Supporting Information

Synthesis and Properties of Cycloparaphenylene-2,7-pyrenylene: A Pyrene-Containing Carbon Nanoring

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1. Experimental Section

General

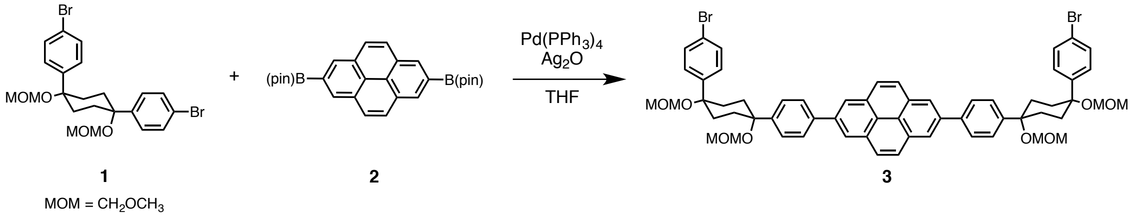
Unless otherwise noted, all materials including dry solvents (dimethylsulfoxide (DMSO)) were obtained from commercial suppliers and used without further purification. Tetrahydrofuran (THF) and *m*-xylene were purified by passing through a solvent purification system (Glass Contour). All reactions were performed using standard vacuum-line and Schlenk techniques. Work-up and purification procedures were carried out with reagent-grade solvents under air. *cis*-1,4-Bis(4-bromophenyl)-1,4-bis(methoxymethoxy)cyclohexane (**1**)[S1] and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrene (**2**)[S2] were synthesized according to reported procedures.

Analytical thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm). The developed chromatogram was analyzed by UV lamp (254 nm). Flash column chromatography was performed with E. Merck silica gel 60 (230–400 mesh). Preparative recycling gel permeation chromatography (GPC) was performed with JAI LC-9204 instrument equipped with JAIGEL-2H/JAIGEL-2H columns using chloroform as an eluent. High-resolution mass spectra (HRMS) were obtained from a JEOL JMS700 (fast atom bombardment mass spectrometry, FAB-MS) or Bruker Daltonics Ultraflex III TOF/TOF (MALDI TOF-MS) with 9-nitroanthracene as matrix. Melting points were measured on a MPA100 Optimelt automated melting point system. Nuclear magnetic resonance (NMR) spectra were recorded on JEOL JNM-ECA-600 (^{1}H 600 MHz, ^{13}C 150 MHz) spectrometer. Chemical shifts for ^{1}H NMR are expressed in parts per million (ppm) relative to $CHCl_3$ (δ 7.26 ppm) or $CHDCl_2$ (δ 5.32 ppm). Chemical shifts for ^{13}C NMR are expressed in ppm relative to $CDCl_3$ (δ 77.0 ppm) or CD_2Cl_2 (δ 53.8 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, m = multiplet, br = broad signal), coupling constant (Hz), and integration.

S1) H. Omachi, S. Matsuura, Y. Segawa and K. Itami, *Angew. Chem. Int. Ed.*, 2010, **49**, 10202.

S2) D. N. Coventry, A. S. Batsanov, A. E. Goeta, J. A. K. Howard, T. B. Marder and R. N. Perutz, *Chem. Commun.*, 2005, 2172.

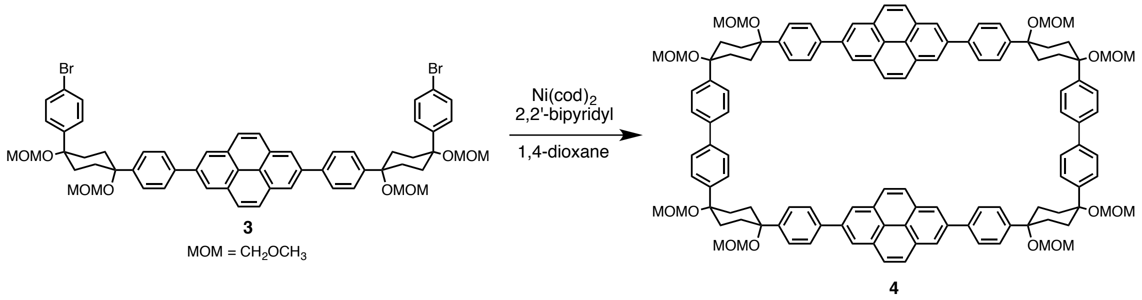
Synthesis of 3



To a 100-mL round-bottom glass flask containing a magnetic stirring bar were added **1** (11.4 g, 22.2 mmol), **2** (1.99 g, 4.39 mmol), $Pd(PPh_3)_4$ (508 mg, 439 μmol), Ag_2O (3.61 g, 15.8 mmol), and dry THF (44 mL). The resultant mixture was heated to reflux for 15 h. After the reaction mixture was cooled down to room temperature, the mixture was passed through short silica gel column chromatography ($CHCl_3$). The crude product was purified by the silica gel column chromatography (hexane/EtOAc = 6:1 to $CHCl_3$/EtOAc = 1:1) to afford **3** (3.23 g, 69%) as a colorless solid. Unreacted **1** (7.07 g) was also recovered by the silica gel column chromatography.

^1H NMR (600 MHz, $CDCl_3$) δ 2.15 (brs, 8H), 2.33–2.47 (m, 8H), 3.43 (s, 6H), 3.46 (s, 6H), 4.46 (s, 4H), 4.53 (s, 4H), 7.35 (d, J = 8.2 Hz, 4H), 7.47 (d, J = 8.2 Hz, 4H), 7.62 (d, J = 8.2 Hz, 4H), 7.86 (d, J = 8.2 Hz, 4H), 8.13 (s, 4H), 8.38 (s, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 33.2 (CH_2), 56.2 (CH_3), 78.1 (4°), 78.3 (4°), 92.3 (CH_2), 92.5 (CH_2), 121.8 (4°), 123.9 (CH), 124.0 (4°), 127.7 (4°), 128.1 (CH), 128.8 (4°), 131.7 (CH), 131.7 (4°), 138.4 (4°), 140.8 (4°); HRMS (FAB) m/z calcd for $C_{60}H_{60}Br_2NaO_{12}$ $[M{\cdot}Na]^+$: 1089.2553, found: 1089.2582; mp: 121.4–123.3 °C.

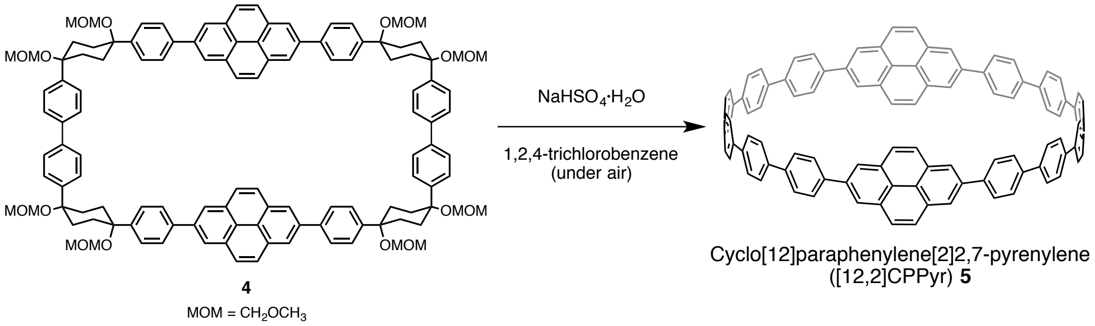
Synthesis of 4



To a 20-mL Schlenk tube containing a magnetic stirring bar were added **3**(336 mg, 315 μmol), nickelbis(1,5-cyclooctadiene) (Ni(cod)$_2$, 176 mg, 692 μmol), 2,2'-bipyridyl (104 mg, 692 μmol), and dry 1,4-dioxane (160 mL). The reaction mixture was stirred at 90 °C for 24 h. After cooled down to room temperature, the mixture was concentrated under reduced pressure. The mixture was extracted with CHCl$_3$. The combined organic phase was dried over Na$_2$SO$_4$ and concentrated under reduced pressure. The crude product was purified by GPC and washed with EtOAc to afford **4** (48.3 mg, 17%) as a white solid.

^{1}H NMR (600 MHz, CDCl$_3$) δ 2.21 (brs, 16H), 2.43 (brs, 16H), 3.45 (s, 12H), 3.47 (s, 12H), 4.49 (s, 8H), 4.54 (s, 8H), 7.47–7.60 (m, 16H), 7.60–7.72 (m, 8H), 7.83 (d, *J* = 7.8 Hz, 8H), 8.08 (s, 8H), 8.34 (s, 8H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 33.6 (CH$_2$), 56.6 (CH$_3$), 78.7 (4°), 78.8 (4°), 92.8 (CH$_2$), 92.9 (CH$_2$), 124.3 (CH), 124.4 (4°), 127.4 (CH), 128.0 (CH), 128.5 (CH), 132.1 (4°), 138.9 (4°), 140.1 (4°), 141.2 (4°); HRMS (FAB) *m*/*z* calcd for $C_{120}H_{120}NaO_{16}$ [M·Na]$^+$: 1839.8474, found 1839.8465; mp: 265–300 °C (dec.).

Synthesis of [12,2]CPPyr 5



To a screw-top test tube containing a magnetic stirring bar were added **4** (10.0 mg, 5.4 μmol), $NaHSO_4·H_2O$ (15 mg, 108 μmol), and dry 1,2,4-trichlorobenzene (6 mL). The flask was stirred at 150 °C for 40 h. After the reaction mixture was cooled down to room temperature, the mixture was diluted with hexane and passed through a short silica gel column chromatography (hexane to CH_2Cl_2) to remove 1,2,4-trichlorobenzene as the first fraction. The crude product was washed with EtOAc to afford [12,2]CPPyr **5** (1.3 mg, 18%) as a pale yellow solid.

^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.68 (d, *J* = 8.4 Hz, 8H), 7.71 (d, *J* = 8.4 Hz, 8H), 7.72 (s, 16H) 7.76 (d, *J* = 8.4 Hz, 8H), 7.93 (d, *J* = 8.4 Hz, 8H), 8.09 (s, 8H), 8.42 (s, 8H); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.8 Hz, 8H), 7.68 (d, *J* = 8.8 Hz, 8H), 7.68 (s, 16H) 7.72 (d, *J* = 8.8 Hz, 8H), 7.88 (d, *J* = 8.8 Hz, 8H), 8.06 (s, 8H), 8.36 (s, 8H); ^{13}C NMR (150 MHz, CD_2Cl_2) δ 124.1 (CH), 124.3 (CH), 127.6 (CH), 127.7 (CH), 127.8 (CH), 128.0 (CH), 128.3 (CH), 128.5 (CH), 132.1 (4°), 133.0 (4°), 139.1 (4°), 139.2 (4°), 139.3 (4°), 139.4 (4°), 139.9 (4°),; HRMS (MALDI) *m*/*z* calcd for $C_{104}H_{64}$ $[M]^+$: 1312.5008, found 1312.5013; mp: >300 °C.

2. Photophysical Measurement

UV/Vis absorption spectrum of **5** was recorded on a Shimadzu UV-3510 spectrometer with a resolution of 0.5 nm. Emission spectrum of **5** was measured with an F-4500 Hitachi spectrometer with a resolution of 0.4 nm upon excitation at 343 nm. Dilute solution in degassed spectral grade chloroform in a 1 cm square quartz cell was used for measurements. Absolute fluorescence quantum yield was determined with a Hamamatsu C9920-02 calibrated integrating sphere system upon excitation at 343 nm. Fluorescence lifetimes were measured with a Hamamatsu Picosecond Fluorescence Measurement System C4780 equipped with a USHO pulsed nitrogen laser (excitation wavelength 337 nm with a repetition rate of 10 Hz).

3. Computational Study

The Gaussian 09 program[S3] running on a SGI Altix4700 system was used for optimization (B3LYP/6-31G(d)).[S4] All structures were optimized without any symmetry assumptions. Zero-point energy, enthalpy, and Gibbs free energy at 298.15 K and 1 atm were estimated from the gas-phase studies. Harmonic vibration frequency calculation at the same level was performed to verify all stationary points as local minima (with no imaginary frequency). Reported energy values were used for biphenyl and *p*-terphenyl.[S5] Visualization of the results was performed by use of GaussView 5.0.9 software.

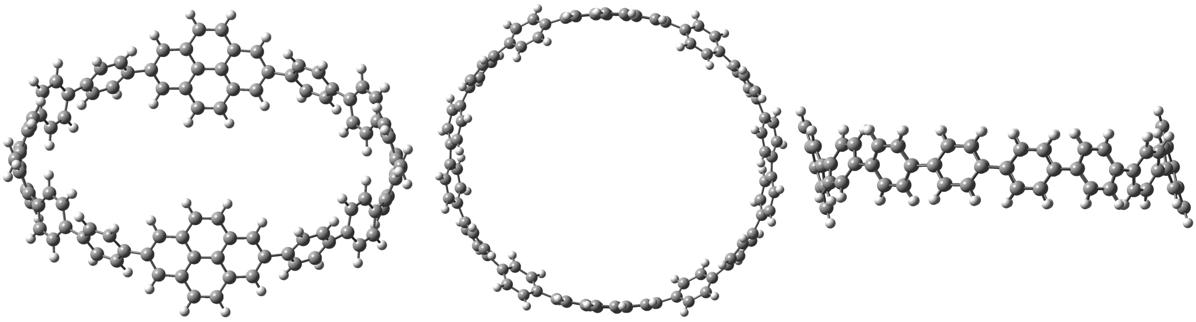
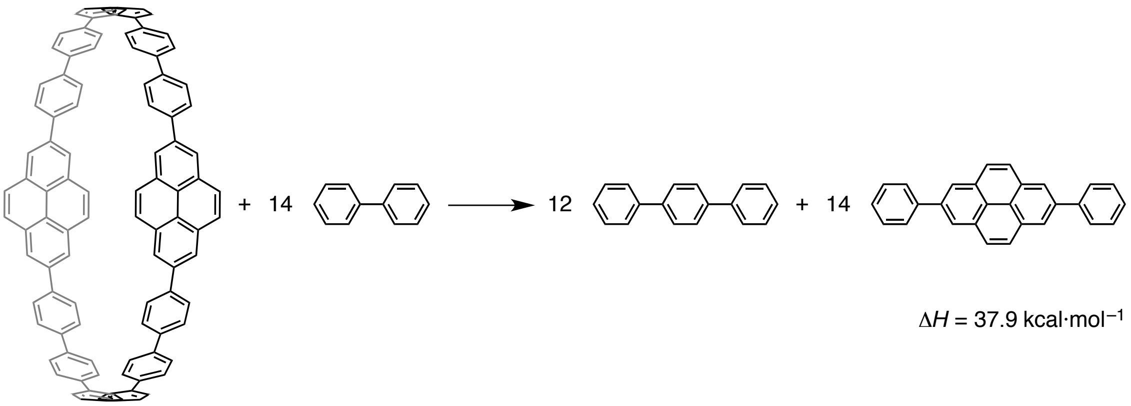


Figure S1. Optimized structures of **5**.

S3) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian 09, Revision A.02*, Gaussian, Inc., Wallingford CT, 2009.

S4) (a) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; (b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B,* 1988, **37**, 785.

S5) Y. Segawa, H. Omachi and K. Itami, *Org. Lett.*, 2010, **12**, 2262.



5

ΔH = 37.9 kcal·mol^{-1}

Scheme S1. Homodesmotic reactions for strain energies (ΔH) of **5**.

Table S1. Uncorrected and thermal-corrected energies of stationary points (Hartree).[a]

compound	*E*	*E* + *ZPE*	*H*	*G*
2,7-diphenylpyrene	-1077.887431	-1077.517874	-1077.497326	-1077.566676
5	-4000.792025	-4000.445868	-4000.369650	-4000.561771

a) *E*: electronic energy; *ZPE*: zero-point energy; *H* (= $E + ZPE + E_{\mathrm{vib}} + E_{\mathrm{rot}} + E_{\mathrm{trans}} + RT$): sum of electronic and thermal enthalpies; *G* (= $H - TS$): sum of electronic and thermal free energies .

Table S2. Cartesian coordinates for optimized compounds.

Optimized structure of 2,7-diphenylpyrene

C	-3.547148	-0.000029	-0.000047
C	-2.831352	1.206689	0.005623
C	-1.430112	1.232875	0.004818
C	-0.711867	-0.000045	-0.000056
C	-1.430127	-1.232961	-0.004907
C	-2.831361	-1.206765	-0.005696
C	-0.680781	2.461213	0.001670
C	0.711894	-0.000047	-0.000047
C	1.430183	1.232862	-0.004912
C	0.680880	2.461214	-0.001821
C	2.831412	1.206657	-0.005656
H	3.373068	2.148745	0.018216
C	3.547188	-0.000075	-0.000020
C	2.831407	-1.206774	0.005685
C	1.430170	-1.232953	0.004880
C	0.680860	-2.461304	0.001803
C	-0.680802	-2.461303	-0.001725
H	-1.229805	-3.399933	-0.002831
H	1.229854	-3.399940	0.002987
H	-1.229781	3.399846	0.002782
H	-3.373012	2.148764	-0.018195
H	-3.373035	-2.148827	0.018172
H	1.229876	3.399850	-0.002975
H	3.373027	-2.148888	-0.018022
C	5.033188	0.000006	0.000094
C	5.755466	-0.932755	0.763391
C	5.755350	0.932756	-0.763378
C	7.149583	-0.933130	0.763425
H	5.217735	-1.646344	1.381554
C	7.149457	0.933323	-0.763424
H	5.217489	1.646122	-1.381683
C	7.853273	0.000167	0.000039
H	7.686832	-1.658903	1.368423
H	7.686611	1.659103	-1.368494
H	8.939908	0.000232	0.000046
C	-5.033249	-0.000007	0.000010
C	-5.755543	-0.932331	-0.763869
C	-5.755423	0.932392	0.763895
C	-7.149651	-0.932732	-0.763876
H	-5.217754	-1.645432	-1.382514
C	-7.149536	0.932903	0.763986
H	-5.217544	1.645483	1.382478
C	-7.853324	0.000110	0.000082
H	-7.686963	-1.658081	-1.369326
H	-7.686754	1.658310	1.369449
H	-8.939959	0.000156	0.000111

Optimized structure of **5**

C	-9.421570	5.621008	1.191185
C	-8.712778	6.815894	1.191551
C	-6.699327	9.007465	1.192086
C	-5.570184	9.816334	1.192103
C	-2.847229	11.016549	1.192094
C	-1.487852	11.301814	1.192096
C	1.487852	11.301814	1.192096
C	2.847229	11.016549	1.192094
C	5.570184	9.816334	1.192103
C	6.699327	9.007465	1.192086
C	8.712778	6.815894	1.191551
C	9.421570	5.621008	1.191185
C	10.384522	2.817659	1.202107
C	10.569027	1.429926	1.229003
C	10.630408	0.680951	2.457754
C	10.630408	-0.680951	2.457754
C	10.569027	-1.429926	1.229003
C	10.384522	-2.817659	1.202107
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C	-9.421570	-5.621008	1.191185
C	-10.384522	-2.817659	1.202107
C	-10.569027	-1.429926	1.229003
C	-10.630408	-0.680951	2.457754
C	-10.630408	0.680951	2.457754
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C	10.612084	-0.710466	0.000000
C	10.569027	-1.429926	-1.229003
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C	10.223819	-3.531632	0.000000
C	9.739895	-4.942228	0.000000
C	9.421570	-5.621008	-1.191185
C	8.712778	-6.815894	-1.191551
C	8.269129	-7.419889	0.000000
C	7.263389	-8.514705	0.000000
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C	5.570184	-9.816334	-1.192103
C	4.921995	-10.191953	0.000000
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C	-0.743187	-11.383629	0.000000
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H	0.996360	11.404173	2.153459
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H	7.106784	8.714138	2.153421
H	8.456689	7.247003	2.153202
H	9.677156	5.191349	2.153359
H	10.302664	3.326650	2.156469
H	5.161380	-10.107538	2.153498
H	3.338376	-10.913071	2.153512
H	0.996360	-11.404173	2.153459
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H	8.456689	-7.247003	2.153202

C	-10.384522	2.817659	1.202107	C	-9.421570	-5.621008	-1.191185	H	7.106784	-8.714138	2.153421
C	-10.223819	3.531632	0.000000	C	-9.739895	-4.942228	0.000000	H	-7.106784	-8.714138	2.153421
C	-9.739895	4.942228	0.000000	C	-10.223819	-3.531632	0.000000	H	-8.456689	-7.247003	2.153202
C	-9.421570	5.621008	-1.191185	C	-10.384522	-2.817659	-1.202107	H	-9.677156	-5.191349	2.153359
C	-8.712778	6.815894	-1.191551	C	-10.569027	-1.429926	-1.229003	H	-10.302664	-3.326650	2.156469
C	-8.269129	7.419889	0.000000	C	-10.612084	-0.710466	0.000000	H	-10.302664	3.326650	2.156469
C	-7.263389	8.514705	0.000000	C	-10.612084	0.710466	0.000000	H	-9.677156	5.191349	-2.153359
C	-6.699327	9.007465	-1.192086	C	-10.569027	1.429926	-1.229003	H	-8.456689	7.247003	-2.153202
C	-5.570184	9.816334	-1.192103	C	-10.384522	2.817659	-1.202107	H	-7.106784	8.714138	-2.153421
C	-4.921995	10.191953	0.000000	C	10.630408	0.680951	-2.457754	H	9.677156	5.191349	-2.153359
C	-3.561938	10.791685	0.000000	C	10.630408	-0.680951	-2.457754	H	10.302664	3.326650	-2.156469
C	-2.847229	11.016549	-1.192094	C	-10.630408	-0.680951	-2.457754	H	10.302664	-3.326650	-2.156469
C	-1.487852	11.301814	-1.192096	C	-10.630408	0.680951	-2.457754	H	9.677156	-5.191349	-2.153359
C	-0.743187	11.383629	0.000000	H	10.640837	1.229134	3.396900	H	8.456689	-7.247003	-2.153202
C	0.743187	11.383629	0.000000	H	10.640837	-1.229134	3.396900	H	7.106784	-8.714138	-2.153421
C	1.487852	11.301814	-1.192096	H	-10.640837	-1.229134	3.396900	H	-7.106784	-8.714138	-2.153421
C	2.847229	11.016549	-1.192094	H	-10.640837	1.229134	3.396900	H	-8.456689	-7.247003	-2.153202
C	3.561938	10.791685	0.000000	H	10.640837	1.229134	-3.396900	H	-9.677156	-5.191349	-2.153359
C	4.921995	10.191953	0.000000	H	10.640837	-1.229134	-3.396900	H	-10.302664	-3.326650	-2.156469
C	5.570184	9.816334	-1.192103	H	-10.640837	-1.229134	-3.396900	H	-10.302664	3.326650	-2.156469
C	6.699327	9.007465	-1.192086	H	-10.640837	1.229134	-3.396900	H	-5.161380	10.107538	-2.153498

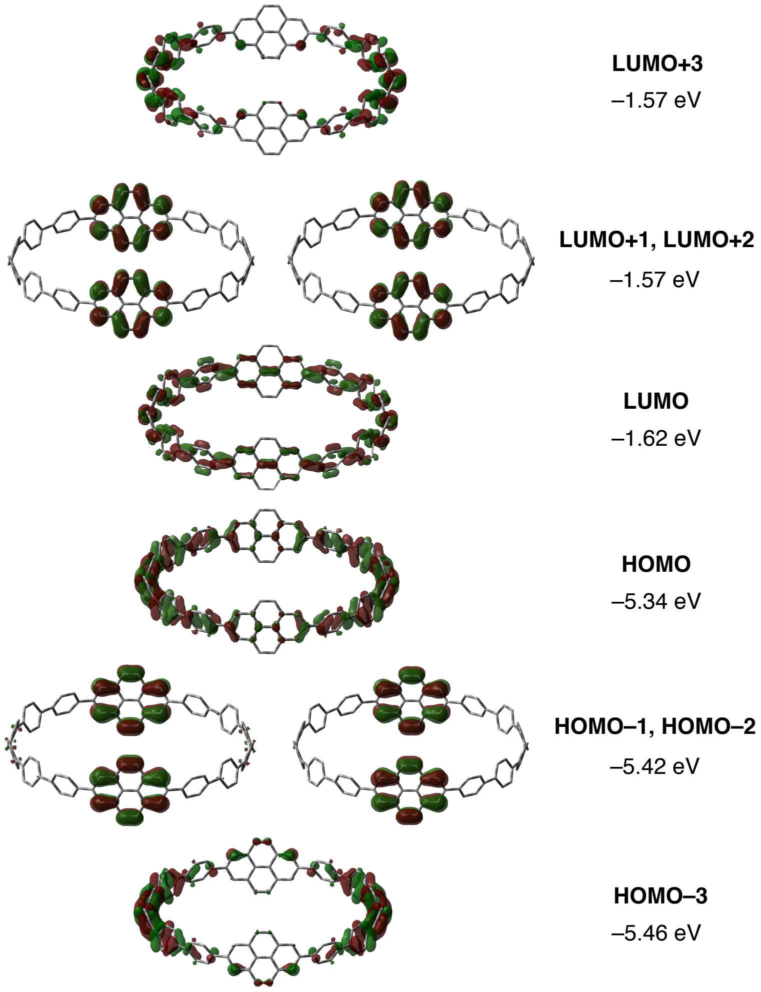


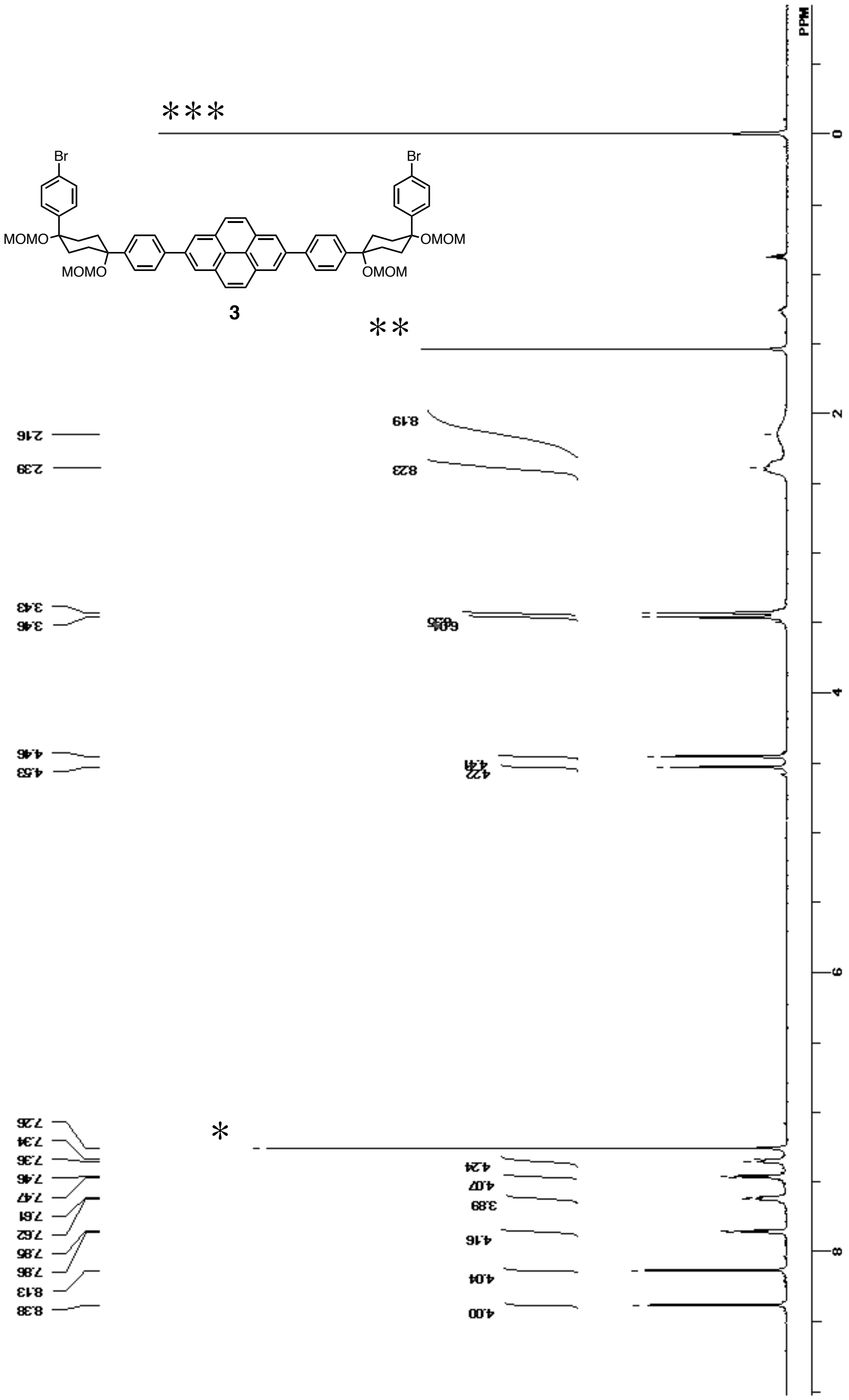
Figure S2. Frontier molecular orbitals of **5**.

Table S3. TD-DFT vertical one-electron excitations (7 states) calculated for the optimized structure of **5**.

	energy	wavelength	Oscillator strength (*f*)	Description
S_3	3.2678 eV	379.41 nm	0.0000	HOMO -> LUMO (0.58653)
S_4	3.4653 eV	357.79 nm	2.9151	HOMO–3 -> LUMO (0.48440) HOMO–1 -> LUMO (0.15985) HOMO -> LUMO+1 (-0.12190) HOMO -> LUMO+3 (0.44413)
S_5	3.5046 eV	353.78 nm	1.3101	HOMO–6 -> LUMO+4 (0.11762) HOMO–4 -> LUMO (0.44700) HOMO–4 -> LUMO+6 (0.10508) HOMO–2 -> LUMO+1 (0.19412) HOMO–1 -> LUMO+2 (0.19141) HOMO -> LUMO+4 (0.43164)
S_9	3.6207 eV	342.43 nm	0.9859	HOMO–5 -> LUMO+1 (0.16553) HOMO–4 -> LUMO (-0.11518) HOMO–3 -> LUMO+2 (0.43718) HOMO–2 -> LUMO+1 (0.22463) HOMO–2 -> LUMO+3 (-0.13415) HOMO–1 -> LUMO+2 (0.39914) HOMO -> LUMO+4 (-0.13483)
S_{11}	3.6737 eV	337.49 nm	1.1748	HOMO–4 -> LUMO (-0.19802) HOMO–3 -> LUMO+2 (-0.40639) HOMO–2 -> LUMO+1 (0.45766) HOMO–2 -> LUMO+3 (-0.20797)
S_{17}	3.7076 eV	334.41 nm	0.5471	HOMO–4 -> LUMO+4 (0.13072) HOMO–3 -> LUMO+2 (-0.27933) HOMO–2 -> LUMO+1 (-0.22407) HOMO–2 -> LUMO+3 (0.31036) HOMO–1 -> LUMO+2 (0.47883)
S_{19}	3.7310 eV	332.31 nm	0.1631	HOMO–3 -> LUMO+2 (0.14207) HOMO–2 -> LUMO+1 (0.33130) HOMO–2 -> LUMO+3 (0.55534) HOMO–1 -> LUMO+2 (-0.18683)

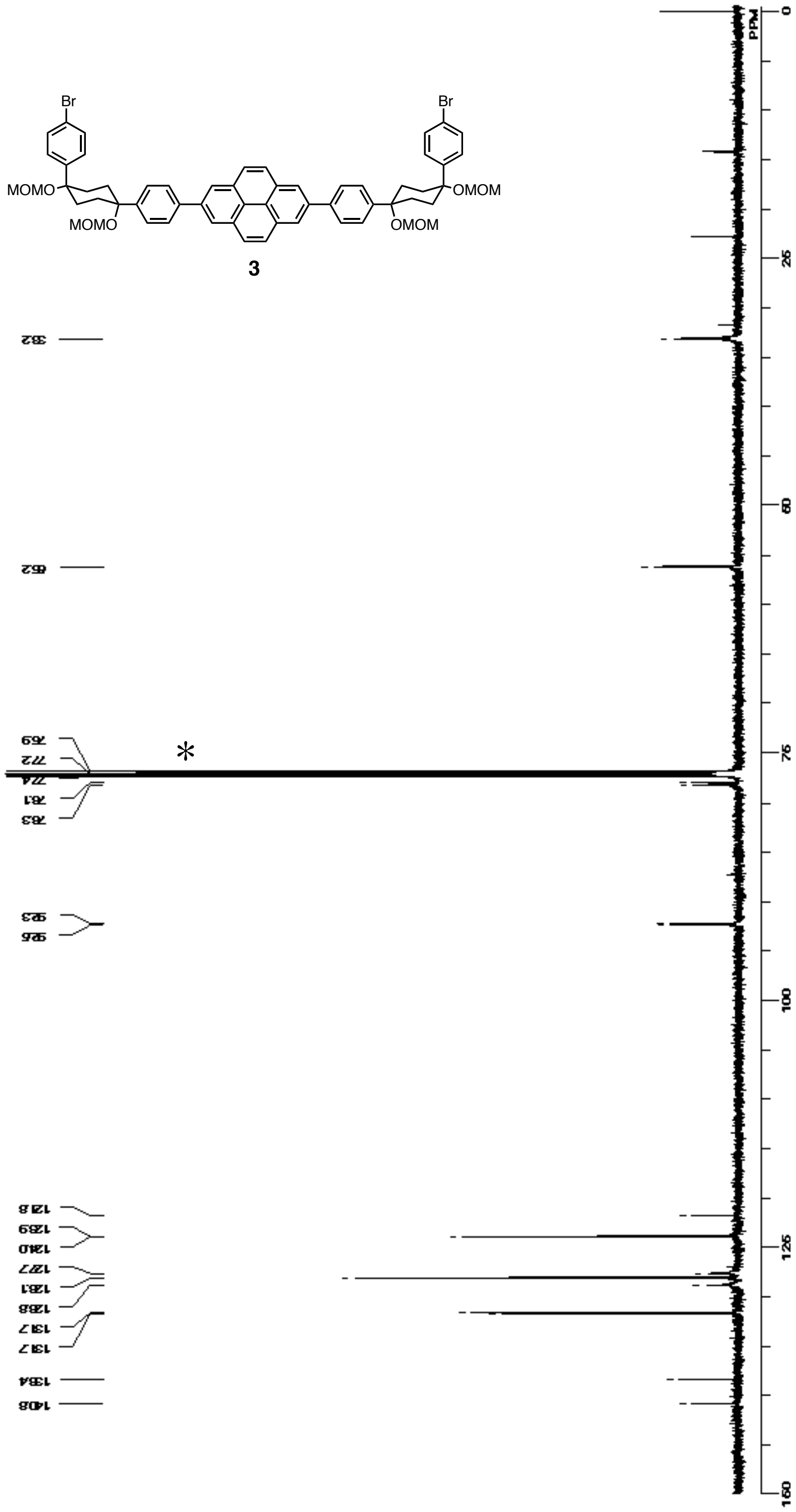
4. ^{1}H NMR and ^{13}C NMR Spectra of New Compounds

^{1}H NMR spectrum of **3** ($CDCl_3$)



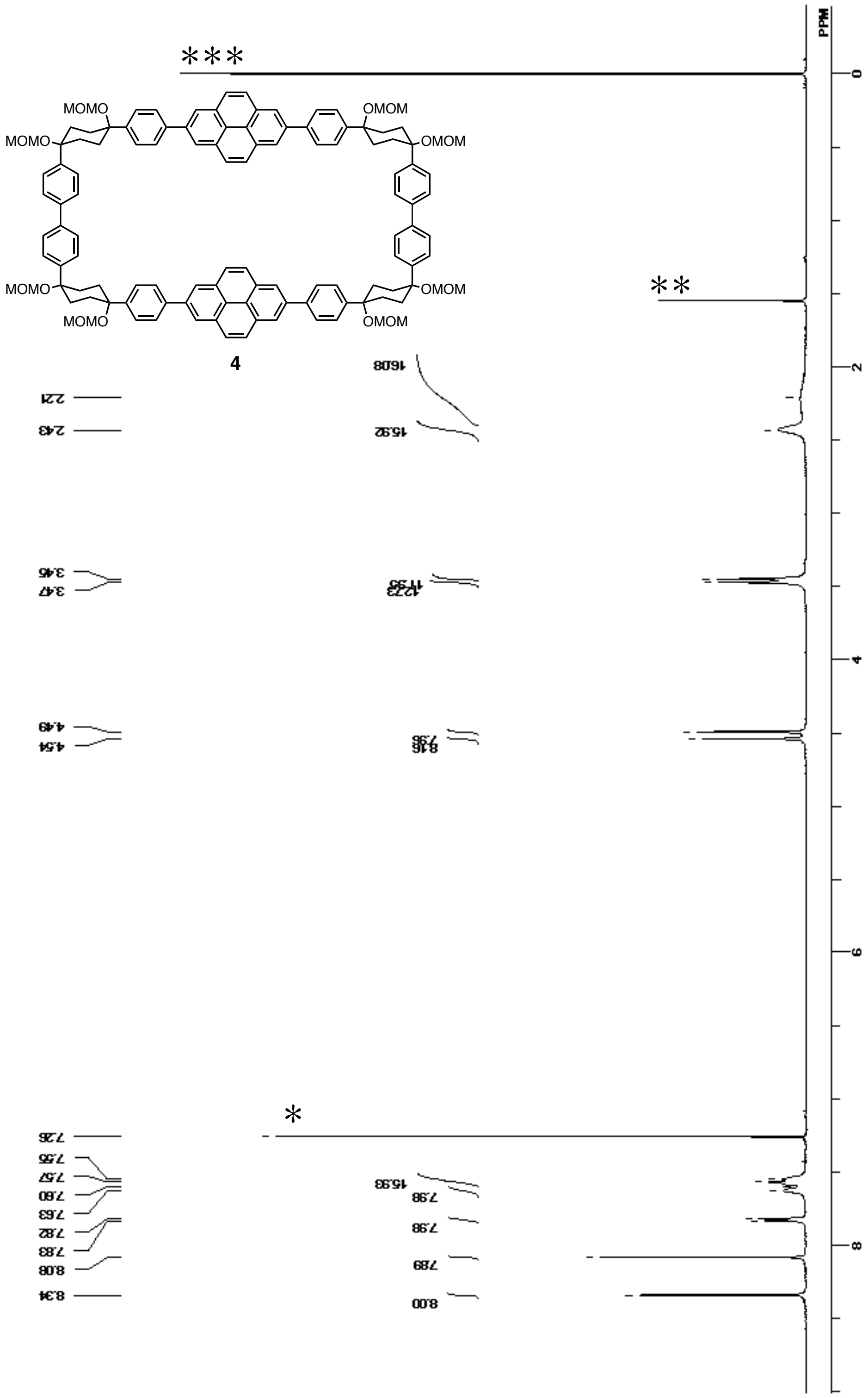
*$CHCl_3$, **H_2O, ***tetramethylsilane (TMS)

^{13}C NMR spectrum of **3** ($CDCl_3$)



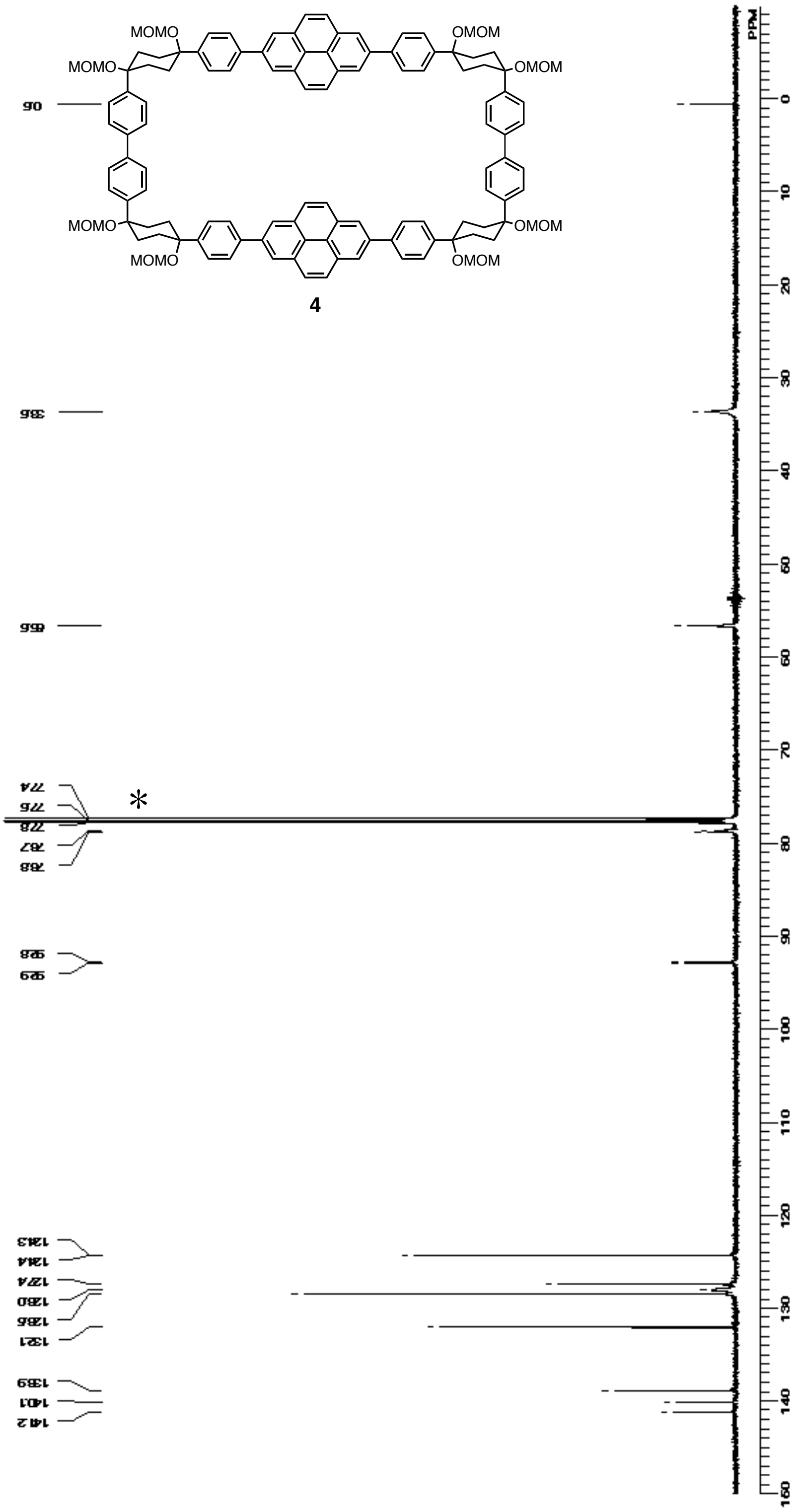
*$CDCl_3$

^{1}H NMR spectrum of **4** ($CDCl_3$)



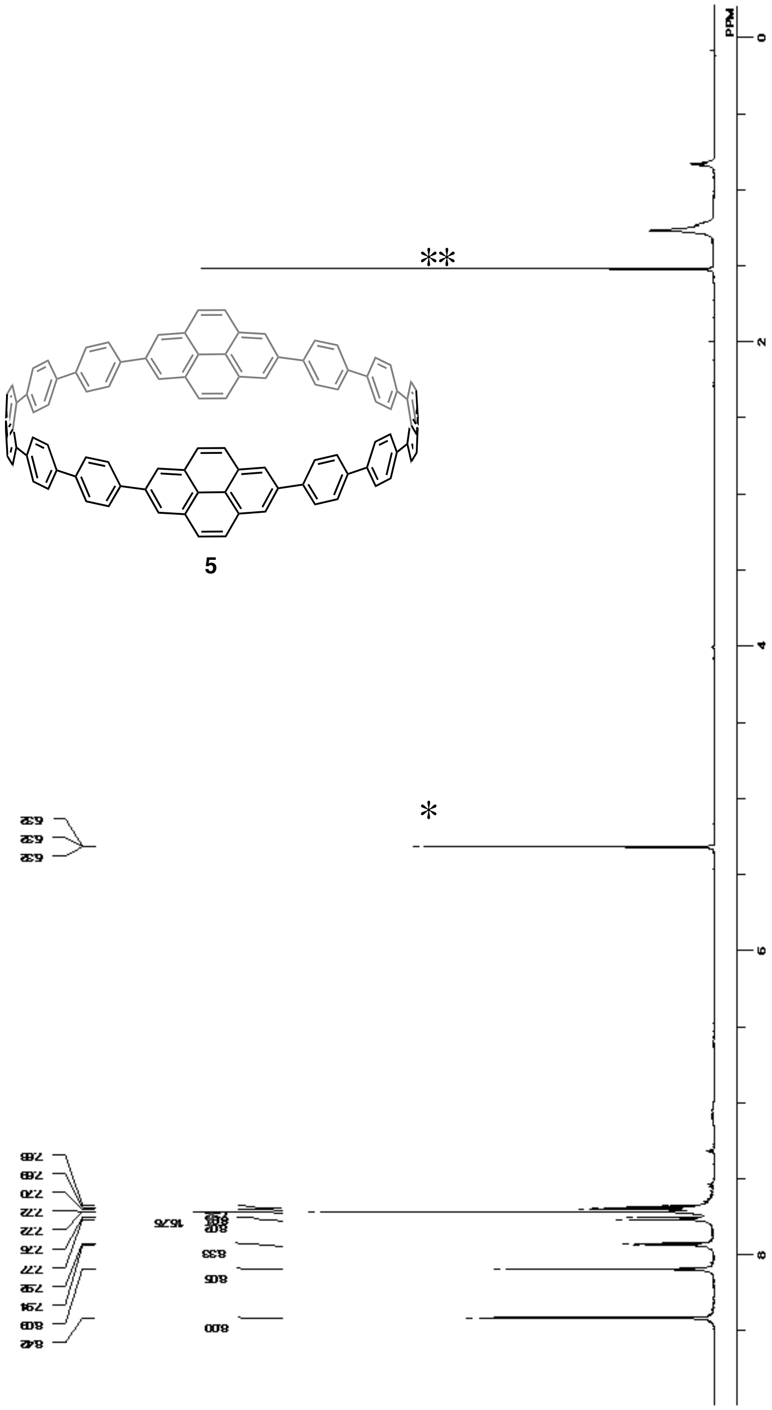
*$CHCl_3$, **H_2O, ***tetramethylsilane (TMS)

^{13}C NMR spectrum of **4** (CDCl$_3$)



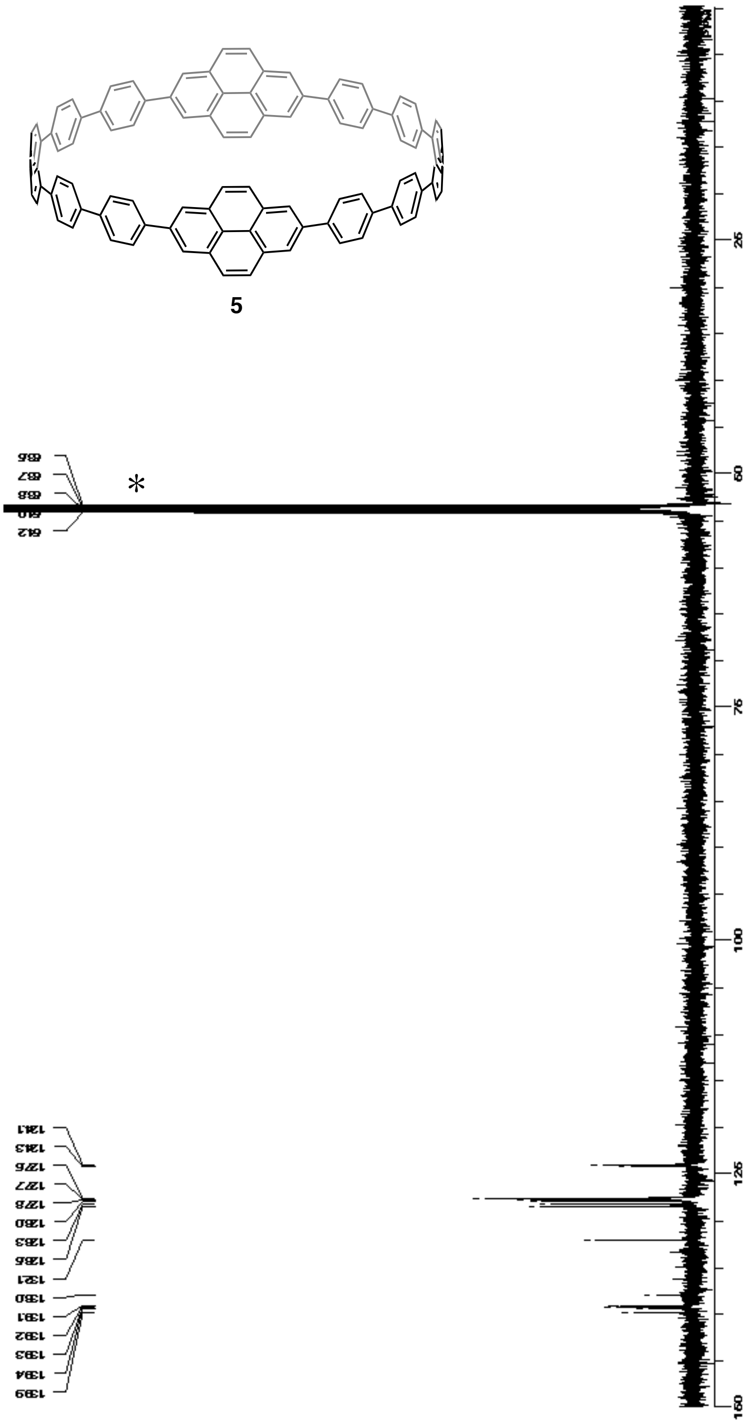
*CDCl$_3$

^{1}H NMR spectrum of **5** (CD_2Cl_2)



*$CHDCl_2$, **H_2O

^{13}C NMR spectrum of **5** (CD_2Cl_2)



5

*CD_2Cl_2