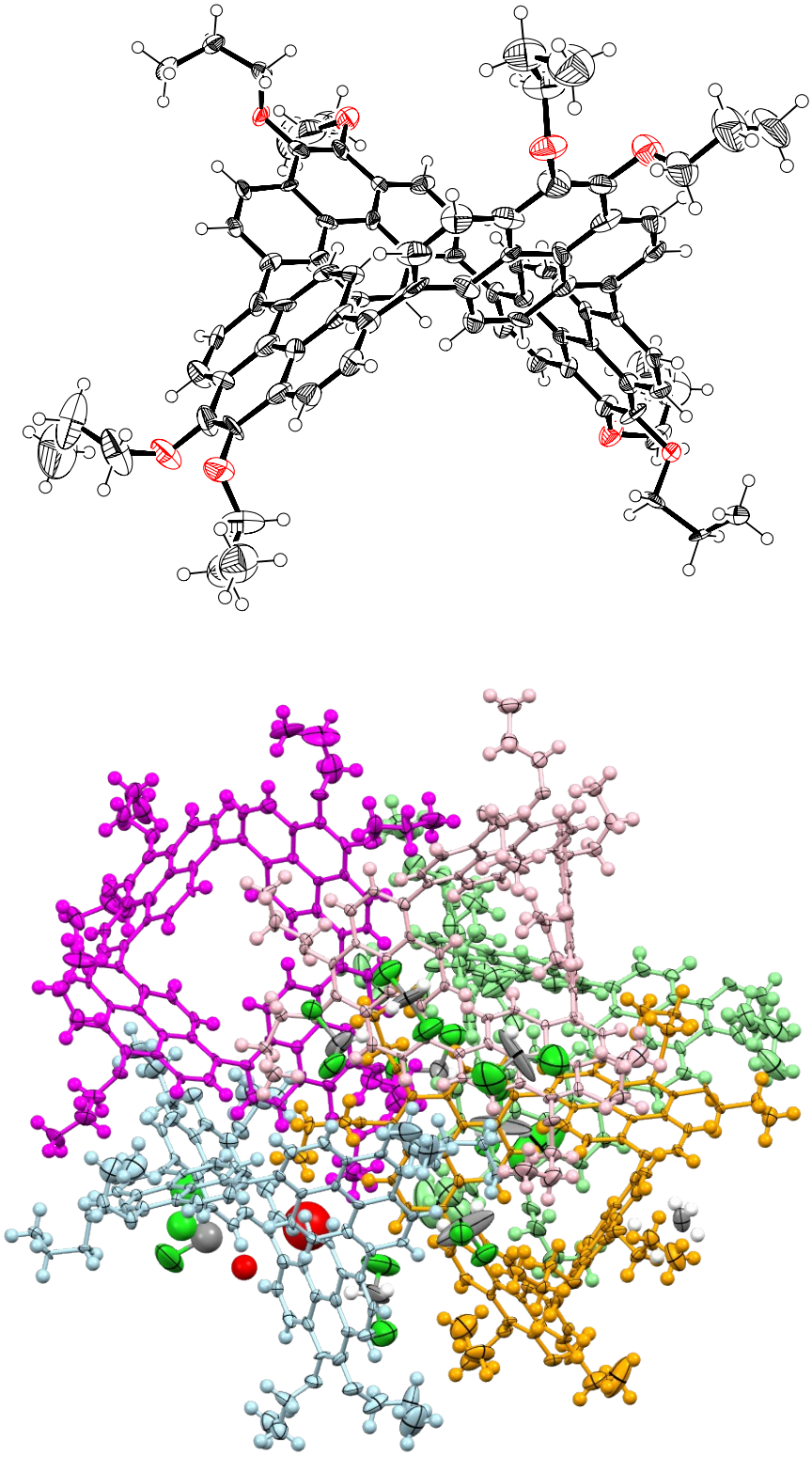


Figure S33. X-ray structure of **CP4**. (top) Monomeric view and (bottom) crystallographic asymmetric unit. The thermal ellipsoids are scaled to the 50% probability. The crystallographic asymmetric unit of **CP4** contains five identical molecules of slightly different structures.

Table S3. Crystal data and structure refinement for **CP6**.

Empirical formula	$C_{132}H_{120}O_{12}$·(dichloromethane)$_2$
Formula weight	2068.12
Temperature	90(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 18.716(4) Å
	b = 15.758(4) Å β = 111.956(4)°
	c = 18.963(5) Å
Volume	5187(2) Å^3
Z	2
Density (calculated)	1.324 g/cm^3
Absorption coefficient	0.182 mm^{-1}
F(000)	2184
Crystal size	0.15 x 0.15 x 0.03 mm^3
Theta range for data collection	1.735 to 25.799°
Index ranges	$-22 \le h \le 16$, $-19 \le k \le 19$, $-23 \le l \le 22$
Reflections collected	29527
Independent reflections	9962 [R(int) = 0.1190]
Completeness to theta = 25.242°	100.0%
Max. and min. transmission	0.995 and 0.839
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9962 / 15 / 738
Goodness-of-fit on F^2	1.101
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0793
R indices (all data)	wR_2 = 0.2405
Largest diff. peak and hole	0.820 and –0.404 e.Å^{-3}

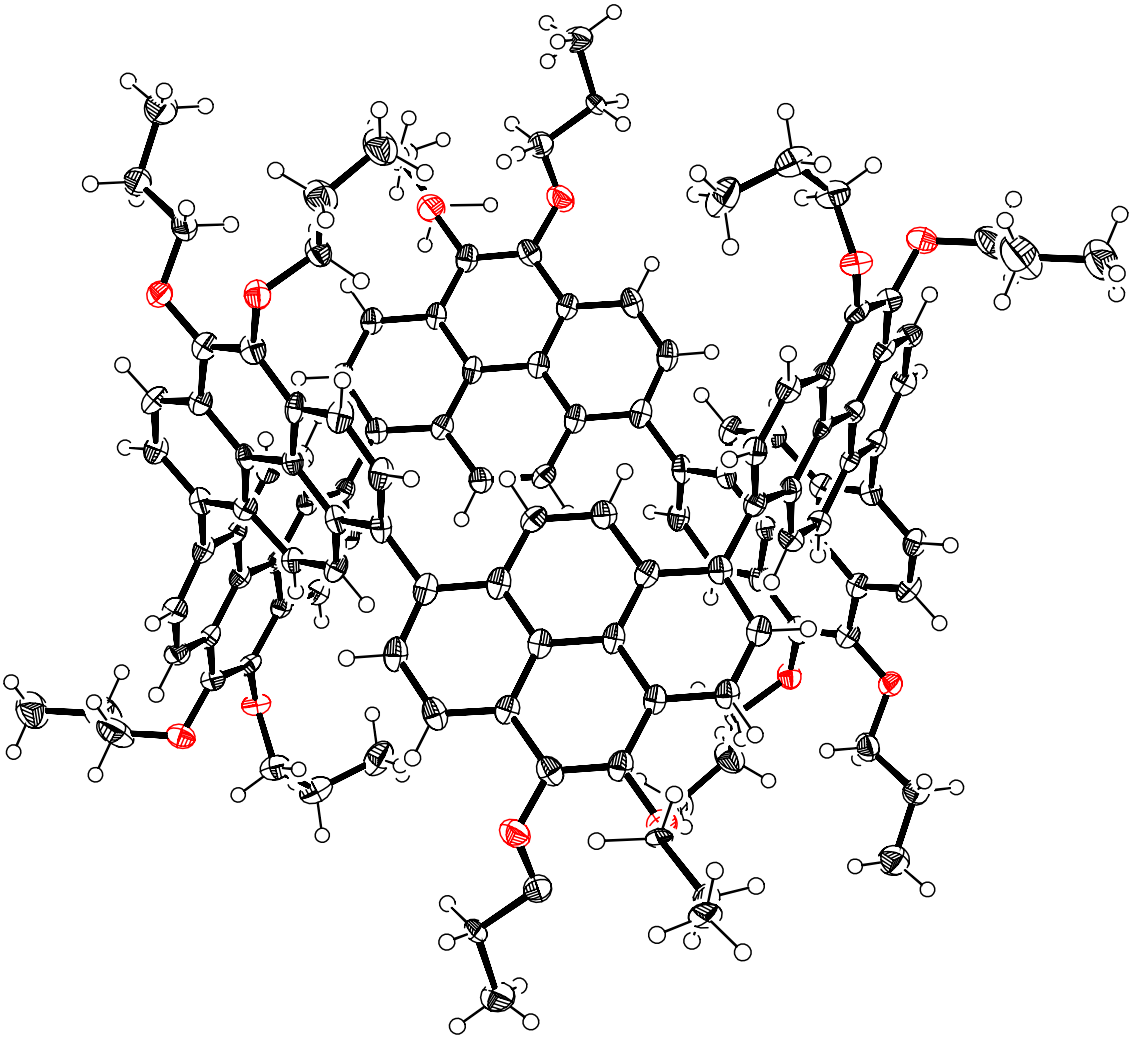


Figure S34. X-ray structure of **CP6**. The thermal ellipsoids are scaled to the 50% probability. Solvent molecules are omitted for clarity.

10. Cartesian Coordinates

The cartesian coordinates (in Å) optimized at the B3LYP/6-31G(d) level are shown.

CP5

1	C	-5.51478	0.3019	1.26341
2	C	3.99135	1.19482	1.29509
3	C	3.74435	2.33527	1.95815
4	C	3.90203	3.50599	1.32537
5	C	4.39676	3.54226	0.0763
6	C	4.7117	2.45452	-0.62493
7	C	4.34492	1.30375	-0.01254
8	C	4.45261	4.63442	-0.68505
9	C	5.14279	4.57261	-1.84809
10	C	4.86749	1.49901	-2.62297
11	C	5.92646	3.68038	-2.50281
12	C	5.24225	2.58947	-1.87815
13	C	6.64745	2.65452	-3.01058
14	C	-6.67605	-0.78666	2.90753
15	C	-5.4728	-0.46656	2.39072
16	C	-4.39329	-0.89404	3.10818
17	C	-4.52508	-1.46178	4.33747
18	C	-5.75732	-1.64581	4.86057
19	C	-6.8251	-1.35155	4.10544
20	C	-3.11551	-0.71101	2.72876
21	C	-2.06609	-1.2182	3.38969
22	C	-2.17729	-1.73809	4.62133
23	C	-3.45245	-1.81628	5.09088
24	C	-1.12446	-2.23521	5.32467
25	C	-1.39819	-2.58642	6.59923
26	C	-2.63345	-2.62491	7.09727
27	C	-3.68419	-2.30954	6.32732
28	C	-4.91844	-2.51475	6.83294
29	C	-5.9779	-2.10252	6.11128
30	C	0.15851	-2.52517	4.95856
31	C	1.11752	-1.88703	4.23606
32	C	2.29708	-2.48624	3.91756
33	C	2.56786	-3.73872	4.34454
34	C	1.6342	-4.37926	5.05857
35	C	0.47093	-3.78873	5.32747
36	C	1.00702	-0.59896	3.86407

37	C	1.9276	0.0115	3.10063
38	C	3.07017	-0.59437	2.72892
39	C	3.24412	-1.86429	3.17549
40	C	3.97411	-0.02336	1.8933
41	C	5.09324	-0.72517	1.62392
42	C	5.29336	-1.95593	2.09261
43	C	4.36303	-2.55129	2.85289
44	C	4.59695	-3.82126	3.24432
45	C	3.72409	-4.38974	4.09732
46	C	4.37847	0.35906	-2.10504
47	C	4.19295	0.22588	-0.79594
48	C	6.19213	2.14366	-4.17402
49	C	5.04513	1.50255	-3.96454
50	C	4.30576	0.7266	-4.78616
51	C	-4.65289	0.3524	0.22015
52	C	-4.63956	1.43491	-0.58655
53	C	-5.5878	2.3873	-0.57881
54	C	-6.55242	2.24111	0.33945
55	C	-6.47094	1.26271	1.24988
56	C	-3.81737	-0.64912	-0.12589
57	C	-3.61509	1.60992	-1.4272
58	C	-3.49615	2.72038	-2.15781
59	C	-4.46993	3.65151	-2.18149
60	C	-5.58358	3.42823	-1.4443
61	C	-2.68704	0.67721	-1.6724
62	C	-1.65969	1.05734	-2.47877
63	C	-1.18516	2.32861	-2.22397
64	C	-2.30237	2.86474	-2.76008
65	C	-2.86236	-0.50811	-1.06304
66	C	4.80563	-0.02212	-5.77869
67	C	4.02656	-0.96419	-6.33615
68	C	2.75392	-1.1845	-5.94039
69	C	2.20163	-0.34574	-5.0432
70	C	2.97898	0.63499	-4.55211
71	C	0.92348	-0.48369	-4.62004
72	C	0.32341	0.41265	-3.79039
73	C	1.0827	1.49054	-3.5131
74	C	2.36663	1.59696	-3.85061
75	C	0.26002	-1.57527	-5.04636
76	C	-0.98931	-1.75314	-4.58483

77	C	-1.55568	-0.88833	-3.73403
78	C	-0.93317	0.22189	-3.29064
79	C	2.0272	-2.20652	-6.44162
80	C	0.81413	-2.46768	-5.89929
81	O	0.10034	-3.54806	-6.36908
82	C	0.32388	-4.73769	-5.64478
83	O	2.57036	-3.10252	-7.33458
84	C	2.2773	-2.81026	-8.68278
85	O	-4.3822	4.7606	-2.98974
86	C	-3.888	5.91164	-2.3404
87	O	-6.56955	4.38789	-1.4214
88	C	-7.59163	4.16984	-2.36764
89	O	-7.24362	-2.30692	6.61619
90	C	-7.74378	-1.21933	7.36265
91	O	3.9815	5.83963	-0.21102
92	O	5.21617	5.83049	-2.43643
93	O	-5.12957	-2.98986	8.10904
94	O	5.76391	-4.49011	2.94487
95	C	2.64435	6.10165	-0.57674
96	C	6.06485	6.03141	-3.54645
97	C	-5.31128	-4.38729	8.17656
98	C	5.67583	-5.30841	1.79895
99	O	3.95857	-5.67986	4.52101
100	C	4.67041	-5.75934	5.73618
101	H	3.44964	2.3422	3.01982
102	H	3.64485	4.42822	1.87182
103	H	7.62659	3.09289	-3.30728
104	H	-7.62464	-0.59848	2.3735
105	H	-7.8629	-1.52513	4.4351
106	H	-2.84282	-0.16385	1.82022
107	H	-1.09759	-1.13919	2.87958
108	H	-0.60576	-2.89358	7.30864
109	H	-2.72906	-2.97989	8.13665
110	H	1.75424	-5.41562	5.41578
111	H	-0.2418	-4.4692	5.83158
112	H	0.13564	0.00232	4.17233
113	H	1.69173	1.03828	2.78106
114	H	5.92465	-0.30808	1.02505
115	H	6.24357	-2.43598	1.80671
116	H	4.17106	-0.54154	-2.7082

117	H	3.7998	-0.74523	-0.45109
118	H	6.74785	2.09847	-5.12348
119	H	-7.36406	2.98011	0.44876
120	H	-7.21427	1.38895	2.05646
121	H	-3.87175	-1.62044	0.39665
122	H	-0.56781	1.66016	-1.59459
123	H	-2.10529	3.77543	-3.352
124	H	-2.15511	-1.34099	-1.21035
125	H	5.8711	0.03324	-6.05628
126	H	4.51445	-1.60769	-7.08725
127	H	0.78421	2.38246	-2.9562
128	H	2.88218	2.52261	-3.53964
129	H	-1.60913	-2.61024	-4.89731
130	H	-2.60413	-1.10993	-3.47243
131	H	0.03329	-4.59874	-4.57969
132	H	-0.30465	-5.53935	-6.09267
133	H	1.3937	-5.03523	-5.71134
134	H	1.1786	-2.84263	-8.85437
135	H	2.67601	-1.80693	-8.95231
136	H	2.76739	-3.5807	-9.31884
137	H	-3.83534	6.73439	-3.0878
138	H	-4.56807	6.21616	-1.51498
139	H	-2.86839	5.719	-1.93896
140	H	-8.09063	3.19445	-2.17219
141	H	-8.33826	4.98883	-2.26672
142	H	-7.17045	4.18583	-3.39746
143	H	-8.76798	-1.48015	7.71095
144	H	-7.0972	-1.02817	8.24745
145	H	-7.79621	-0.30817	6.7262
146	H	2.3541	7.08752	-0.14994
147	H	2.54951	6.14201	-1.68467
148	H	1.97373	5.31448	-0.16508
149	H	5.97407	7.09742	-3.85401
150	H	7.12528	5.84062	-3.26713
151	H	5.74362	5.3972	-4.40303
152	H	-4.41185	-4.91136	7.78369
153	H	-5.45858	-4.66627	9.24371
154	H	-6.2105	-4.68875	7.59526
155	H	6.66782	-5.78614	1.6374
156	H	4.91087	-6.10201	1.94868

157	H	5.41707	-4.6951	0.90736
158	H	4.10133	-5.25367	6.54773
159	H	4.79666	-6.83441	5.99433
160	H	5.67388	-5.29173	5.62641

Linear Pyrenylene 5-mer (P5)

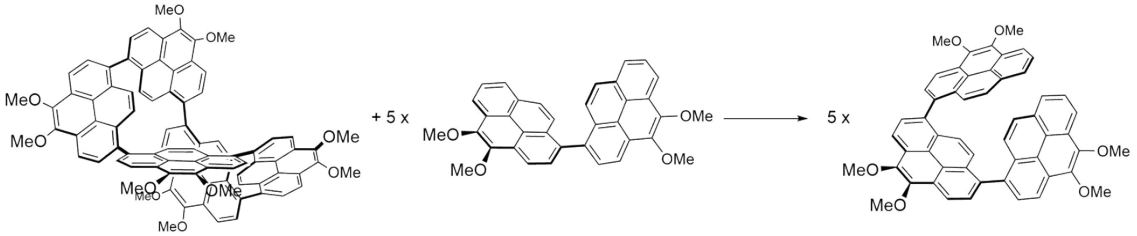
1	C	-0.72182	-1.1849	-3.40225
2	C	-2.07053	-1.29596	-3.47367
3	C	-2.57165	-2.52864	-3.67073
4	C	-1.77438	-3.59255	-3.81576
5	C	-0.43571	-3.47782	-3.76229
6	C	0.09265	-2.2597	-3.5254
7	C	1.43544	-2.13883	-3.42168
8	C	2.01451	-0.94681	-3.14627
9	C	1.19705	0.11806	-3.06705
10	C	-0.13196	-0.00325	-3.14988
11	C	2.20662	-3.23203	-3.59055
12	C	3.54229	-3.08194	-3.54665
13	C	4.10483	-1.89723	-3.28285
14	C	3.35706	-0.81056	-3.01765
15	C	0.33867	-4.566	-3.96564
16	C	1.67439	-4.45696	-3.79314
17	C	4.00665	0.31866	-2.63716
18	O	2.46318	-5.56837	-3.99256
19	O	-0.20337	-5.81362	-4.18267
20	C	3.67061	1.11165	-1.59057
21	C	4.29622	2.2875	-1.34984
22	C	5.29581	2.69051	-2.15999
23	C	5.69002	1.86264	-3.14366
24	C	5.07147	0.69762	-3.36728
25	C	3.93276	3.07655	-0.31395
26	C	4.54514	4.26713	-0.15314
27	C	5.56762	4.65649	-0.94564
28	C	5.89359	3.89282	-2.01182
29	C	2.97143	2.69261	0.55825
30	C	2.59147	3.47495	1.59755
31	C	3.14783	4.69739	1.67501
32	C	4.11634	5.07491	0.83286
33	C	2.73098	0.73368	-0.70591
34	C	2.36242	1.51955	0.31093

35	O	6.1771	5.88254	-0.79571
36	O	6.93258	4.29241	-2.82303
37	C	-2.94836	-0.26205	-3.47036
38	C	-2.70862	0.74866	-4.32409
39	C	-3.57816	1.7528	-4.4779
40	C	-4.72883	1.80631	-3.78324
41	C	-4.99946	0.79637	-2.93074
42	C	-4.11307	-0.21639	-2.77952
43	C	-5.57499	2.84646	-3.9597
44	C	-6.77012	2.8278	-3.32478
45	C	-7.0624	1.78463	-2.51533
46	C	-6.17421	0.80175	-2.26146
47	C	-8.27161	1.70692	-1.93091
48	C	-8.57081	0.73635	-1.06077
49	C	-7.67768	-0.21551	-0.73753
50	C	-6.48314	-0.17469	-1.37551
51	C	-5.57547	-1.15192	-1.2059
52	C	-4.41245	-1.15563	-1.86523
53	C	1.70172	3.13066	2.56185
54	C	0.7296	4.01519	2.85232
55	C	-0.25949	3.71542	3.70268
56	C	-0.30838	2.52752	4.33082
57	C	0.70188	1.66186	4.11752
58	C	1.69791	1.96409	3.25115
59	C	0.69364	0.491	4.78752
60	C	1.70015	-0.38971	4.61761
61	C	2.72396	-0.07137	3.8124
62	C	2.72603	1.09757	3.16099
63	C	-0.30806	0.20017	5.64292
64	C	-0.29214	-0.98815	6.28007
65	C	0.69823	-1.87103	6.09438
66	C	1.7037	-1.56657	5.26579
67	C	-1.34552	2.22562	5.14359
68	C	-1.2994	1.08845	5.87507
69	O	-2.34767	0.79531	6.71877
70	O	-2.36323	3.12374	5.37754
71	C	-8.01343	-1.07685	0.25493
72	C	-9.1991	-1.72321	0.36891
73	C	-9.49344	-2.4632	1.46511
74	C	-8.61422	-2.56795	2.48118

75	C	-7.43097	-1.94205	2.35507
76	C	-7.14	-1.21605	1.26947
77	C	-10.09588	-1.72292	-0.6369
78	C	-11.27345	-2.35059	-0.53595
79	C	-11.57413	-3.04079	0.57335
80	C	-10.6712	-3.11309	1.5718
81	C	-12.75681	-3.67191	0.66369
82	C	-13.04569	-4.38691	1.75696
83	C	-12.14219	-4.47604	2.74204
84	C	-10.94871	-3.85304	2.66513
85	C	-10.04236	-3.98687	3.65811
86	C	-8.90177	-3.2613	3.6056
87	O	-7.98725	-3.38905	4.62763
88	O	-10.32064	-4.71131	4.7958
89	C	-8.15497	-2.44853	5.66542
90	C	-9.85561	-6.04241	4.75377
91	O	-5.31005	3.84712	-4.87106
92	C	-4.46268	4.87443	-4.39944
93	O	-7.70406	3.8021	-3.60924
94	C	-7.79153	4.84563	-2.66172
95	C	2.70289	-6.31607	-2.82065
96	C	-0.32269	-6.1561	-5.54594
97	C	7.34194	5.84805	-0.00091
98	C	6.52981	5.08031	-3.92167
99	C	-2.17358	1.27298	8.03465
100	C	-3.48998	2.93605	4.5498
101	H	-3.65423	-2.69639	-3.81259
102	H	-2.2772	-4.55205	-4.0213
103	H	1.57694	1.14198	-2.91987
104	H	-0.70391	0.92415	-2.98683
105	H	4.23508	-3.92855	-3.68501
106	H	5.20575	-1.87995	-3.19864
107	H	6.50743	2.11994	-3.83754
108	H	5.41446	0.11542	-4.24068
109	H	2.89733	5.39745	2.49153
110	H	4.56055	6.06728	1.01655
111	H	2.21251	-0.23625	-0.77505
112	H	1.52847	1.14526	0.92586
113	H	-1.82712	0.74498	-4.9899
114	H	-3.30724	2.50806	-5.23333

115	H	-9.05918	2.45951	-2.09835
116	H	-9.54985	0.80717	-0.55442
117	H	-5.74858	-2.01574	-0.544
118	H	-3.72628	-1.98146	-1.6174
119	H	0.65755	4.98681	2.33221
120	H	-1.04387	4.47984	3.83015
121	H	3.5836	-0.75215	3.68623
122	H	3.62302	1.30956	2.55675
123	H	-1.08175	-1.28749	6.98868
124	H	0.69583	-2.83479	6.63116
125	H	2.52318	-2.29392	5.13681
126	H	-6.6666	-1.96241	3.14947
127	H	-6.18228	-0.66561	1.2846
128	H	-9.90375	-1.22912	-1.60298
129	H	-11.97436	-2.30779	-1.3877
130	H	-13.50162	-3.62141	-0.14866
131	H	-14.0138	-4.90969	1.83688
132	H	-12.43022	-5.09356	3.6086
133	H	-7.36381	-2.62842	6.42705
134	H	-8.04955	-1.41481	5.26738
135	H	-9.15258	-2.57281	6.14166
136	H	-8.74804	-6.06201	4.65226
137	H	-10.14188	-6.53931	5.70745
138	H	-10.32476	-6.5864	3.90403
139	H	-4.32076	5.61013	-5.22225
140	H	-4.92096	5.39055	-3.53066
141	H	-3.47098	4.47473	-4.09824
142	H	-6.85256	5.43627	-2.64629
143	H	-8.62887	5.51458	-2.96147
144	H	-7.99026	4.45068	-1.64239
145	H	1.74531	-6.70039	-2.40492
146	H	3.35503	-7.1776	-3.08675
147	H	3.22097	-5.68685	-2.06316
148	H	-0.7815	-7.16793	-5.60994
149	H	-0.97775	-5.42501	-6.06978
150	H	0.67974	-6.18112	-6.0275
151	H	8.10766	5.18861	-0.46598
152	H	7.74623	6.88266	0.06624
153	H	7.09782	5.48487	1.02213
154	H	7.43574	5.33595	-4.51519

155	H	5.82205	4.51055	-4.56395
156	H	6.05029	6.0198	-3.56835
157	H	-2.0922	2.38237	8.03584
158	H	-3.06328	0.97372	8.63232
159	H	-1.26195	0.82447	8.48832
160	H	-4.24329	3.71318	4.80851
161	H	-3.20329	3.04785	3.48043
162	H	-3.9324	1.92992	4.72172



Total energy –2645909.921 –1059122.567 x 5 –1588303.879 x 5 (kcal/mol)
= 3.360 kcal/mol

Figure S35. A hypothetical homodesmotic reaction for the calculation of strain energy of **CP5**. Propyl groups were replaced by Me groups.

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