Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Corannulene-based nanographene containing helical motifs

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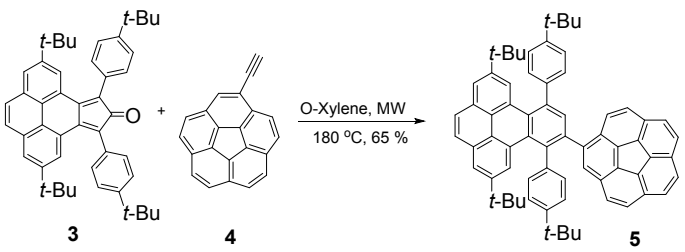
1 General Information

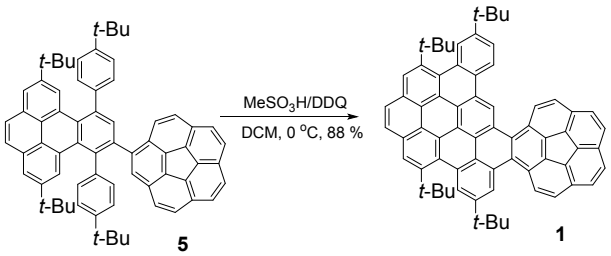
Unless otherwise noted, all materials including dry solvent were obtained from commercial suppliers and used without further purification. All reactions were performed with dry solvents under Argon in dried glassware with standard vacuum-line techniques. Compounds **3**[S1], **4**[S2], **6**[S1] and **7**[S3] were prepared according to the reported literatures. Work-up and purification procedures were carried out with reagent-grade solvents under air.

Analytical TLC was carried out using tapered silica plates with a preadsorbent zone. NMR spectra were recorded on BRUKER AVENCE 400 MHz or JOEL 400 MHz. Chemical shifts were reported relative to the standard solvent signals on literature. The chemical shift references were as follows: (^{1}H) dichloromethane-d, 5.32 ppm; (^{13}C) dichloromethane-d, 53.84; (^{1}H) chloroform-d, 7.26 ppm; (^{13}C) chloroform-d, 77.16 ppm. Mass spectra (ESI, MALDI) were acquired on GCT and FT-ICR spectrometer (Bruker Daltonics Inc. APEXII, BIFLEX III), respectively. UV-Vis, Fluorescence, CD and CPL spectra were recorded in a quartz cell (light path 10 mm). Fluorescence spectra were measured on FS5 and FLS980, and UV-Vis spectra were recorded on Shimadzu UV 3600. CD spectra were recorded on a ChirascanTM Circular Dichroism spectrometer (Applied Photophysics Ltd, Surrey, United Kingdom). CPL spectra were gained with Chirascan-CPL, Applied Photophysics. The absolute fluorescence quantum yield was determined by an absolute method using an integrating sphere excited at 350 nm for **1** and 398 nm for **2** using a 150 W Xenon lamp. The fluorescence Electronic Supplementary Material (ESI) for lifetimes were excited with a supercontinuum ultrafast fiber laser, using the time correlated single-photon-counting (TCSPC) method. Typically, 10000 counts were collected at the peak channel, and the decay curves were fitted by least-squares deconvolution with original Edinburgh Instrument software; the quality of the parameters were judged by the reduced χ^2 values and the randomness of the weighted residuals.

2 Synthesis



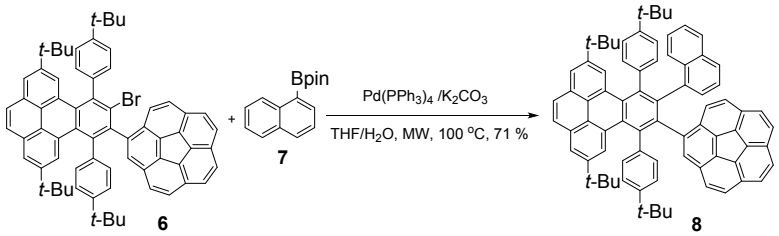
Into an oven-dried (2-5) mL glass reaction vial equipped with a Teflon coated magnetic stirring bar was added **3** (30 mg, 0.05 mmol) and **4** (15 mg, 0.06 mmol). The vial was then sealed with a PTFE-Silicon septum in an Intellivent Cap and purged repeatedly with argon. Anhydrous O-Xylene (3 mL) was added to this solid mixture, and the vial was then irradiated with microwaves in a CEM Discover Microwave Unit, at 180 °C for 1 h. The reaction mixture was cooled and then washed with excess methylene chloride. The organic solution was extracted three times with water, dried with magnesium sulfate, and filtered. Removal of the solvent under reduced pressure, the residue was purified by flash chromatography (light petroleum ether/dichloromethane = 8/1, v/v, R_f = 0.30.) to give **5** (27 mg, 65 %) as a white solid. m.p. = 260-262 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K), δ = 8.37 (d, 1 H, *J* = 1.20 Hz), 8.26 (d, 1 H, *J* = 1.12 Hz), 7.97 (d, 1 H, *J* = 1.20 Hz), 7.95 (d, 1 H, *J* = 1.16 Hz), 7.94 (s, 2 H), 7.79-7.78 (2 H), 7.77-7.75 (d, 2 H, *J* = 6.12 Hz), 7.73-7.72 (d, 1 H, *J* = 5.80 Hz), 7.70 (1 H), 7.65-7.61 (2 H), 7.54-7.53 (d, 1 H, *J* = 5.88 Hz), 7.47-7.46 (d, 1 H, *J* = 5.40 Hz), 7.40-7.39 (5 H), 7.20-7.19 (d, 1 H, *J* = 5.04 Hz), 7.01 (1 H), 6.95 (1 H), 1.33 (s, 18 H), 1.14 (s, 18 H), 1.09 (s, 18 H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K), δ = 150.6, 150.1, 147.7, 143.4, 141.0, 139.8, 139.7, 139.3, 137.1, 136.6, 134.6, 133.3, 132.9, 132.5, 132.3, 131.8, 131.7, 131.6, 131.5, 131.4, 131.3, 130.3, 129.6, 128.6, 128.1, 127.9, 127.8, 127.7, 127.1, 126.6, 126.4, 124.6, 124.2, 122.9, 122.8, 78.2, 78.1, 77.9, 77.6, 35.7, 35.4, 35.2, 32.3, 32.0. FT-IR (ATR): ῡ = 3032, 2961, 2930, 2866, 1686, 1607, 1510, 1476, 1460, 1393, 1364, 1265, 1113, 1017, 883, 833, 785, 735, 662, 583 cm^{-1}. HR-MS (MALDI-TOF): m/z: $[M+H]^+$ Calcd for $C_{68}H_{61}$ 877.4695, found 877.4761.



5 1

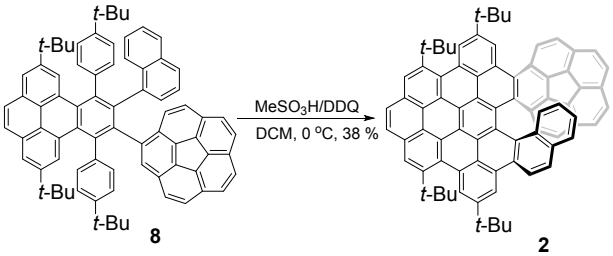
To a solution of **5** (26 mg, 0.03 mmol) in dichloromethane (13 mL), $MeSO_3H$ (1.71 mL) was added slowly at 0 °C. Subsequently DDQ (20 mg, 0.09 mmol) was added in one portion. The reaction mixture was quenched after stirring for 12 h at 0 °C with a saturated solution of $NaHCO_3$ (70 mL). The solution was stirred vigorously for another 30 min. The organic layer was separated and the aqueous phase was extracted with dichloromethane (2 × 50 mL), washed with water (50 mL), dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The residue was purified by column

chromatography on SiO_2 (light petroleum ether/ dichloromethane = 8:1, v/v, R_f = 0.29) to give the product **1** (23 mg, 88 %) as a yellow solid. m.p. = 275-277 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 11.24 (s, 1 H), 9.72 (s, 1 H), 9.33-9.32 (d, 1 H, *J* = 8.60 Hz), 9.17-9.15 (d, 1 H, *J* = 8.84 Hz), 9.07 (s, 1H), 9.05-9.03 (d, 1 H, *J* = 5.72 Hz), 9.02 (s, 1 H), 8.92 (s, 1 H), 8.74 (s, 1 H), 8.53-8.50 (d, 2 H, *J* = 7.84 Hz), 8.09-8.07 (t, 2 H, *J* = 11.24 Hz), 8.01-7.99 (d, 1 H, *J* = 8.56 Hz), 7.95-7.90 (dd, 4 H, J_1 = 8.72 Hz, J_2 = 8.64 Hz), 1.88 (s, 9 H), 1.85 (s, 9 H), 1.77 (s, 9 H), 1.61 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K), δ = 147.0, 146.7, 146.1, 145.5, 139.1, 137.7, 137.5, 136.3, 136.2, 132.7, 132.2, 131.9, 131.7, 131.0, 130.9, 130.6, 130.5, 130.4, 130.3, 129.9, 129.8, 129.7, 129.4, 129.3, 129.2, 129.1, 128.3, 127.9, 127.8, 127.6, 125.8, 125.6, 125.4, 125.3, 125.0, 124.9, 123.9, 123.4, 122.8, 22.2, 39.9, 39.7, 36.6, 36.2, 36.1, 35.8, 32.9, 32.6, 30.6, 30.2. FT-IR (ATR): ῡ = 2961, 2926, 2864, 1670, 1609, 1597, 1478, 1460, 1385, 1364, 1308, 1262, 891, 831, 719, 683, 642, 583 cm^{-1}. HR-MS (MALDI-TOF): m/z: $[M+H]^+$ Calcd for $C_{68}H_{55}$ 871.4226, found 871.4215.



Into an oven-dried (2-5) mL glass reaction vial equipped with a Teflon coated magnetic stirring bar was added **6** (20 mg, 0.021 mmol), **7** (10 mg, 0.039 mmol), $Pd(PPh_3)_4$ (3.6 mg, 0.003 mmol) and K_2CO_3 (26 mg, 0.188 mmol) in THF (3 mL) and H2O (1.5 mL) under Argon atmosphere, and the vial was then irradiated with microwaves in a CEM Discover Microwave Unit, at 100 °C for 1 h. The reaction mixture was cooled and then washed with excess methylene chloride. The organic solution was extracted three times with water, dried with magnesium sulfate, and filtered. Removal of the solvent under reduced pressure, the residue was purified by flash chromatography (light petroleum ether/dichloromethane = 5/1, v/v, R_f = 0.25.) to give **8** (15 mg, 71 %) as a yellow solid. m.p. = 247-249 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.42 (d, 1 H, *J* = 1.76 Hz), 8.31-8.30 (d, 1 H, *J* = 1.48 Hz), 7.94-7.92 (3 H), 7.90-7.89 (d, 1 H, *J* = 1.80 Hz), 7.85-7.83 (d, 1 H, *J* = 1.80 Hz), 7.70-7.69 (d, 2 H, *J* = 3.28 Hz), 7.67-7.65 (d, 1 H, *J* = 8.36 Hz), 7.63-7.61 (d, 1 H, *J* = 8.72 Hz), 7.53 (s, 2 H), 7.48-7.46 (d, 1 H, *J* = 7.76 Hz), 7.44-7.41 (d, 1 H, *J* = 8.88 Hz), 7.37-7.36 (d, 1 H, *J* = 3.4 Hz), 7.30-7.28 (d, 1 H, *J* = 7.44 Hz), 7.23-7.21 (d, 1 H, *J* = 7.00 Hz), 7.04-7.02 (d, 3 H, *J* = 10.24 Hz), 6.95 (d, 1 H, *J* = 1.52 Hz), 6.92 (s, 1 H), 6.89-6.87 (1 H), 6.85-6.83

(1 H), 6.77-6.74 (dd, 1H, J_1 = 2.04 Hz, J_2 = 2.08 Hz), 6.70-6.67 (2 H), 6.23-6.22 (1 H), 6.00-5.99 (1 H), 1.09-1.06 (18 H), 0.97 (s, 9 H), 0.68 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K), δ = 148.7, 148.6, 148.3, 147.0, 146.9, 140.7, 140.2, 139.9, 139.6, 139.3, 139.2, 139.1, 139.0, 138.6, 135.8, 135.6, 135.5, 135.4, 135.3, 135.2, 134.8, 134.4, 134.3, 133.0, 132.8, 132.6, 132.4, 132.2, 132.1, 132.0, 131.8, 131.4, 130.9, 130.7, 130.5, 130.4, 130.3, 130.2, 130.1, 130.0, 129.9, 129.7, 129.5, 129.4, 128.1, 127.8, 127.7, 127.5, 127.2, 127.0, 126.8, 126.6, 126.5, 126.4, 126.3, 125.7, 125.5, 125.1, 125.0, 124.9, 124.7, 124.6, 124.5, 124.2, 124.0, 123.8, 122.1, 122.0, 35.0, 34.9, 34.9, 34.2, 33.8, 31.6, 31.6, 31.5, 31.2, 30.9. FT-IR (ATR): ῡ = 3030, 2963, 2924, 2855, 1665, 1609, 1508, 1460, 1400, 1364, 1269, 1119, 1017, 883, 831, 733, 698, 673, 662, 586 cm^{-1}. HR-MS (MALDI-TOF): m/z: $[M+H]^+$ Calcd for $C_{78}H_{67}$ 1003.5165, found 1003.5236.



8 **2**

To a solution of **8** (16 mg, 0.016 mmol) in dichloromethane (12 mL), $MeSO_3H$ (1.6 mL) was added slowly at 0 °C. Subsequently DDQ (18 mg, 0.084 mmol) was added in one portion. The reaction mixture was quenched after stirring for 12 h at 0 °C with a saturated solution of $NaHCO_3$ (70 mL). The solution was stirred vigorously for another 30 min. The organic layer was separated and the aqueous phase was extracted with dichloromethane (2 × 50 mL). The combined organic phase was washed with water (50 mL), dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on SiO_2 (light petroleum ether/dichloromethane = 5:1, v/v, R_f = 0.24.) to give the product as a green solid (6 mg, 38 %), m.p. > 300 °C.[1] H NMR (400 MHz, $CDCl_3$, 298 K) δ = 9.79 (s, 1 H), 9.30 (s, 1 H), 9.13-9.10 (d, 2 H, J = 10.04 Hz), 9.09-9.08 (d, 1 H, J = 5.88 Hz), 9.06-9.04 (d, 2 H, J = 5.80 Hz), 8.95-8.93 (d, 1 H, J = 5.84 Hz), 8.58 (s, 2 H), 8.09-8.08 (d, 1 H, J = 5.52 Hz), 7.94-7.92 (d, 2 H, J = 5.88 Hz), 7.74-7.72 (d, 1 H, J = 5.72 Hz), 7.68-7.66 (d, 1 H, J = 5.76 Hz), 7.62-7.58 (dd, 2 H, J_1 = 5.24 Hz, J_2 = 5.68 Hz), 7.50-7.48 (d, 1H, J = 5.68 Hz), 7.12-7.09 (t, 1 H, J = 9.68 Hz), 7.02-6.99 (2 H), 6.84-6.82 (d, 1 H, J = 5.84 Hz), 1.88 (18 H), 1.84 (18 H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K), δ = 146.2, 145.5, 145.1, 138.0, 137.2, 135.9, 135.8, 135.1, 132.6, 131.9, 131.1, 131.0, 130.7, 130.6, 130.6, 130.5, 130.4, 130.3, 130.2, 129.9, 129.8, 129.6, 129.5, 129.4, 129.0, 128.8, 128.3,

128.2, 127.8, 127.7, 127.5, 127.4, 127.3, 127.1, 126.9, 126.8, 126.7, 126.4, 125.8, 125.1, 124.6, 124.2, 123.8, 123.4, 123.0, 122.5, 121.8, 121.4, 121.3, 120.1, 119.8, 118.9, 39.1, 39.0, 36.0, 35.3, 35.1, 35.0, 32.2, 31.6, 29.8. FT-IR (ATR): $\tilde{\upsilon}$ = 2963, 2922, 2853, 1743, 1680, 1610, 1477, 1462, 1398, 1385, 1362, 1262, 1096, 1020, 827, 797 cm^{-1}. HR-MS (MALDI-TOF): m/z: $[M+H]^+$ Calcd for $C_{78}H_{59}$ 995.4539, found 995.4618.

3 X-ray Crystallography

Crystals suitable for X-ray analysis were obtained by slow diffusion of acetonitrile into chloroform solution of **1**, toluene solution of **2** and 1,2-Dichloroethane solution of **5**, respectively. Single crystal X-ray diffraction data were collected on a Super Nova, Dual, Cu at zero, AtlasS2 diffractometer. The crystal was kept at 100.00(10) K during data collection. Using Olex2[S4], the structure was solved with the ShelXT[S5] structure solution program using Direct Methods and refined with the ShelXL[S6] refinement package using Least Squares minimization. The disordered solvent molecules were removed with the SQUEEZE routine in PLATON[S7] and the solvent-free model was employed for the final refinement. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were positioned by geometric idealization. Additional crystal and refinement information is summarized in **Table S1-S3**.

Crystal Structure Data of compound **5** (CCDC number: **1976758**).

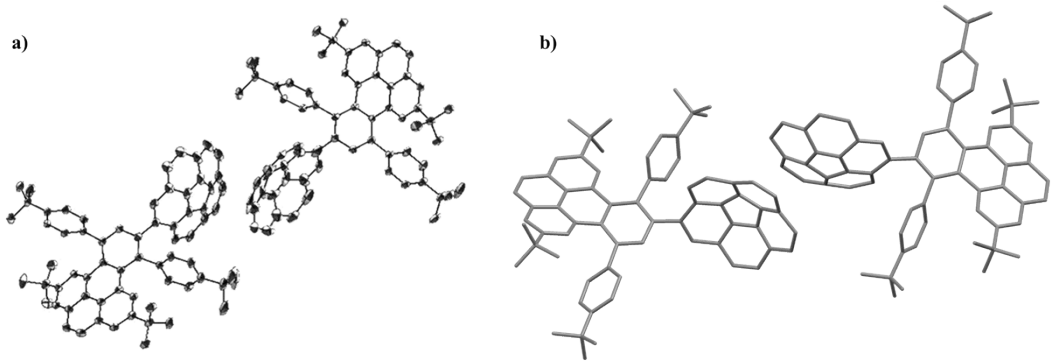


Figure S1. Crystal structure of **5** was obtained by slow diffusion of acetonitrile into 1,2-Dichloroethane solution. The thermal ellipsoids are set at a 50 % probability level. Hydrogen atoms are omitted for clarity.

Table S1. Crystal data and structure refinement for compound **5**.

Identification code	**5**
Empirical formula	$C_{136}H_{120}$
Formula weight	1754.31
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1

a/Å	18.5396(2)
b/Å	18.9417(2)
c/Å	19.29380(10)
α/°	91.1760(10)
β/°	114.0070(10)
γ/°	115.3930(10)
Volume/Å^3	5433.04(10)
Z	2
ρ_{calc}g/cm^3	1.072
μ/mm^{-1}	0.453
F(000)	1872.0
Crystal size/mm^3	0.1 × 0.02 × 0.02
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.16 to 151.76
Index ranges	-19 ≤ h ≤ 23, -23 ≤ k ≤ 23, -23 ≤ l ≤ 23
Reflections collected	71651
Independent reflections	21828 [R_{int} = 0.0405, R_{sigma} = 0.0373]
Data/restraints/parameters	21828/972/1435
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0778, wR_2 = 0.2181
Final R indexes [all data]	R_1 = 0.0883, wR_2 = 0.2278
Largest diff. peak/hole / e Å^{-3}	0.64/-0.44

Crystal Structure Data of compound **1** (CCDC number: **1976760**).

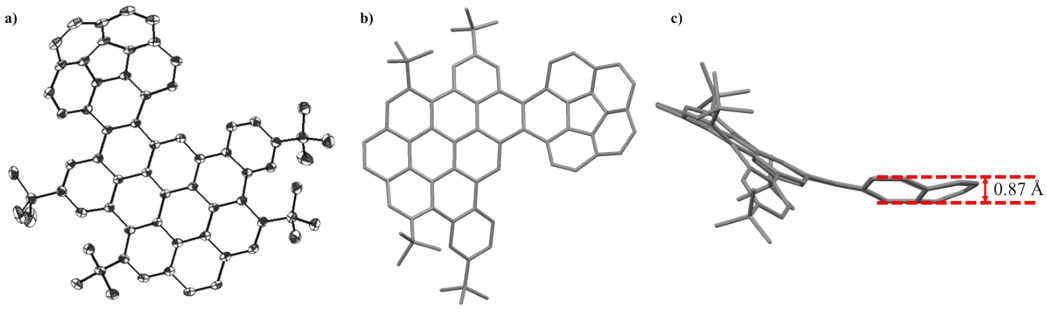


Figure S2. Crystal structure of **1** was obtained by slow diffusion of acetonitrile into chloroform solution. The thermal ellipsoids are set at a 50 % probability level. Hydrogen atoms are omitted for clarity.

Table S2. Crystal data and structure refinement for compound **1**.

Identification code	**1**
Empirical formula	$C_{68}H_{54}$
Formula weight	871.11
Temperature/K	100.01(10)
Crystal system	monoclinic
Space group	C2/c
a/Å	31.3551(6)
b/Å	9.78470(10)

c/Å	32.8326(6)
α/°	90
β/°	111.219(2)
γ/°	90
Volume/Å^3	9390.1(3)
Z	8
ρ_{calc}g/cm^3	1.232
μ/mm^{-1}	0.524
F(000)	3696.0
Crystal size/mm^3	0.200 × 0.100 × 0.060
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.532 to 133.2
Index ranges	-30 ≤ h ≤ 37, -11 ≤ k ≤ 11, -39 ≤ l ≤ 36
Reflections collected	15503
Independent reflections	8281 [R_{int} = 0.0116, R_{sigma} = 0.0143]
Data/restraints/parameters	8281/46/655
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0439, wR_2 = 0.1162
Final R indexes [all data]	R_1 = 0.0473, wR_2 = 0.1193
Largest diff. peak/hole / e Å^{-3}	0.33/-0.31

Crystal Structure Data of compound **2** (CCDC number: **1976761**).

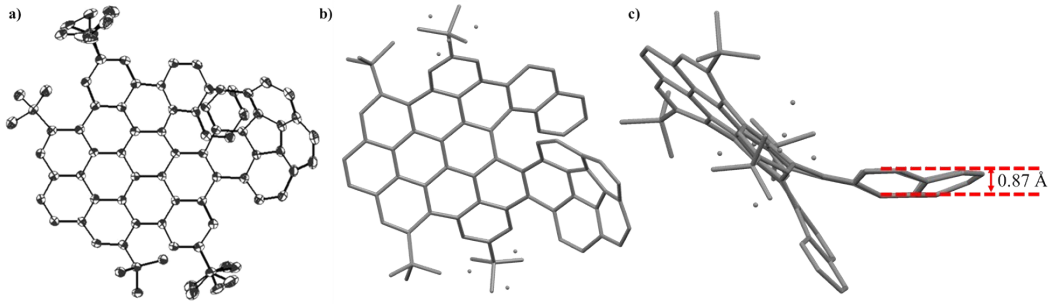


Figure S3. Crystal structure of **2** was obtained by slow diffusion of acetonitrile into toluene solution. The thermal ellipsoids are set at a 50 % probability level. Hydrogen atoms are omitted for clarity.

Table S3. Crystal data and structure refinement for compound **2**.

Identification code	**2**
Empirical formula	$C_{39}H_{29}$
Formula weight	497.62
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	18.1041(3)
b/Å	13.2301(2)
c/Å	25.0781(4)
α/°	90

β/°	104.108(2)
γ/°	90
Volume/Å^3	5825.51(17)
Z	8
ρ_{calc}g/cm^3	1.135
μ/mm^{-1}	0.484
F(000)	2104.0
Crystal size/mm^3	0.100 × 0.100 × 0.100
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.89 to 151.988
Index ranges	-22 ≤ h ≤ 21, -15 ≤ k ≤ 16, -31 ≤ l ≤ 31
Reflections collected	36721
Independent reflections	11596 [R_{int} = 0.0497, R_{sigma} = 0.0418]
Data/restraints/parameters	11596/18/784
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0717, wR_2 = 0.1903
Final R indexes [all data]	R_1 = 0.0842, wR_2 = 0.2072
Largest diff. peak/hole / e Å^{-3}	0.26/-0.31

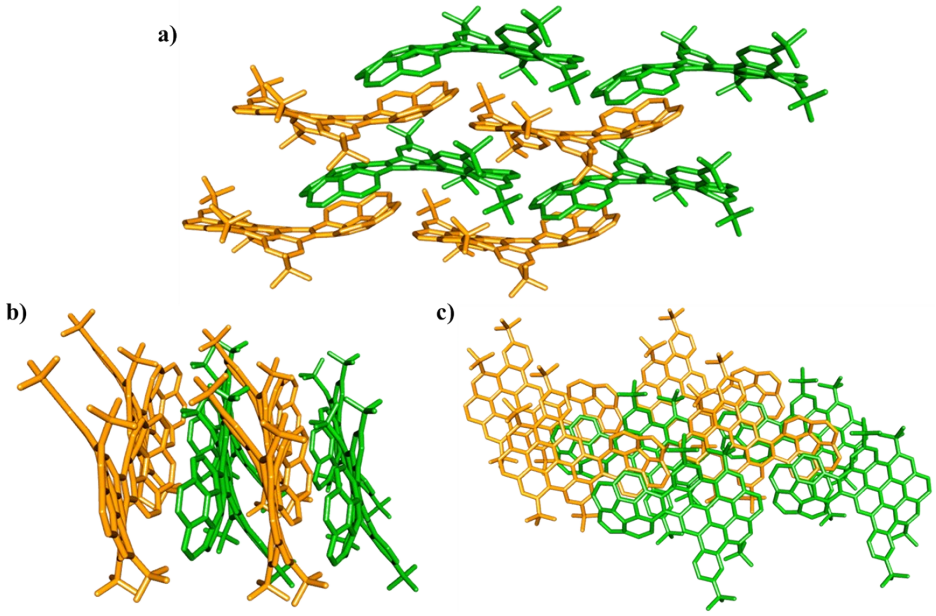


Figure S4. Crystal packing pattern of **1** from the top and side views. Hydrogen atoms are omitted for clarity.

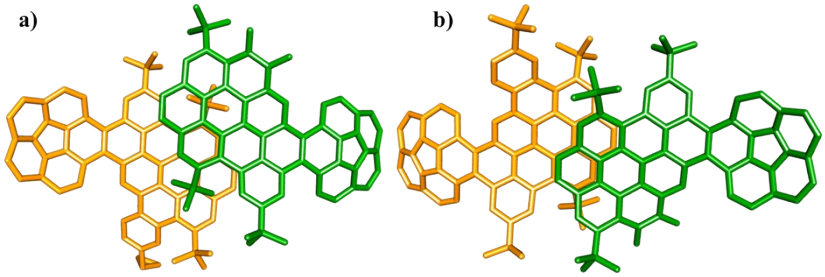


Figure S5. The two packing modes of **1** in the solid phase. Hydrogen atoms are omitted

for clarity.

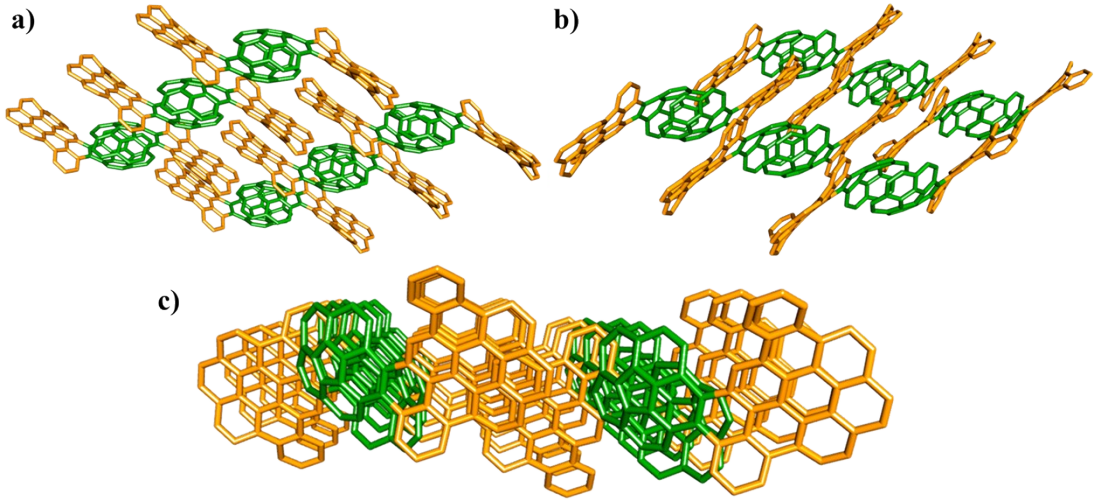


Figure S6. The plane-convex π-π interaction between the planar nanographene regions and corannulene units of **1** in the solid phase. Hydrogen atoms and *t*-Bu groups are omitted for clarity.

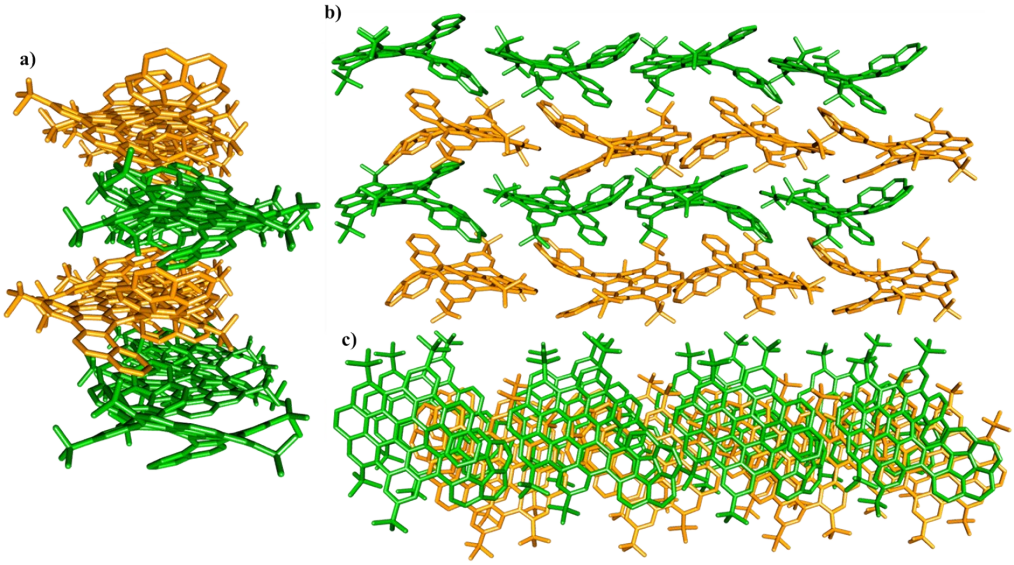


Figure S7. Crystal packing pattern of **2** from the top and side views. Hydrogen atoms are omitted for clarity.

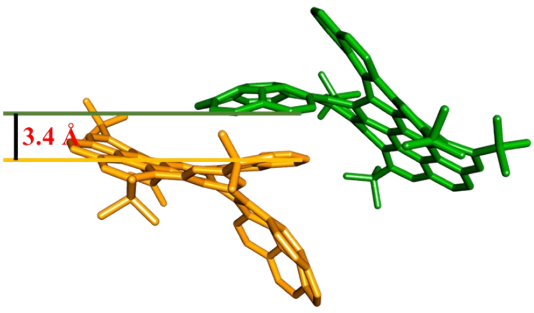


Figure S8. The π-π distances of **2** in the solid phase. Hydrogen atoms are omitted for

clarity.

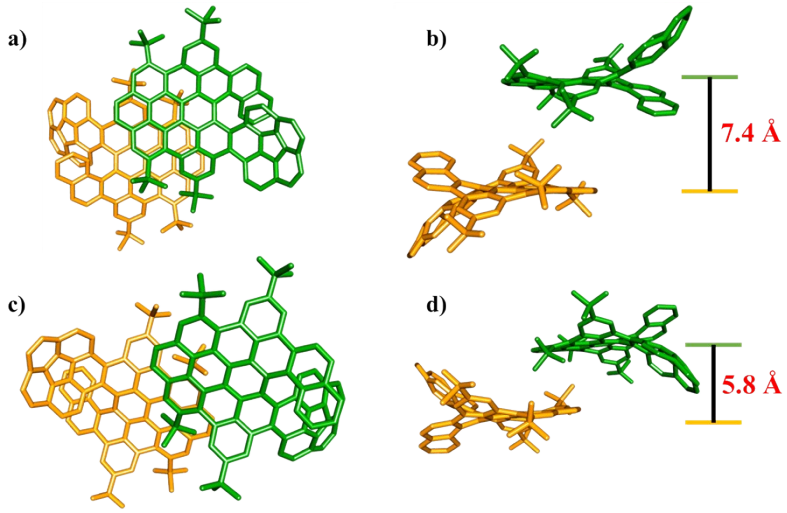
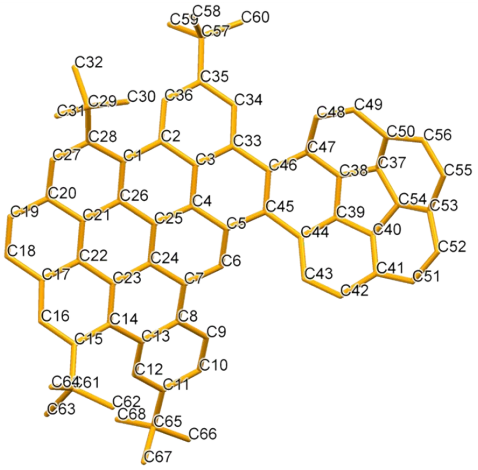
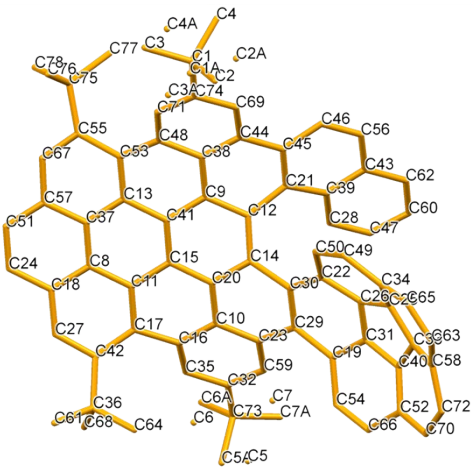


Figure S9. The two packing modes and their distances of **2** in the solid phase. Hydrogen atoms are omitted for clarity.



The dihedral angles
C43-C44-C5-C6 = 37°

Figure S10. Selected dihedral angles for **1** are listed, hydrogen atoms are omitted for clarity.



The dihedral angles
C30-C14-C21-C39 = 41°

Figure S11. Selected dihedral angles for **2** are listed, hydrogen atoms are omitted for

clarity.

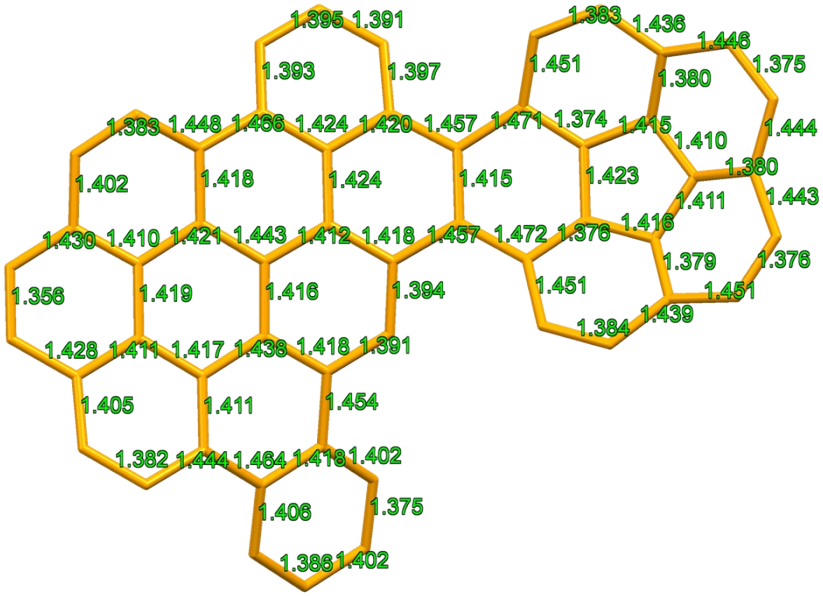


Figure S12. Bond lengths for **1** are listed, *t*-Bu groups and hydrogen atoms are omitted for clarity.

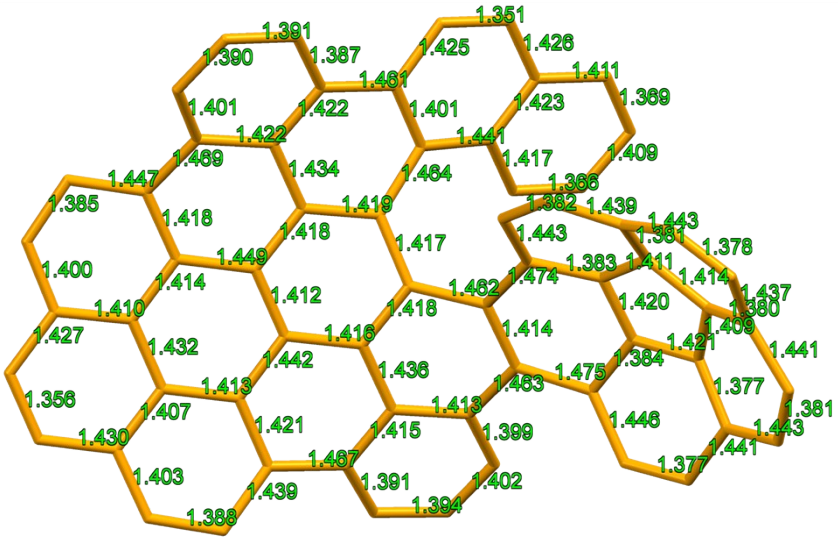


Figure S13. Bond lengths for **2** are listed, *t*-Bu groups and hydrogen atoms are omitted for clarity.

4 Optical Resolution by Chiral HPLC

Chiral HPLC analysis of **2**, was performed on an Agilent 1260 instrument equipped with a COSMOSIL Cholester column (10 mm × 250 mm, absorption intensity at 398 nm). A mixture of DCM/MeOH (65/35) was used as the eluent with a flow rate of 2 mL/min at 298K.

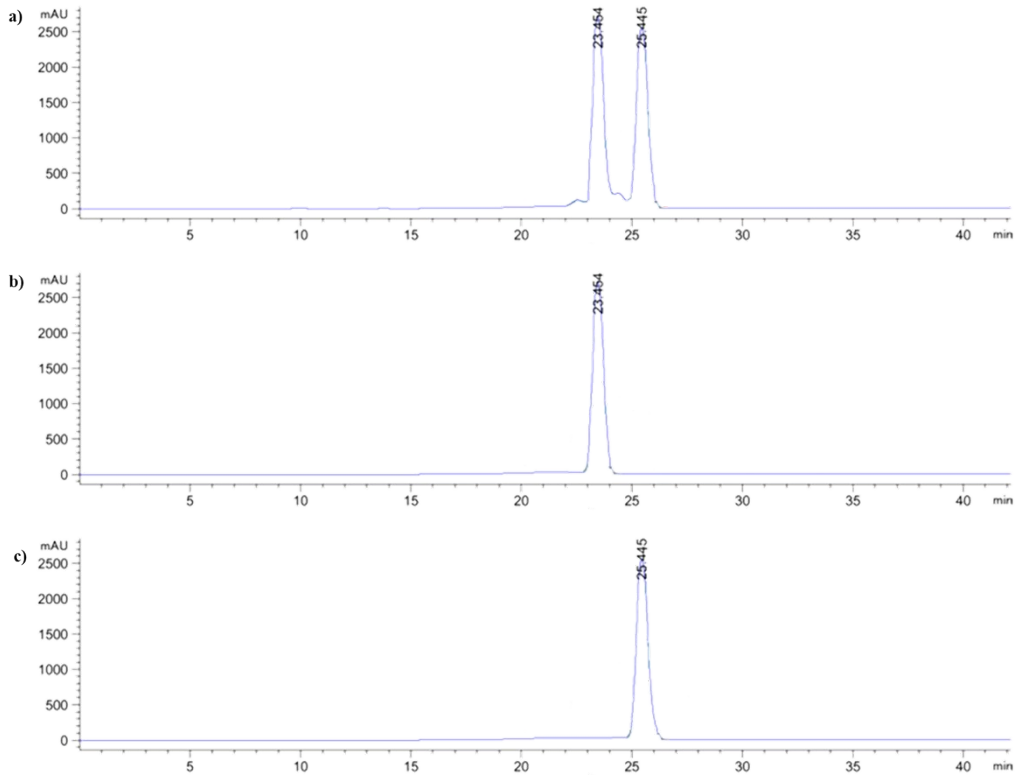


Figure S14. HPLC analysis of (a) 2, (b) the separated **P-2** and (c) the separated **M-2**.

5 Photophysical Study

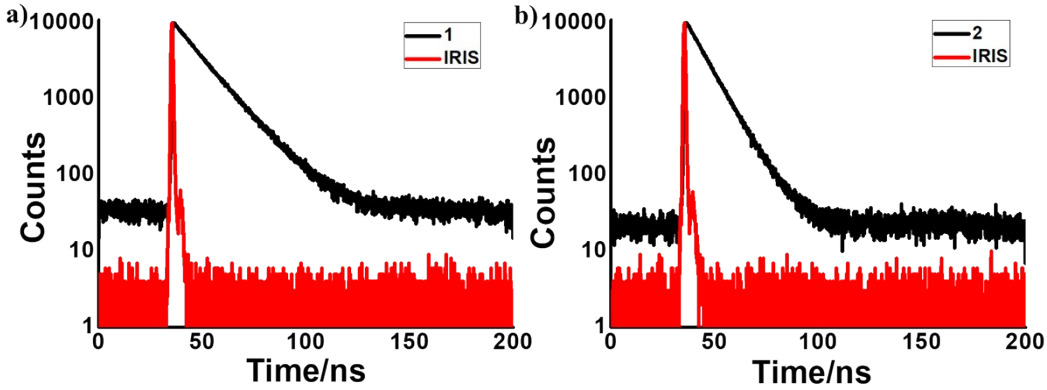


Figure S15. Fluorescence lifetimes measured at 487 nm and 580 nm for **1** and **2** in $CHCl_3$ (1.0×10^{-5} M), respectively.

6 Computational Study

All calculations were performed using the Gaussian 09[S8] program package. The geometries of bowls **1**, **2** (*t*-Bu groups on pyrene units are omitted) and transition states were optimized at the B3LYP level of density functional theory (DFT) with the 6-31G(d) basis set. Harmonic vibration frequency calculations at the same level were

performed to verify all stationary points as local minima (with no imaginary frequency) or transition states (with one imaginary frequency). Transition states were also verified by IRC calculations. Zero-point energy and Gibbs free energy at 298 K and 1 atm were estimated from the gas-phase studies. The first sixty vertical transition energies for bowls **1** and **2** were calculated by time-dependent density functional theory (TD-DFT) at the B3LYP/6-31G(d)/PCM level (over optimized geometries at the same level). All bright states (oscillator strength $f > 0.1$) and corresponding main single electron transition for **1** and **2** are listed in **Table S4** and **5**. UV-vis spectra of **1** and **2** and CD spectra of **2** were simulated according to TD-DFT results. Nucleus independent chemical shifts (NICS) calculations of **1** and **2** are at the GIAO-B3LYP/6-311+G(2d,p)/PCM computational level and were all carried out according to published procedures.[S9] The ACID plots were generated with Gaussian 09 using the CSGT method and ACID 2.0.0.[S10]

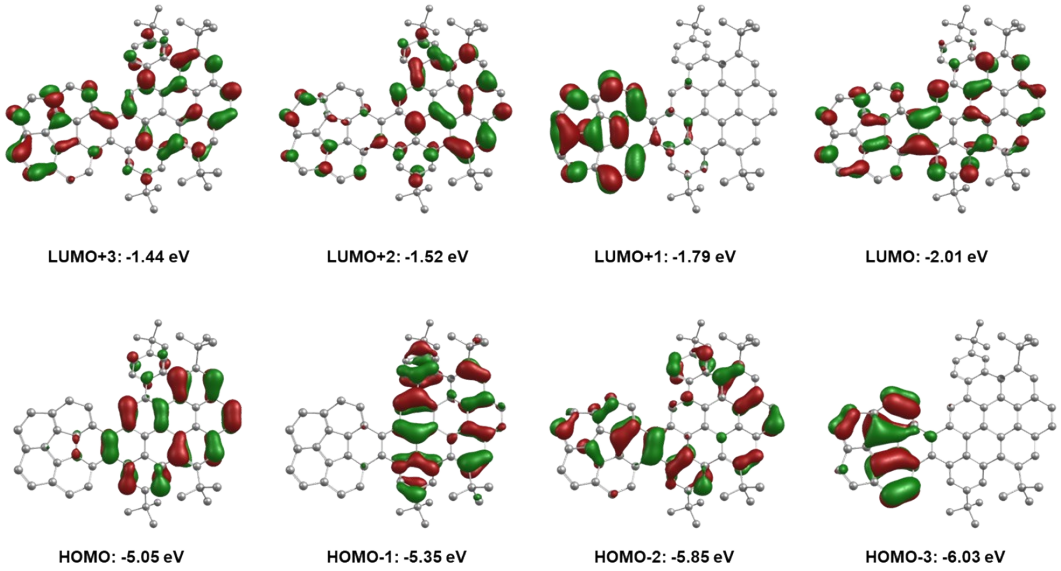


Figure S16. Kohn-Sham frontier orbitals and frontier orbital energies for **1** at the optimized S0 geometry at B3LYP/6-31G(d) level of theory in chloroform solution.

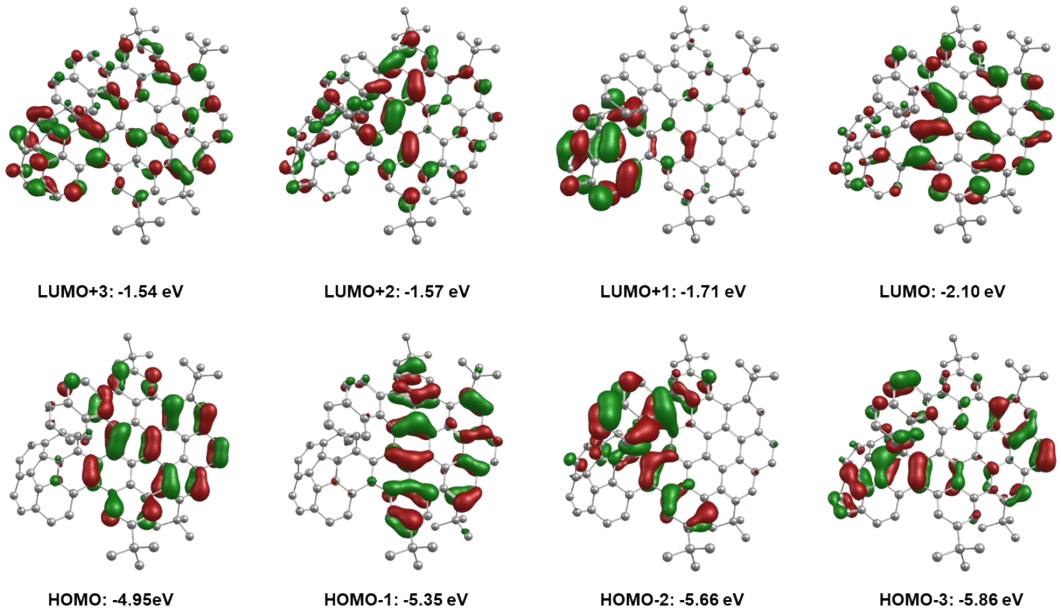


Figure S17. Kohn-Sham frontier orbitals and frontier orbital energies for **2** at the optimized S0 geometry at B3LYP/6-31G(d) level of theory in chloroform solution.

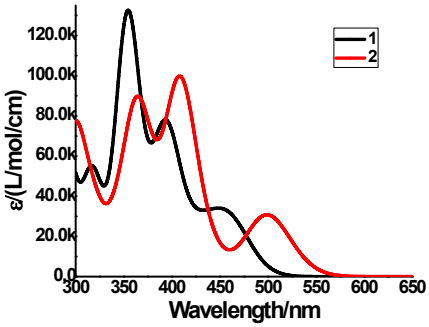


Figure S18. Simulated UV-vis spectra of **1** and **2** at the B3LYP/6-31G(d)/PCM level of theory.

Table S4. TD-DFT singlet excitation energies E, excitation wavelengths λ, oscillator strengths $f > 0.1$, and orbital contributions for **1** at the optimized S0 ground state geometry in chloroform.

Energy (eV)	Wavelength (nm)	Osc. Strength	Major contributions
2.68	462	0.2402	H→L (89%)
2.88	431	0.2109	H-1→L (18%) H→L+1 (67%)
3.10	400	0.1556	H→L+2 (53%) H→L+3 (22%)
3.15	393	0.4442	H-1→L (15%) H-1→L+1 (12%) H-1→L+2 (11%) H→L+3 (48%)

3.17	391	0.1596	H-1→L+1 (75%)
3.45	360	0.3325	H-3→L (17%) H-2→L+1 (14%) H-1→L+2 (30%)
3.46	359	0.1254	H-3→L (35%) H-3→L+1 (22%) H-1→L+2 (17%)
3.52	352	0.6336	H-4→L (19%) H-1→L+2 (23%) H-1→L+3 (36%)
3.53	351	0.2207	H-5→L (16%) H-4→L (26%) H-1→L+3 (23%)
3.89	319	0.1662	H-5→L+1 (20%) H→L+5 (26%)
3.96	313	0.1709	H-7→L (25%) H-5→L+1 (22%) H-2→L+3 (11%)
4.25	292	0.1459	H-7→L+1 (12%) H-6→L+2 (12%) H→L+6 (14%)
4.34	286	0.1459	H-5→L+3 (61%) H-7→L (25%) H-4→L+2 (12%)
4.66	266	0.1333	H-8→L+3 (42%) H-2→L+5 (19%)
4.92	252	0.1189	H-9→L+2 (14%) H-6→L+4 (12%) H-3→L+5 (29%) H→L+10 (11%)

Table S5. TD-DFT singlet excitation energies E, excitation wavelengths λ, oscillator strengths $f > 0.1$, and orbital contributions for **2** at the optimized S0 ground state geometry in chloroform.

Energy (eV)	Wavelength (nm)	Osc. Strength	Major contributions
2.48	499	0.3014	H→L (94%)
2.83	438	0.1055	H→L+1 (76%) H→L+2 (11%)
3.03	409	0.8266	H-1→L (34%) H→L+2 (23%) H→L+3 (29%)
3.33	373	0.1342	H-4→L (30%) H-1→L+2 (34%)

			H-1→L+3 (19%)
3.39	365	0.2475	H-6→L (10%) H-1→L+2 (34%) H-1→L+3 (17%) H→L+5 (19%)
3.43	362	0.3117	H-7→L (12%) H-2→L+2 (12%) H-1→L+3 (27%) H→L+5 (15%)
3.63	342	0.1504	H-2→L+3 (51%) H-1→L+4 (16%)
3.88	319	0.1034	H-6→L+1 (36%) H-4→L+2 (12%) H→L+6 (10%)
4.16	298	0.1232	H-7→L+2 (31%) H-6→L+2 (12%) H-5→L+3 (31%)
4.23	293	0.1209	H-7→L+3 (10%) H-3→L+4 (35%) H-1→L+6 (19%)
4.44	279	0.1132	H-8→L+3 (23%) H-3→L+5 (14%) H-1→L+7 (11%) H-2→L+8 (11%)

Table S6. Uncorrected and thermal-corrected (298 K) energies of stationary points (Hartree)[a]

optimized structures	**imaginary frequencies**	**E(H)**	**E+ZPE(H)**	**G(H)**
M-1	0	-1994.95049863	-1994.385342	-1994.444133
TS_1	1	-1994.93245780	-1994.367694	-1994.426340
concave-**M-1**	0	-1994.94491146	-1994.379939	-1994.439047
TS_2	1	-1994.94196310	-1994.377873	-1994.436635
P-1	0	-1994.95049868	-1994.385342	-1994.444132
P-2	0	-2378.44602014	-2377.775434	-2377.840264
TS_1'	1	-2378.42738530	-2377.757169	-2377.821517
concave-**P-2**	0	-2378.43571893	-2377.765301	-2377.830388

[a)] E: electronic energy; ZPE: zero-point energy; G: sum of electronic and thermal free energies.

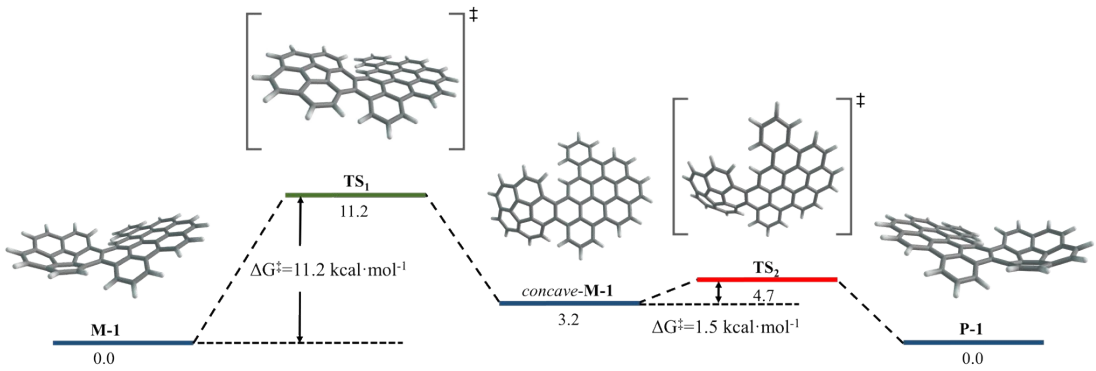


Figure S19. Isomerization between **M-1**, *concave*-**M-1** and **P-1.**

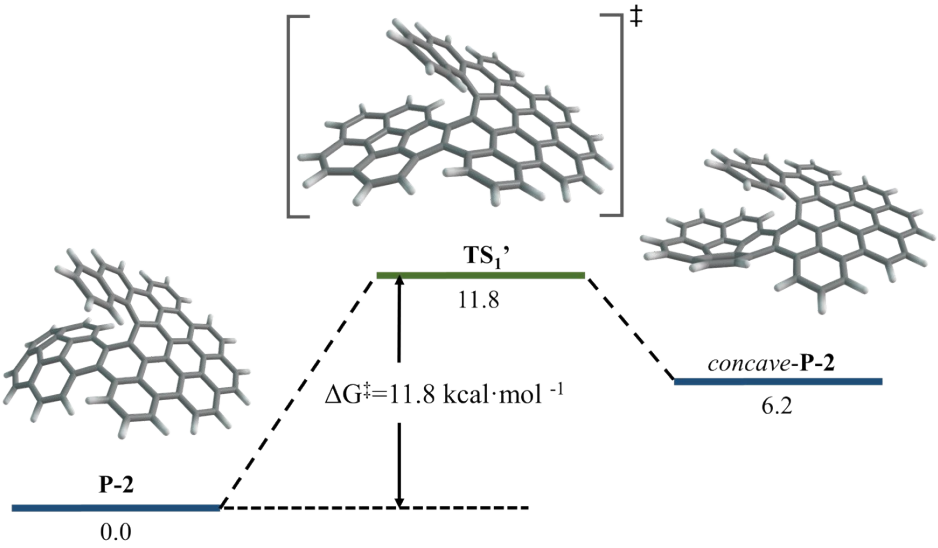


Figure S20. Isomerization between **P-2** and *concave*-**P-2**.

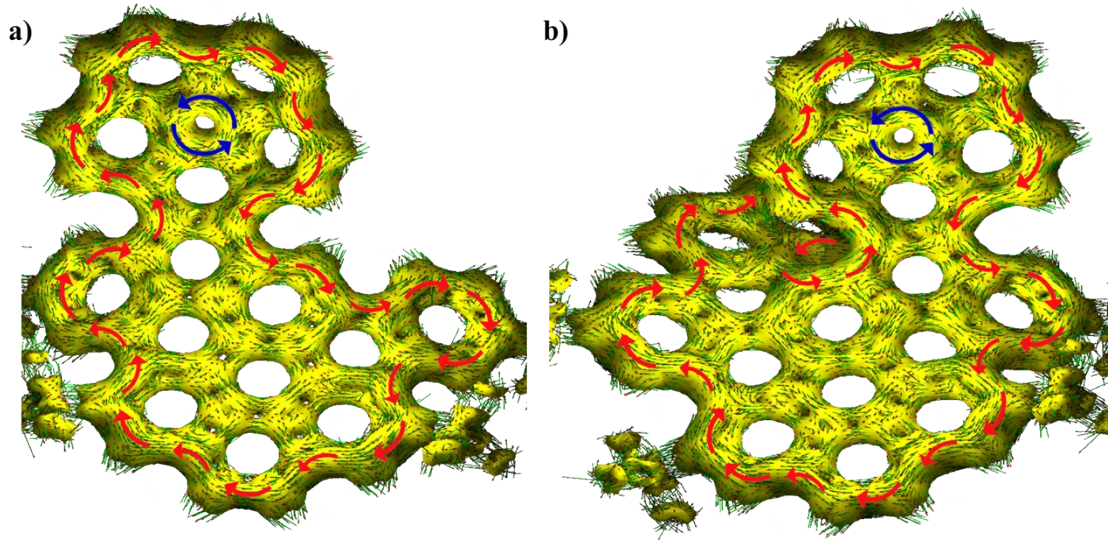
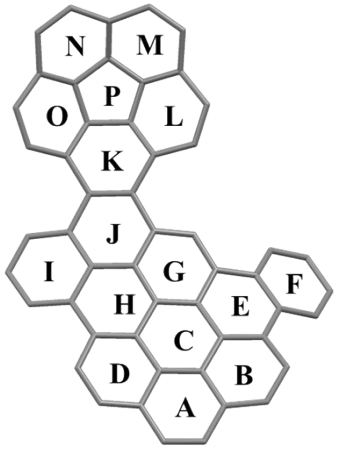


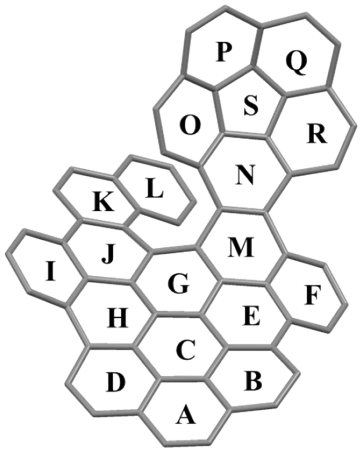
Figure S21. ACID plots of **1** (a) and **2** (b) (Iso value: 0.03 a.u.). The direction of external magnetic vector is orthogonal with respect to the central ring plane and points upward.

Table S7. NICS(1)$_{ZZ}$ and NICS(-1)$_{ZZ}$ for **1** at the optimized S0 geometry at the GIAO-B3LYP/6-311+G(2d,p) level of theory in chloroform solution. The position 1 Å above the ring center is defined as "1" and the position 1 Å under the ring center is defined as "-1".



Ring	NICS(1)zz	NICS(-1)zz	Average Value
A	-19.01	-17.91	-18.46
B	-31.08	-27.87	29.47
C	-2.23	-1.28	-1.76
D	-30.67	-28.28	-29.48
E	-4.87	-8.21	-6.54
F	-21.78	-27.26	-24.52
G	-26.56	-30.34	-28.45
H	-1.89	-6.94	-4.41
I	-24.37	-32.05	-28.21
J	-4.59	-6.85	-5.72
K	-13.34	-4.95	-9.14
L	-22.94	-13.64	-18.29
M	-22.84	-14.27	-18.56
N	-22.72	-14.61	-18.66
O	-22.32	-13.35	-17.83
P	14.04	12.66	13.35

Table S8. NICS(1)$_{ZZ}$ and NICS(-1)$_{ZZ}$ for **2** at the optimized S0 geometry at the GIAO-B3LYP/6-311+G(2d,p) level of theory in chloroform solution. The position 1 Å above the ring center is defined as "1" and the position 1 Å under the ring center is defined as "-1".



Ring	NICS(1)zz	NICS(-1)zz	Average Value
A	-18.43	-18.63	-18.53
B	-30.74	-27.67	-29.21
C	-1.64	-1.58	-1.61
D	-28.36	-30.61	-29.48
E	-0.44	-5.73	-3.08
F	-24.09	-30.62	-27.35
G	-26.96	-28.02	-27.49
H	-5.18	-3.23	-4.20
I	-28.68	-23.80	-26.24
J	-1.60	-3.71	-2.65
K	-21.96	-23.29	-22.63
L	-28.12	-30.34	-29.23
M	-4.42	-3.10	-3.76
N	-15.81	-6.45	-11.13
O	-23.32	-15.44	-19.38
P	-23.06	-14.42	-18.74
Q	-21.64	-14.13	-17.89
R	-21.87	-12.71	-17.29
S	14.08	12.83	13.45

7 NMR, IR and Mass Spectra

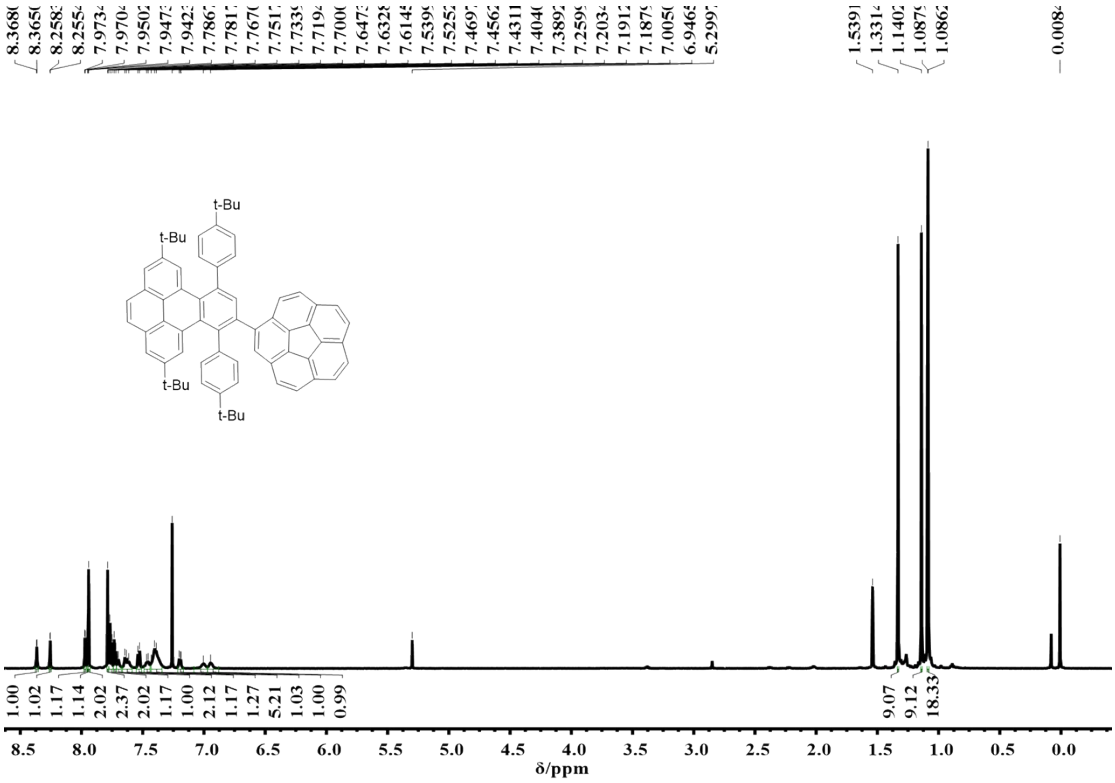


Figure S22. ^{1}H NMR spectrum of the compound **5** (400 MHz, $CDCl_3$, 298 K).

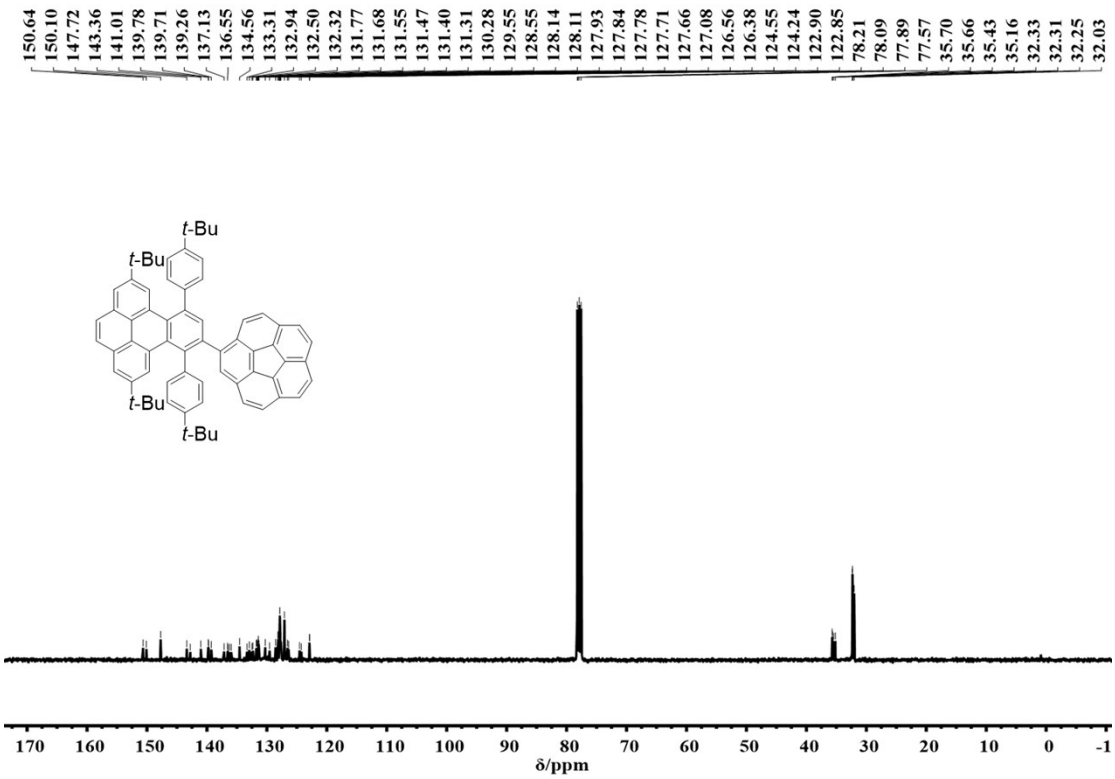


Figure S23. ^{13}C NMR spectrum of the compound **5** (100 MHz, $CDCl_3$, 298 K).

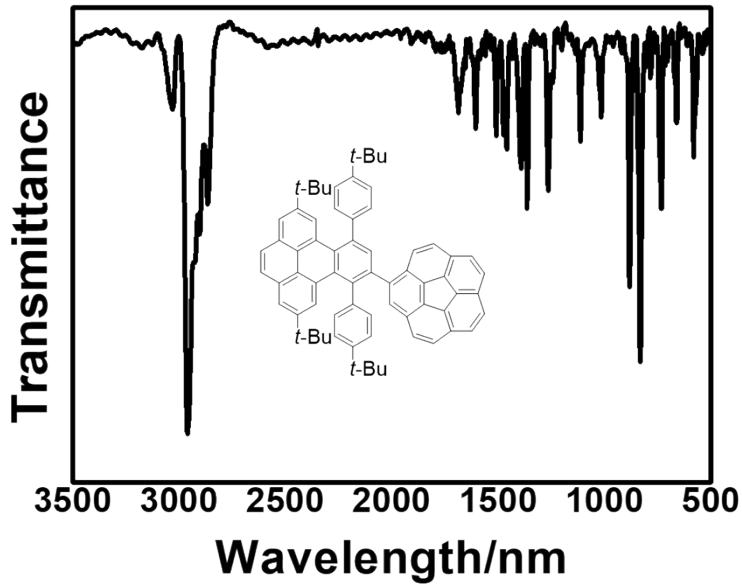


Figure S24. The FT-IR spectrum of **5**.

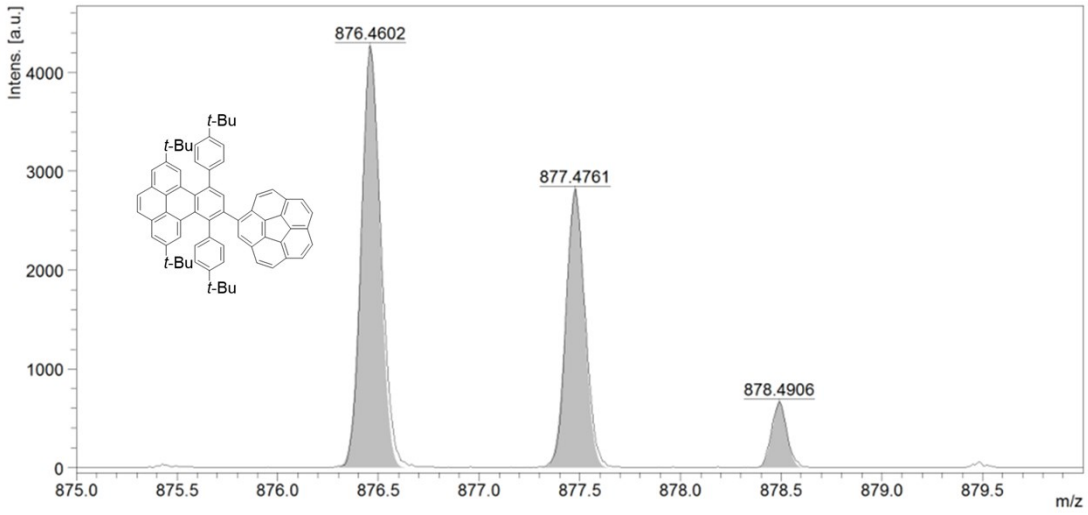


Figure S25. HRMS (MALDI-TOF) spectrum of the compound **5**.

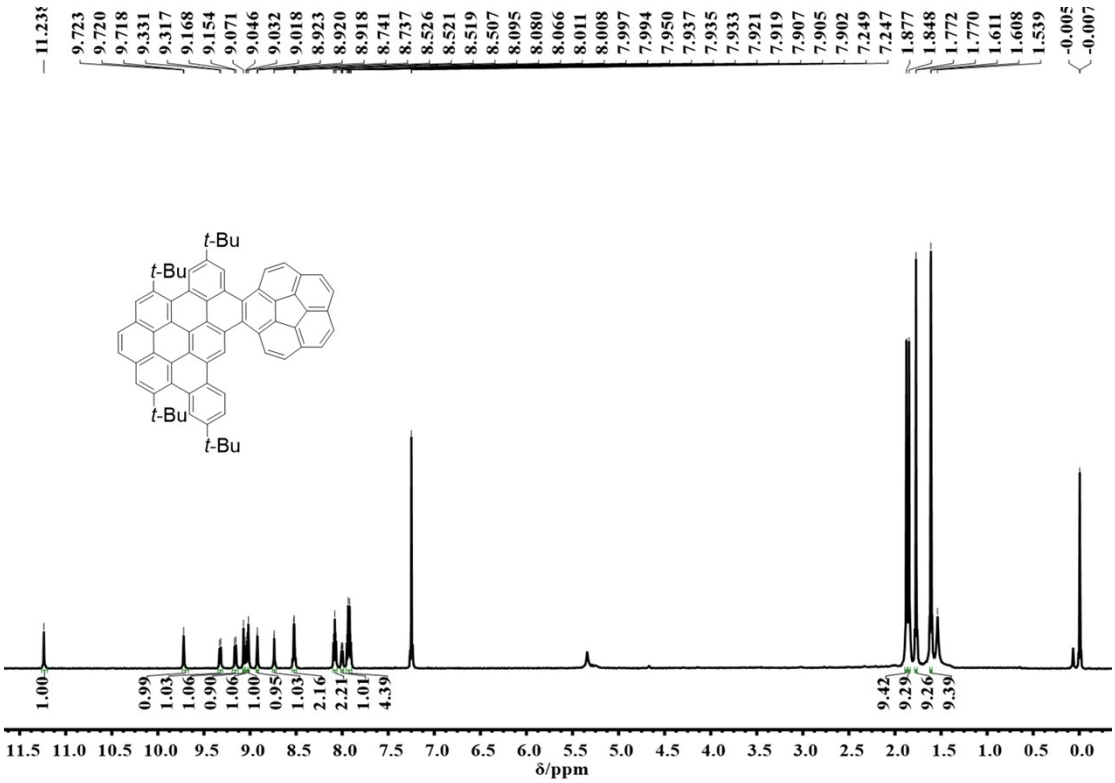


Figure S26. ^{1}H NMR spectrum of the compound **1** (400 MHz, $CDCl_3$, 298 K).

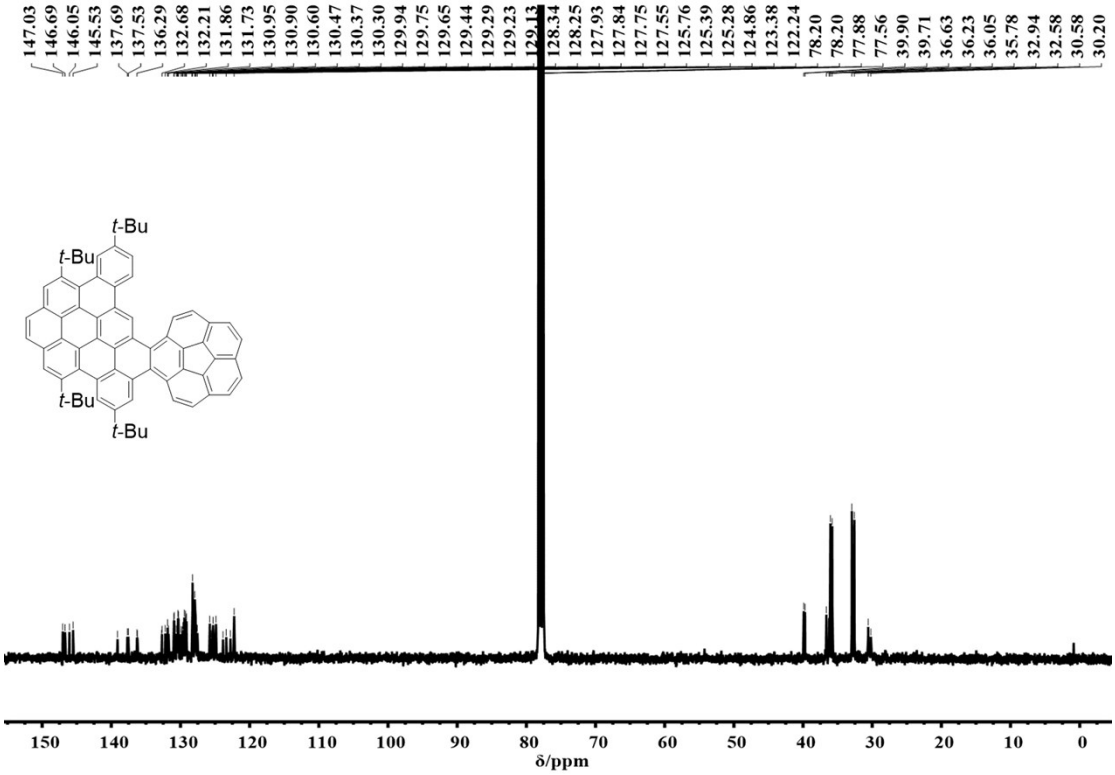


Figure S27. ^{13}C NMR spectrum of the compound **1** (100 MHz, $CDCl_3$, 298 K).

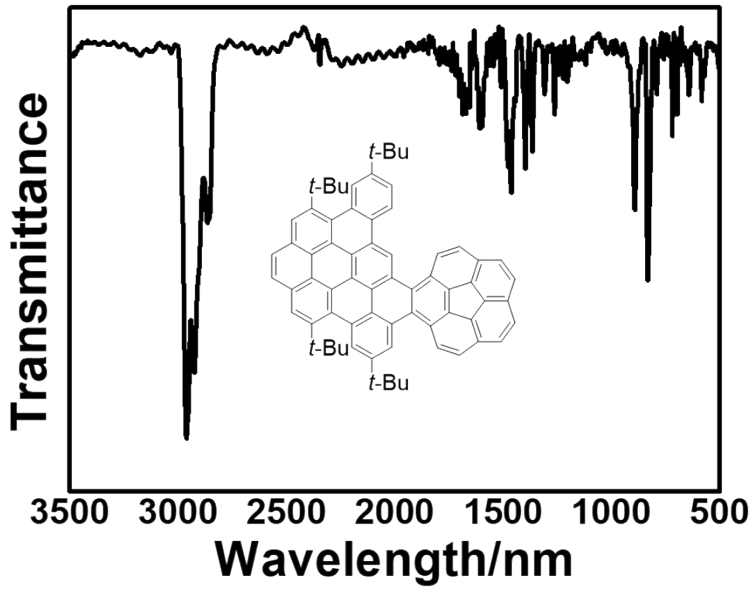


Figure S28. The FT-IR spectrum of **1**.

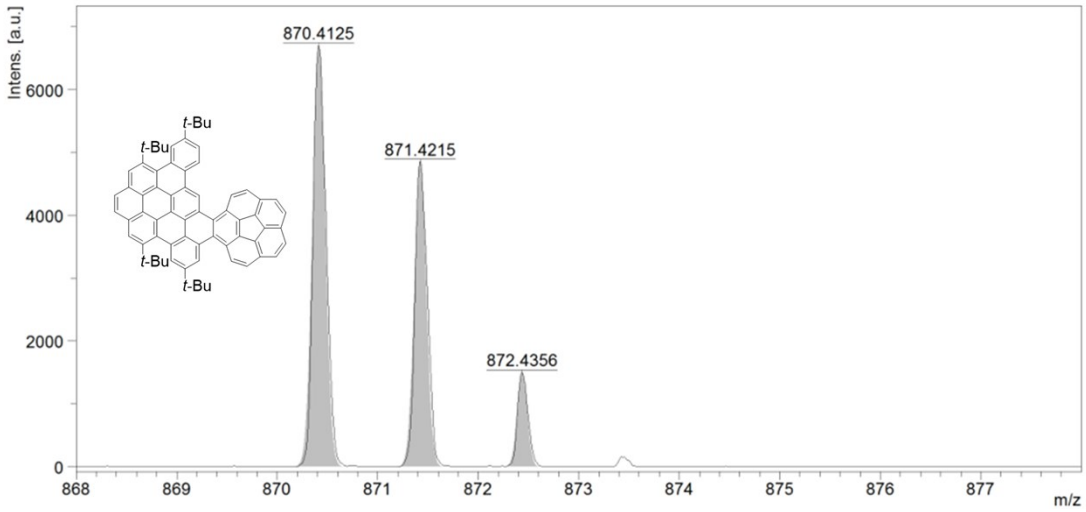


Figure S29. HRMS (MALDI-TOF) spectrum of the compound **1**.

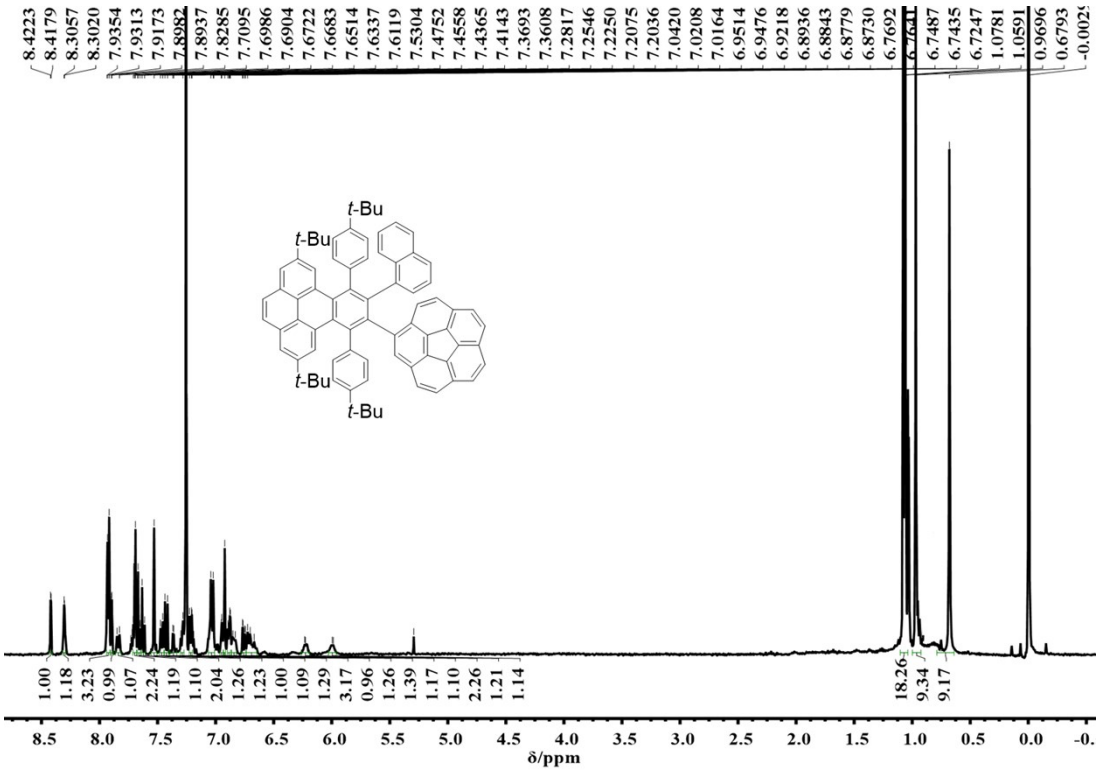


Figure S30. ^{1}H NMR spectrum of the compound **8** (400 MHz, $CDCl_3$, 298 K).

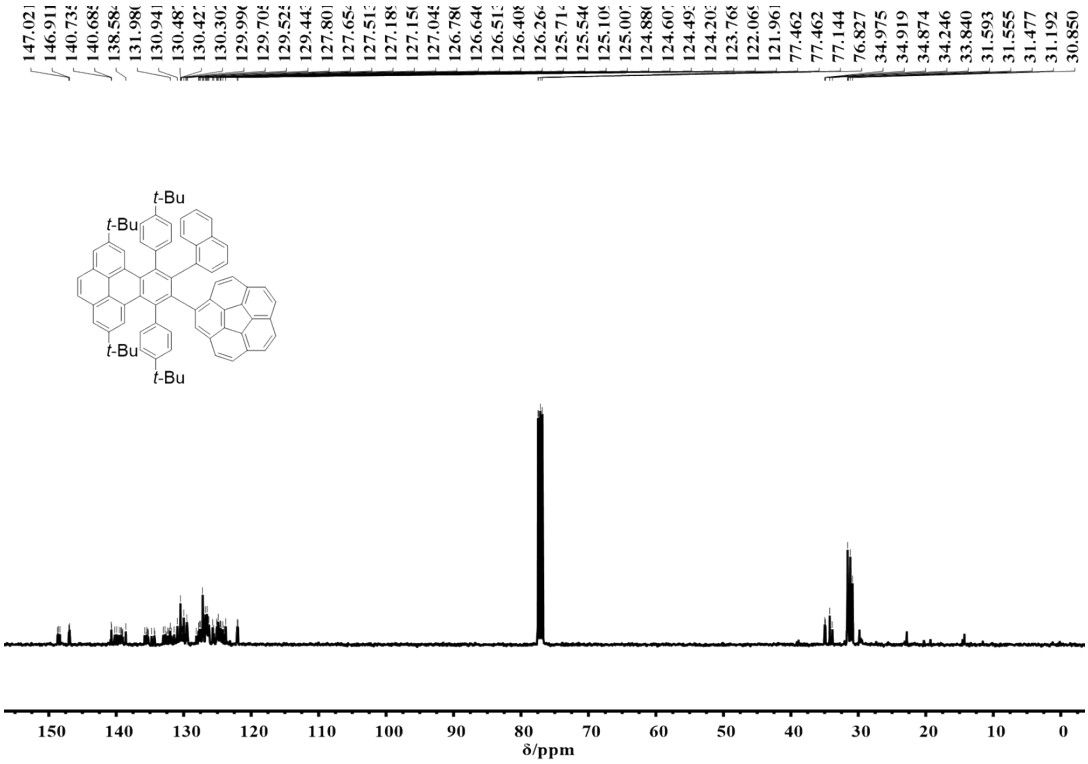


Figure S31. ^{13}C NMR spectrum of the compound **8** (100 MHz, $CDCl_3$, 298 K).

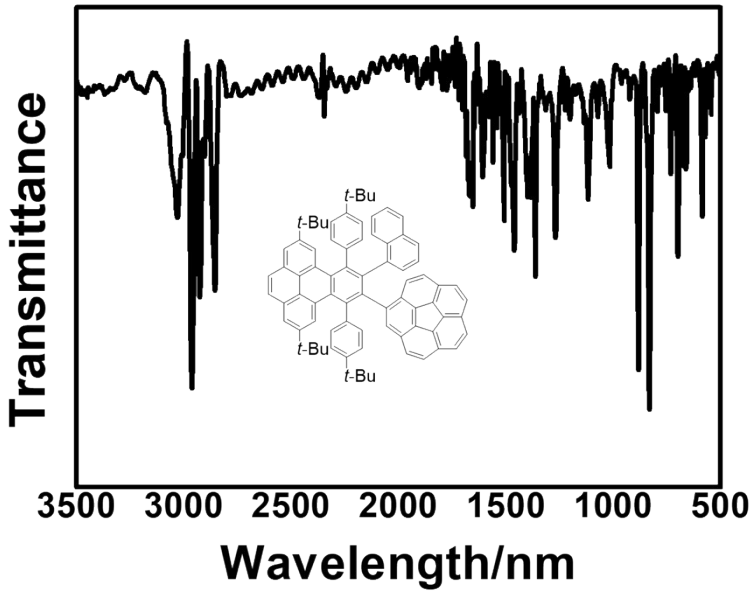


Figure S32. The FT-IR spectrum of **8**.

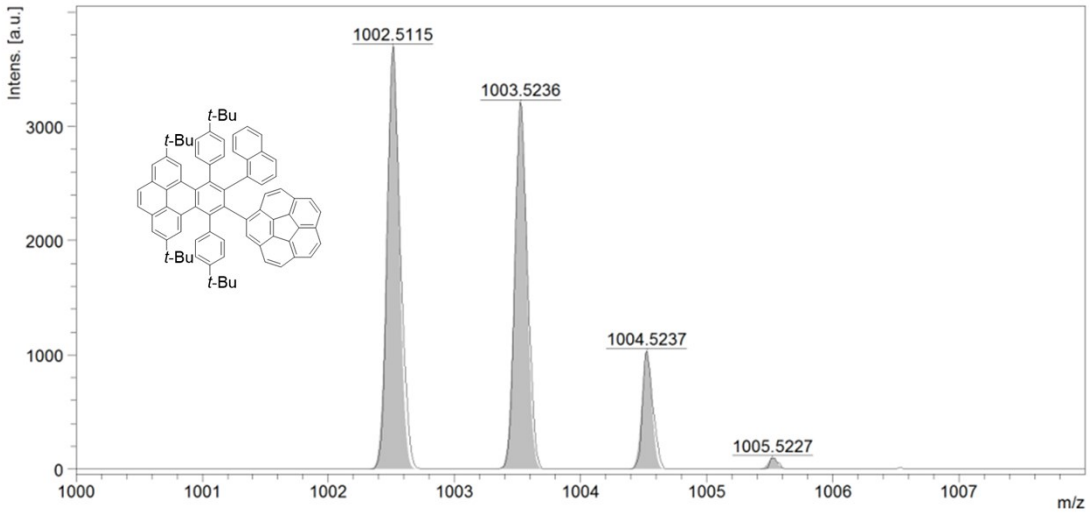


Figure S33. HRMS (MALDI-TOF) spectrum of the compound **8**.

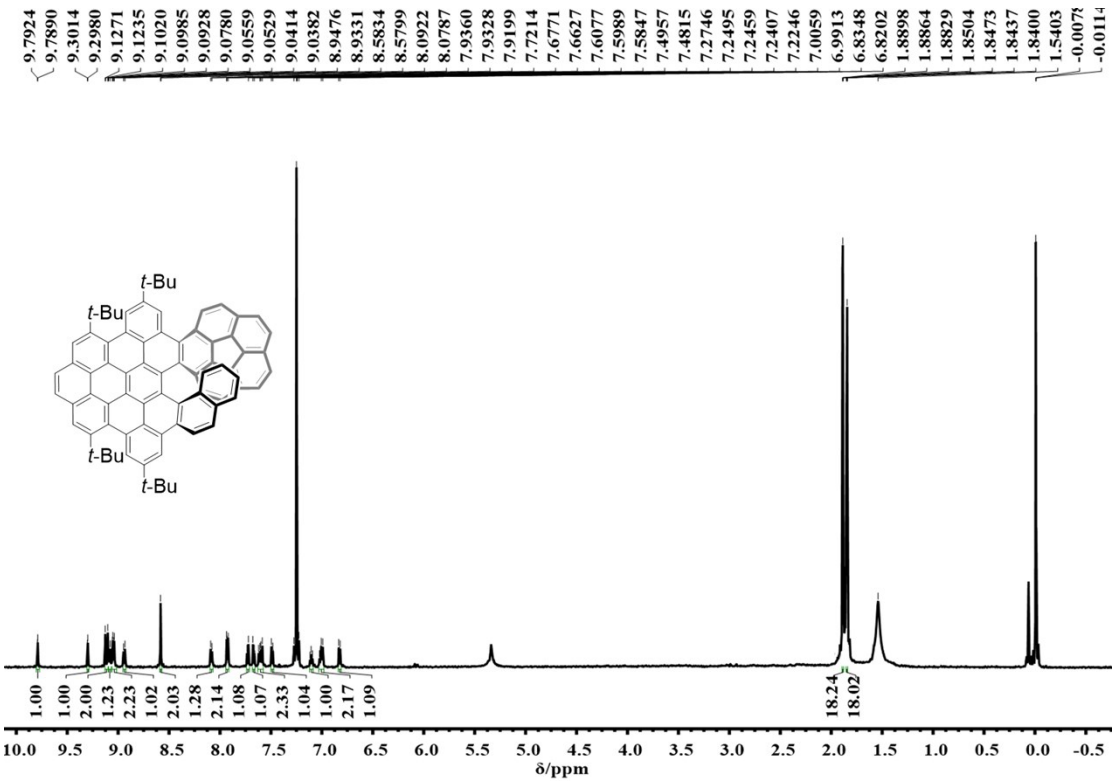


Figure S34. ^{1}H NMR spectrum of the compound **2** (400 MHz, $CDCl_3$, 298 K).

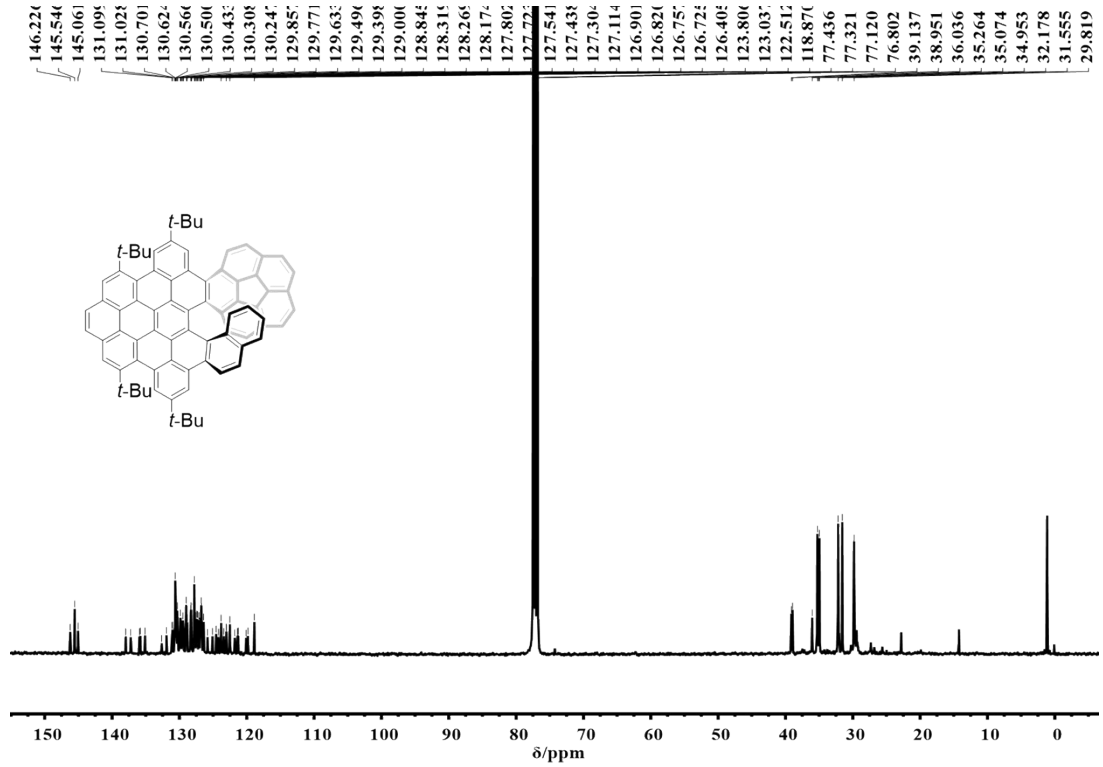


Figure S35. ^{13}C NMR spectrum of the compound **2** (100 MHz, $CDCl_3$, 298 K).

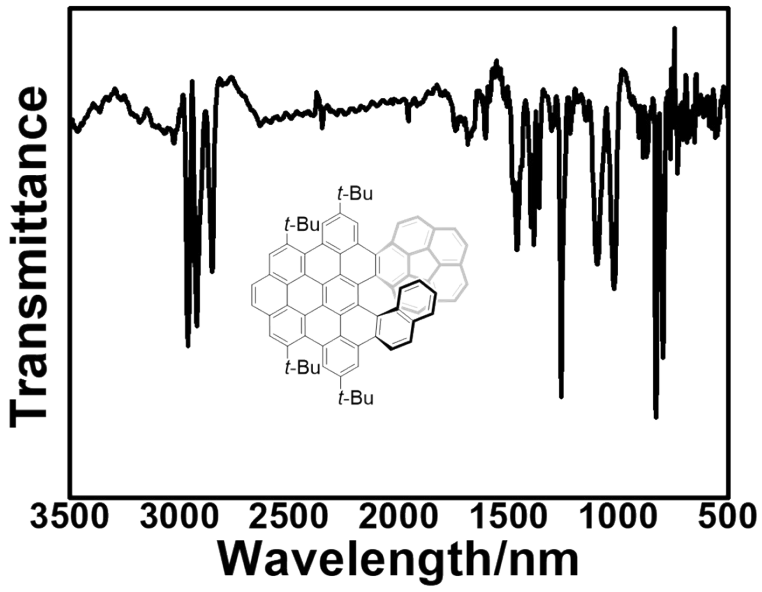


Figure S36. The FT-IR spectrum of **2**.

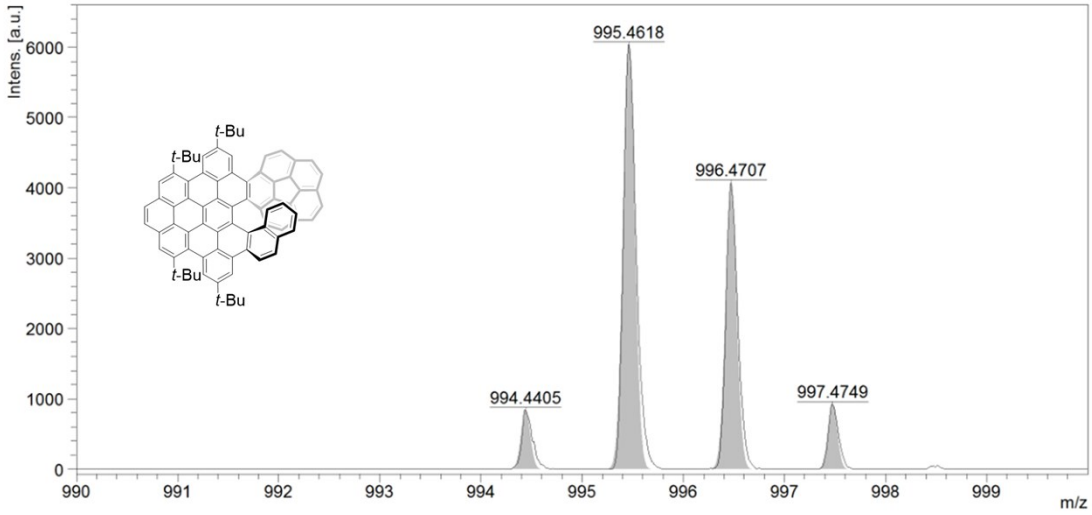


Figure S37. HRMS (MALDI-TOF) spectrum of the compound **2**.

8 Cartesian coordinates of optimized species

Optimized S0 geometry of **M-1**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.335870	-2.275410	0.393057
2	6	0	-2.212124	-0.693532	0.083582
3	6	0	-4.975115	-0.213943	-0.452174
4	6	0	-1.847933	1.706194	0.447444
5	6	0	-3.099283	-1.803335	-0.145263

6	6	0	-4.117584	0.881675	-0.128074
7	6	0	-1.242054	-3.375652	0.327966
8	6	0	-2.623225	-3.133515	-0.067710
9	6	0	1.512841	-0.063492	0.437989
10	6	0	-2.389379	3.058643	0.592978
11	6	0	4.252043	-0.551177	0.720450
12	6	0	3.763052	0.779361	0.568984
13	6	0	-2.723031	0.631779	0.127576
14	6	0	-1.578818	4.144079	0.996712
15	1	0	-0.532063	3.981844	1.226418
16	6	0	-3.518517	-4.190792	-0.364779
17	6	0	0.070038	0.159965	0.426208
18	6	0	2.000925	-1.394425	0.587609
19	6	0	-0.483000	1.434522	0.594278
20	1	0	0.182761	2.237637	0.867681
21	6	0	-6.712433	-2.367639	-1.057218
22	1	0	-7.365629	-3.205900	-1.286951
23	6	0	-0.824005	-0.936961	0.262673
24	6	0	-7.192917	-1.089800	-1.068529
25	1	0	-8.235270	-0.893290	-1.307380
26	6	0	-4.831214	-3.951222	-0.700070
27	1	0	-5.491901	-4.781636	-0.936928
28	6	0	-4.470775	-1.551761	-0.449128
29	6	0	1.041176	-2.489642	0.710681
30	6	0	-4.636349	2.198422	-0.075646
31	6	0	-3.764979	3.302602	0.320308
32	6	0	-5.346091	-2.635465	-0.738068
33	6	0	-6.345181	0.016976	-0.756767
34	6	0	6.016295	0.794022	0.125572
35	6	0	3.451055	-1.667057	0.557840
36	6	0	2.448135	1.061571	0.247343
37	6	0	-0.782502	-4.649610	0.698452
38	1	0	-1.461318	-5.494847	0.701917
39	6	0	-6.826895	1.344314	-0.733211
40	1	0	-7.870378	1.530376	-0.975541

41	6	0	5.638992	-0.535913	0.432781
42	6	0	1.419326	-3.767635	1.155539
43	1	0	2.414187	-3.926245	1.549625
44	6	0	-6.002159	2.393869	-0.398838
45	6	0	4.853545	1.599738	0.189256
46	6	0	-4.255571	4.622045	0.457540
47	1	0	-5.300955	4.831634	0.264109
48	6	0	2.280787	2.334408	-0.428351
49	1	0	1.299645	2.639661	-0.771430
50	6	0	4.189354	-2.852267	0.164320
51	1	0	3.660853	-3.776109	-0.035294
52	6	0	-3.438941	5.666657	0.848851
53	6	0	6.333411	-1.633037	-0.053357
54	6	0	7.114387	1.108698	-0.658095
55	6	0	4.716519	2.761633	-0.554551
56	6	0	-2.085400	5.424446	1.124133
57	1	0	-1.435293	6.235176	1.441134
58	6	0	7.597791	-1.319988	-0.683907
59	1	0	8.236221	-2.130196	-1.029031
60	6	0	5.552849	-2.840087	-0.107990
61	1	0	6.007771	-3.756523	-0.477462
62	6	0	0.519166	-4.829180	1.148797
63	6	0	3.350547	3.145185	-0.791878
64	1	0	3.137931	4.041900	-1.369800
65	6	0	7.971774	-0.014785	-0.968223
66	1	0	8.891608	0.152584	-1.524221
67	6	0	7.072704	2.430201	-1.246193
68	1	0	7.923844	2.785346	-1.822966
69	6	0	5.929778	3.214917	-1.200405
70	1	0	5.923712	4.156549	-1.744841
71	1	0	-3.849115	6.667862	0.947964
72	1	0	-6.422298	3.392496	-0.390486
73	1	0	-3.162272	-5.214926	-0.355187
74	1	0	0.837091	-5.804963	1.505694

Optimized S0 geometry of *concave*-**M-1**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.461117	-2.358952	-0.151303
2	6	0	-2.258123	-0.662022	-0.065814
3	6	0	-5.041484	-0.012187	0.040505
4	6	0	-1.687007	1.717370	0.097890
5	6	0	-3.241056	-1.715444	-0.081394
6	6	0	-4.069175	1.030973	0.110220
7	6	0	-1.427201	-3.409390	-0.145315
8	6	0	-2.845219	-3.073278	-0.149144
9	6	0	1.510826	-0.264260	-0.478741
10	6	0	-2.096502	3.106978	0.310078
11	6	0	-2.671086	0.694515	0.041144
12	6	0	-1.151192	4.147041	0.463344
13	1	0	-0.090845	3.922755	0.448357
14	6	0	-3.852627	-4.068951	-0.207627
15	6	0	0.094087	0.050429	-0.270171
16	6	0	1.929169	-1.594978	-0.160573
17	6	0	-0.343988	1.363658	-0.067768
18	1	0	0.400767	2.134180	0.017977
19	6	0	-6.998845	-2.054470	-0.082593
20	1	0	-7.735679	-2.852450	-0.131330
21	6	0	-0.877614	-0.990350	-0.166201
22	6	0	-7.391736	-0.750172	0.001066
23	1	0	-8.447230	-0.490126	0.020672
24	6	0	-5.189083	-3.747997	-0.189872
25	1	0	-5.937866	-4.534757	-0.239671
26	6	0	-4.629479	-1.378257	-0.049925
27	6	0	0.934693	-2.660390	-0.113293
28	6	0	-4.482561	2.379937	0.236461
29	6	0	-3.480121	3.434822	0.363056
30	6	0	-5.614281	-2.403547	-0.106714
31	6	0	-6.428943	0.302186	0.069112
32	6	0	-0.974201	-4.739138	-0.131682

33	1	0	-1.681539	-5.559593	-0.113191
34	6	0	-6.812803	1.657444	0.166669
35	1	0	-7.871356	1.905326	0.180298
36	6	0	1.326127	-4.009522	-0.152779
37	1	0	2.375024	-4.263467	-0.231213
38	6	0	-5.871966	2.657408	0.251262
39	6	0	-3.846043	4.787784	0.553660
40	1	0	-4.893159	5.061965	0.603761
41	6	0	-2.900418	5.786363	0.692686
42	6	0	-1.536903	5.461607	0.650725
43	1	0	-0.783755	6.235676	0.769271
44	6	0	0.382658	-5.031214	-0.154755
45	6	0	4.215227	-0.962620	-0.446205
46	6	0	3.799252	0.286089	-0.972654
47	6	0	6.025565	0.432430	-0.447161
48	6	0	3.350862	-1.889505	0.088091
49	6	0	2.496455	0.745638	-0.918128
50	6	0	5.580739	-0.862775	-0.103713
51	6	0	4.931243	1.139376	-0.994093
52	6	0	2.412930	2.170610	-1.225283
53	1	0	1.456623	2.629550	-1.442060
54	6	0	4.001207	-2.819652	0.994060
55	1	0	3.414173	-3.579338	1.499009
56	6	0	6.187890	-1.644888	0.861786
57	6	0	7.111699	1.047801	0.148566
58	6	0	4.858917	2.519286	-1.006307
59	6	0	7.436709	-1.100719	1.358036
60	1	0	8.017655	-1.669086	2.080985
61	6	0	5.340277	-2.701118	1.360879
62	1	0	5.721654	-3.383765	2.117039
63	6	0	3.522813	3.007527	-1.256767
64	1	0	3.355199	4.067408	-1.435223
65	6	0	7.874553	0.174372	1.019113
66	1	0	8.780825	0.548827	1.489976
67	6	0	7.138901	2.485255	-0.022866

68	1	0	7.983563	3.054486	0.358841
69	6	0	6.069856	3.183475	-0.575202
70	1	0	6.124354	4.269392	-0.605675
71	1	0	0.711412	-6.066423	-0.184881
72	1	0	-3.576065	-5.114336	-0.277321
73	1	0	-6.218983	3.680910	0.327390
74	1	0	-3.216060	6.815387	0.840795

Optimized S0 geometry of **P-1**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.335824	-2.275365	-0.393005
2	6	0	-2.212073	-0.693497	-0.083451
3	6	0	-4.975113	-0.213997	0.452156
4	6	0	-1.847882	1.706261	-0.447158
5	6	0	-3.099223	-1.803319	0.145361
6	6	0	-4.117615	0.881635	0.127979
7	6	0	-1.242029	-3.375582	-0.328092
8	6	0	-2.623154	-3.133485	0.067823
9	6	0	1.512861	-0.063473	-0.437799
10	6	0	-2.389339	3.058734	-0.592668
11	6	0	-2.723001	0.631806	-0.127457
12	6	0	-1.578645	4.144327	-0.995705
13	1	0	-0.531648	3.982319	-1.224470
14	6	0	-3.518319	-4.190794	0.365175
15	6	0	0.070078	0.160006	-0.425972
16	6	0	2.000939	-1.394397	-0.587498
17	6	0	-0.482957	1.434565	-0.594036
18	1	0	0.182825	2.237628	-0.867604
19	6	0	-6.712295	-2.367715	1.057461
20	1	0	-7.365464	-3.205962	1.287323
21	6	0	-0.823951	-0.936911	-0.262476
22	6	0	-7.192858	-1.089906	1.068564
23	1	0	-8.235235	-0.893462	1.307364

24	6	0	-4.830994	-3.951258	0.700564
25	1	0	-5.491608	-4.781652	0.937683
26	6	0	-4.470706	-1.551790	0.449275
27	6	0	1.041199	-2.489601	-0.710708
28	6	0	-4.636480	2.198326	0.075245
29	6	0	-3.765116	3.302543	-0.320709
30	6	0	-5.345941	-2.635523	0.738361
31	6	0	-6.345201	0.016883	0.756665
32	6	0	-0.782585	-4.649462	-0.698992
33	1	0	-1.461552	-5.494580	-0.702813
34	6	0	-6.827007	1.344183	0.732904
35	1	0	-7.870494	1.530186	0.975258
36	6	0	1.419282	-3.767504	-1.155865
37	1	0	2.414161	-3.926097	-1.549919
38	6	0	-6.002339	2.393723	0.398376
39	6	0	-4.255840	4.621889	-0.458490
40	1	0	-5.301414	4.831309	-0.265937
41	6	0	-3.439115	5.666601	-0.849357
42	6	0	-2.085327	5.424621	-1.123511
43	1	0	-1.435094	6.235472	-1.439947
44	6	0	0.519058	-4.829001	-1.149414
45	6	0	4.252062	-0.551101	-0.720785
46	6	0	3.763067	0.779446	-0.569246
47	6	0	6.016361	0.794101	-0.125931
48	6	0	3.451067	-1.666958	-0.557920
49	6	0	2.448205	1.061531	-0.247236
50	6	0	5.639037	-0.535846	-0.433181
51	6	0	4.853597	1.599832	-0.189566
52	6	0	2.280856	2.334209	0.428741
53	1	0	1.299750	2.639248	0.772083
54	6	0	4.189288	-2.852158	-0.164293
55	1	0	3.660703	-3.775903	0.035518
56	6	0	6.333342	-1.632965	0.053150
57	6	0	7.114319	1.108657	0.657992
58	6	0	4.716554	2.761541	0.554559

59	6	0	7.597657	-1.320006	0.683885
60	1	0	8.235939	-2.130283	1.029120
61	6	0	5.552780	-2.839988	0.107993
62	1	0	6.007717	-3.756337	0.477651
63	6	0	3.350607	3.144991	0.792201
64	1	0	3.138101	4.041555	1.370392
65	6	0	7.971638	-0.014840	0.968279
66	1	0	8.891360	0.152551	1.524453
67	6	0	7.072626	2.430008	1.246382
68	1	0	7.923697	2.784960	1.823373
69	6	0	5.929717	3.214744	1.200604
70	1	0	5.923518	4.156227	1.745293
71	1	0	0.836925	-5.804686	-1.506624
72	1	0	-3.161912	-5.214873	0.355762
73	1	0	-3.849397	6.667714	-0.948951
74	1	0	-6.422491	3.392334	0.389934

Optimized S0 geometry of **TS_1**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.404012	-2.296212	0.290177
2	6	0	-2.263566	-0.686704	0.045303
3	6	0	-5.038821	-0.159868	-0.365442
4	6	0	-1.839850	1.701885	0.388413
5	6	0	-3.180439	-1.780754	-0.131398
6	6	0	-4.148905	0.920330	-0.080264
7	6	0	-1.335464	-3.377715	0.292784
8	6	0	-2.725454	-3.117567	-0.057682
9	6	0	1.489076	-0.118097	0.122315
10	6	0	-2.351574	3.060526	0.575859
11	6	0	-2.749036	0.645891	0.110159
12	6	0	-1.507593	4.125887	0.963680
13	1	0	-0.457182	3.940801	1.157488
14	6	0	-3.650100	-4.161468	-0.308329

15	6	0	0.051355	0.125775	0.246564
16	6	0	1.969626	-1.471335	0.307342
17	6	0	-0.472983	1.407475	0.449267
18	1	0	0.214090	2.198825	0.692051
19	6	0	-6.837596	-2.284171	-0.885663
20	1	0	-7.515215	-3.111137	-1.083442
21	6	0	-0.872506	-0.953524	0.152885
22	6	0	-7.295256	-0.997683	-0.883421
23	1	0	-8.343129	-0.783928	-1.079516
24	6	0	-4.970821	-3.900613	-0.594232
25	1	0	-5.654779	-4.720897	-0.798055
26	6	0	-4.558736	-1.506341	-0.377871
27	6	0	0.981627	-2.525333	0.559314
28	6	0	-4.640714	2.245793	-0.003673
29	6	0	-3.733220	3.330990	0.363589
30	6	0	-5.464140	-2.576034	-0.621915
31	6	0	-6.416095	0.095310	-0.611764
32	6	0	-0.893376	-4.648151	0.692303
33	1	0	-1.590007	-5.476957	0.748102
34	6	0	-6.871722	1.431594	-0.570459
35	1	0	-7.920704	1.636683	-0.769869
36	6	0	1.338356	-3.794141	1.045532
37	1	0	2.331668	-3.963652	1.428982
38	6	0	-6.014975	2.466243	-0.270536
39	6	0	-4.194406	4.656717	0.536256
40	1	0	-5.243318	4.885787	0.389321
41	6	0	-3.344518	5.682261	0.907053
42	6	0	-1.986042	5.413023	1.127373
43	1	0	-1.310586	6.207855	1.431407
44	6	0	0.416633	-4.834757	1.112258
45	6	0	4.172605	-0.719400	-0.143664
46	6	0	3.700762	0.588493	-0.340521
47	6	0	5.964300	0.635115	-0.469604
48	6	0	3.416539	-1.809554	0.190286
49	6	0	2.403710	1.003255	-0.223480

50	6	0	5.572412	-0.685015	-0.232988
51	6	0	4.811044	1.418972	-0.552020
52	6	0	2.318150	2.448409	-0.477449
53	1	0	1.357816	2.939293	-0.563831
54	6	0	4.286925	-2.985077	0.340581
55	1	0	3.868377	-3.971174	0.485198
56	6	0	6.428641	-1.722971	0.023414
57	6	0	7.252362	1.104967	-0.450476
58	6	0	4.795040	2.784559	-0.658722
59	6	0	7.821982	-1.297728	-0.000315
60	1	0	8.610127	-2.025783	0.177212
61	6	0	5.685837	-2.941782	0.283434
62	1	0	6.212526	-3.881043	0.436336
63	6	0	3.430623	3.279883	-0.659858
64	1	0	3.233216	4.337604	-0.818684
65	6	0	8.209088	0.030235	-0.218092
66	1	0	9.273706	0.251341	-0.193625
67	6	0	7.294131	2.554155	-0.600901
68	1	0	8.252979	3.067100	-0.621037
69	6	0	6.140617	3.341540	-0.703080
70	1	0	6.275640	4.416415	-0.798920
71	1	0	0.727558	-5.800628	1.500870
72	1	0	-3.310967	-5.191594	-0.303441
73	1	0	-6.416138	3.472431	-0.245231
74	1	0	-3.732793	6.688932	1.034755

Optimized S0 geometry of **TS_2**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.405288	-2.275346	-0.352154
2	6	0	-2.256089	-0.662322	-0.110297
3	6	0	-5.052983	-0.154457	0.280356
4	6	0	-1.826488	1.745656	-0.177232
5	6	0	-3.185273	-1.762877	-0.013207

6	6	0	-4.145859	0.939176	0.148518
7	6	0	-1.328105	-3.364561	-0.359876
8	6	0	-2.739198	-3.100450	-0.129257
9	6	0	1.524143	-0.078792	-0.486178
10	6	0	-2.311720	3.128021	-0.135108
11	6	0	-2.744133	0.671949	-0.049538
12	6	0	-1.444224	4.231988	-0.300504
13	1	0	-0.388186	4.070482	-0.479233
14	6	0	-3.684499	-4.149412	-0.005102
15	6	0	0.071014	0.163271	-0.379514
16	6	0	1.954721	-1.439593	-0.369511
17	6	0	-0.469109	1.452503	-0.335845
18	1	0	0.199565	2.282683	-0.383034
19	6	0	-6.883877	-2.298935	0.524748
20	1	0	-7.570776	-3.136821	0.615203
21	6	0	-0.861402	-0.922276	-0.262954
22	6	0	-7.337566	-1.015279	0.614836
23	1	0	-8.392627	-0.810093	0.778528
24	6	0	-5.017481	-3.898334	0.210909
25	1	0	-5.718529	-4.723424	0.310206
26	6	0	-4.575546	-1.498357	0.192156
27	6	0	0.990518	-2.525877	-0.474077
28	6	0	-4.625633	2.269808	0.224979
29	6	0	-3.695447	3.384845	0.072544
30	6	0	-5.499627	-2.574615	0.309096
31	6	0	-6.439312	0.087314	0.492129
32	6	0	-0.843409	-4.659833	-0.604358
33	1	0	-1.525989	-5.499788	-0.652063
34	6	0	-6.887773	1.423267	0.573339
35	1	0	-7.945100	1.614994	0.738913
36	6	0	1.413313	-3.833355	-0.772570
37	1	0	2.454637	-4.022652	-0.997682
38	6	0	-6.010579	2.474252	0.443607
39	6	0	-4.135565	4.728472	0.117843
40	1	0	-5.184847	4.947768	0.274588

41	6	0	-3.262310	5.788087	-0.038336
42	6	0	-1.900014	5.536311	-0.253269
43	1	0	-1.202855	6.358941	-0.386092
44	6	0	0.505398	-4.883234	-0.842550
45	6	0	4.249819	-0.796582	-0.509028
46	6	0	3.850747	0.540976	-0.770293
47	6	0	6.090049	0.526505	-0.236738
48	6	0	3.368459	-1.786517	-0.153104
49	6	0	2.547369	1.000812	-0.644719
50	6	0	5.617583	-0.799876	-0.159824
51	6	0	5.005686	1.352383	-0.612076
52	6	0	2.523434	2.461584	-0.578686
53	1	0	1.601991	3.018101	-0.629203
54	6	0	3.990614	-2.881684	0.569208
55	1	0	3.380756	-3.702146	0.930848
56	6	0	6.207247	-1.768893	0.632516
57	6	0	7.196812	0.981697	0.457729
58	6	0	4.975743	2.704319	-0.329860
59	6	0	7.473388	-1.368891	1.211926
60	1	0	8.040759	-2.084659	1.802556
61	6	0	5.332941	-2.874290	0.937497
62	1	0	5.696983	-3.694113	1.552736
63	6	0	3.652812	3.258177	-0.428212
64	1	0	3.501909	4.330581	-0.325906
65	6	0	7.944279	-0.064544	1.125746
66	1	0	8.863242	0.187898	1.650151
67	6	0	7.262937	2.421806	0.586566
68	1	0	8.126687	2.878297	1.064754
69	6	0	6.206336	3.240940	0.209211
70	1	0	6.283351	4.308243	0.403769
71	1	0	0.853778	-5.882286	-1.089556
72	1	0	-3.356973	-5.180623	-0.062159
73	1	0	-3.633785	6.808322	0.000631
74	1	0	-6.405109	3.480660	0.513168

Optimized S0 geometry of **P-2**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.774063	-1.802844	-0.408872
2	6	0	2.001260	1.404159	0.091205
3	6	0	0.692920	-2.600551	0.591592
4	6	0	3.430311	-2.076056	-0.015058
5	6	0	0.682894	1.132064	0.553114
6	6	0	4.248570	0.612903	-0.595809
7	6	0	0.176869	-0.197420	0.382353
8	6	0	2.489698	-0.993534	0.058765
9	6	0	1.657157	-3.644857	0.719383
10	6	0	3.034727	-3.395171	0.307842
11	6	0	5.716407	-2.863903	-0.504042
12	6	0	-3.081934	-2.242013	0.269556
13	6	0	1.117012	-1.261012	0.305749
14	6	0	-0.055210	2.228595	1.180806
15	6	0	-2.174141	0.471770	-0.330590
16	6	0	-0.683670	-2.850212	0.872620
17	6	0	7.052841	-2.575481	-0.919855
18	1	0	7.762493	-3.396030	-0.992282
19	6	0	-4.534157	0.781790	-0.956779
20	6	0	-3.508599	0.134961	-0.224889
21	6	0	5.291781	-4.174794	-0.189081
22	1	0	6.004457	-4.991976	-0.269690
23	6	0	-1.183819	0.798112	2.939279
24	1	0	-0.506525	-0.020426	2.735040
25	6	0	-1.677085	-1.853525	0.486175
26	6	0	-1.238607	-0.521551	0.222116
27	6	0	-3.953504	-1.184780	0.075717
28	6	0	-0.066163	-5.056588	1.690603
29	6	0	-5.619775	-0.116909	-1.090147
30	6	0	-4.297845	1.801425	-1.865567
31	6	0	1.246275	-4.869068	1.271241

32	1	0	1.966193	-5.664421	1.429156
33	6	0	5.176142	-0.466136	-0.717258
34	6	0	2.406054	2.757895	-0.177770
35	6	0	-1.045953	2.016618	2.221999
36	6	0	-5.253545	-1.335805	-0.467955
37	6	0	2.904044	0.336469	-0.171413
38	6	0	3.997199	-4.429106	0.206961
39	6	0	-1.871819	3.110398	2.631722
40	6	0	1.480757	3.821573	0.042120
41	6	0	0.269893	3.550632	0.816379
42	6	0	-0.563668	4.620114	1.262695
43	1	0	-0.348476	5.634511	0.949030
44	6	0	-2.137176	0.643764	3.924785
45	1	0	-2.204656	-0.299466	4.459931
46	6	0	3.687756	3.023687	-0.748129
47	6	0	-2.931538	2.257765	-1.892416
48	1	0	-2.648231	3.062463	-2.567199
49	6	0	-1.925790	1.620221	-1.176824
50	1	0	-0.909230	1.956720	-1.337954
51	6	0	7.435830	-1.299644	-1.221342
52	1	0	8.455132	-1.089732	-1.536179
53	6	0	-5.783837	-2.555076	-0.860427
54	6	0	4.651614	1.936472	-0.888487
55	6	0	-3.673301	-3.535956	-0.015767
56	1	0	-3.075047	-4.434368	0.072118
57	6	0	5.990222	2.155603	-1.297170
58	6	0	-1.630610	4.401284	2.085924
59	1	0	-2.267238	5.227869	2.391847
60	6	0	6.514278	-0.211520	-1.125987
61	6	0	-6.546679	-0.038068	-2.116821
62	6	0	-1.023631	-4.066886	1.486610
63	1	0	-2.036180	-4.227267	1.835434
64	6	0	-3.012162	1.700762	4.252475
65	1	0	-3.771598	1.563712	5.017319
66	6	0	-2.866931	2.916488	3.622533

67	1	0	-3.496901	3.759916	3.895301
68	6	0	-6.442773	1.155782	-2.927135
69	1	0	-7.170972	1.331097	-3.716066
70	6	0	-5.369949	2.028444	-2.810210
71	1	0	-5.294485	2.854886	-3.513531
72	6	0	-4.955297	-3.684952	-0.532287
73	1	0	-5.287463	-4.687465	-0.793208
74	6	0	6.890558	1.120097	-1.412538
75	1	0	7.913734	1.323404	-1.719119
76	6	0	1.816347	5.106237	-0.410743
77	1	0	1.121198	5.929253	-0.294860
78	6	0	-6.905736	-2.464231	-1.770245
79	1	0	-7.423544	-3.372641	-2.070089
80	6	0	3.974462	4.332429	-1.169208
81	1	0	4.922117	4.557678	-1.644587
82	6	0	-7.271396	-1.265823	-2.365507
83	1	0	-8.064794	-1.276524	-3.109689
84	6	0	3.042934	5.352002	-1.019374
85	1	0	3.277701	6.352528	-1.372130
86	1	0	6.332716	3.162683	-1.506082
87	1	0	-0.348243	-5.985452	2.178725
88	1	0	3.710382	-5.453195	0.419053

Optimized S0 geometry of *concave*-**P-2**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.077068	-1.480658	-0.123768
2	6	0	1.963170	1.428746	0.100710
3	6	0	0.970839	-2.704796	0.026632
4	6	0	3.715176	-1.901096	-0.030135
5	6	0	0.613301	1.012211	0.269361
6	6	0	4.362891	0.890202	-0.196805
7	6	0	0.275723	-0.333549	-0.092826
8	6	0	2.674131	-0.910344	-0.021173

9	6	0	2.001276	-3.689784	0.114610
10	6	0	3.399381	-3.278277	0.040312
11	6	0	6.121584	-2.445919	-0.139771
12	6	0	1.308025	-1.310954	-0.040113
13	6	0	-0.319351	1.980868	0.851385
14	6	0	-0.405296	-3.093388	0.058202
15	6	0	7.478148	-2.010634	-0.245423
16	1	0	8.264512	-2.761424	-0.254302
17	6	0	5.778103	-3.813853	-0.060998
18	1	0	6.571028	-4.557586	-0.077141
19	6	0	-1.576796	0.306449	2.273153
20	1	0	-0.795270	-0.427386	2.129999
21	6	0	-1.447510	-2.105609	-0.189306
22	6	0	-1.063565	-0.763043	-0.503322
23	6	0	0.297601	-5.415096	0.276947
24	6	0	1.633414	-5.036270	0.267782
25	1	0	2.392080	-5.802807	0.371538
26	6	0	5.398674	-0.091604	-0.219839
27	6	0	2.279268	2.830735	0.027104
28	6	0	-1.443876	1.592227	1.684709
29	6	0	2.995901	0.465016	-0.065159
30	6	0	4.463870	-4.213350	0.022845
31	6	0	-2.428031	2.571435	2.030727
32	6	0	1.233374	3.792874	0.151059
33	6	0	-0.061046	3.354308	0.669444
34	6	0	-1.053513	4.306636	1.050380
35	1	0	-0.879765	5.361238	0.872565
36	6	0	-2.659336	-0.017311	3.065479
37	1	0	-2.721479	-1.008130	3.506728
38	6	0	3.610839	3.251842	-0.265188
39	6	0	7.785181	-0.683384	-0.336883
40	1	0	8.820096	-0.360167	-0.418224
41	6	0	4.683899	2.264163	-0.294756
42	6	0	6.047514	2.631774	-0.402182
43	6	0	-2.221721	3.924709	1.645742

44	1	0	-2.975062	4.664940	1.904231
45	6	0	6.759038	0.310528	-0.328976
46	6	0	-0.707515	-4.463596	0.153992
47	1	0	-1.733032	-4.797248	0.079223
48	6	0	-3.676803	0.926975	3.314996
49	1	0	-4.535317	0.656550	3.923507
50	6	0	-3.549562	2.203793	2.815372
51	1	0	-4.295063	2.962900	3.040443
52	6	0	7.051298	1.689882	-0.417772
53	1	0	8.089474	2.004317	-0.491681
54	6	0	1.518362	5.136324	-0.134269
55	1	0	0.736754	5.885584	-0.089903
56	6	0	3.841685	4.612120	-0.528528
57	1	0	4.833458	4.954297	-0.800688
58	6	0	2.804618	5.535029	-0.483730
59	1	0	3.001206	6.578608	-0.713710
60	1	0	6.321174	3.679590	-0.450381
61	1	0	0.035294	-6.466310	0.359279
62	1	0	4.251809	-5.275367	0.061303
63	6	0	-3.209654	-0.434475	-1.526360
64	6	0	-3.658465	-1.662594	-0.977420
65	6	0	-5.498820	-0.405761	-1.489929
66	6	0	-1.985558	0.128403	-1.226721
67	6	0	-2.876072	-2.478511	-0.192385
68	6	0	-4.352600	0.329627	-1.868535
69	6	0	-5.068575	-1.632108	-0.935085
70	6	0	-3.653072	-3.369875	0.648713
71	1	0	-3.150885	-4.038101	1.340297
72	6	0	-1.900141	1.523063	-1.628755
73	1	0	-0.943736	2.028324	-1.620600
74	6	0	-4.346932	1.706947	-1.987413
75	6	0	-6.715318	0.179390	-1.188180
76	6	0	-5.822725	-2.369622	-0.040091
77	6	0	-5.654324	2.316531	-1.878585
78	1	0	-5.756692	3.390573	-2.017507

79	6	0	-3.015771	2.272026	-1.981899
80	1	0	-2.872885	3.328264	-2.197445
81	6	0	-5.044523	-3.313792	0.723246
82	1	0	-5.538769	-3.953095	1.451592
83	6	0	-6.779307	1.592413	-1.495853
84	1	0	-7.713195	2.130817	-1.349695
85	6	0	-7.596692	-0.668774	-0.408556
86	1	0	-8.599330	-0.320104	-0.170551
87	6	0	-7.174659	-1.875591	0.135994
88	1	0	-7.863745	-2.420060	0.777882

Optimized S0 geometry of **TS_1'**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.895360	-1.721915	-0.398209
2	6	0	2.036466	1.405931	0.119020
3	6	0	0.797009	-2.632230	0.423719
4	6	0	3.544626	-2.034549	-0.064290
5	6	0	0.696908	1.085718	0.482566
6	6	0	4.331130	0.690427	-0.497050
7	6	0	0.233346	-0.244613	0.218423
8	6	0	2.579227	-0.974939	0.006852
9	6	0	1.781051	-3.655464	0.568605
10	6	0	3.164086	-3.370199	0.200941
11	6	0	5.859874	-2.761901	-0.502354
12	6	0	1.203118	-1.280993	0.174972
13	6	0	-0.093444	2.127814	1.138084
14	6	0	-0.583466	-2.909775	0.664729
15	6	0	7.203798	-2.432878	-0.859994
16	1	0	7.930757	-3.237120	-0.942998
17	6	0	5.449102	-4.091382	-0.252832
18	1	0	6.178681	-4.892577	-0.342240
19	6	0	-1.319906	0.565787	2.710848
20	1	0	-0.617846	-0.229394	2.499684

21	6	0	-1.591482	-1.953053	0.205451
22	6	0	-1.155138	-0.601747	-0.080201
23	6	0	0.070361	-5.106346	1.492432
24	6	0	1.386908	-4.892509	1.102118
25	1	0	2.121220	-5.671869	1.273005
26	6	0	5.282474	-0.366180	-0.633641
27	6	0	2.433476	2.778746	-0.040945
28	6	0	-1.150406	1.832746	2.090918
29	6	0	2.974661	0.370769	-0.149054
30	6	0	4.147748	-4.383093	0.093255
31	6	0	-2.016211	2.887581	2.521529
32	6	0	1.484715	3.814778	0.207661
33	6	0	0.238915	3.476870	0.894633
34	6	0	-0.633419	4.504031	1.364719
35	1	0	-0.407607	5.540748	1.145916
36	6	0	-2.334310	0.333907	3.617234
37	1	0	-2.423237	-0.645067	4.080090
38	6	0	3.736854	3.097342	-0.531349
39	6	0	7.573121	-1.138506	-1.092248
40	1	0	8.598680	-0.897737	-1.361465
41	6	0	4.722282	2.033788	-0.701928
42	6	0	6.070415	2.293543	-1.051820
43	6	0	-1.752202	4.217295	2.092993
44	1	0	-2.416343	5.014847	2.417061
45	6	0	6.629461	-0.070911	-0.980355
46	6	0	-0.903054	-4.136891	1.268709
47	1	0	-1.910474	-4.323841	1.608468
48	6	0	-3.244605	1.356416	3.956853
49	1	0	-4.051828	1.158815	4.656763
50	6	0	-3.073706	2.614956	3.425174
51	1	0	-3.731343	3.431642	3.713603
52	6	0	6.991577	1.279093	-1.188750
53	1	0	8.020705	1.513625	-1.449698
54	6	0	1.823851	5.132013	-0.136565
55	1	0	1.113038	5.937765	0.002667

56	6	0	4.024581	4.435647	-0.844660
57	1	0	4.990680	4.704707	-1.255649
58	6	0	3.074094	5.432938	-0.666493
59	1	0	3.312134	6.458471	-0.935191
60	1	0	6.403209	3.314642	-1.198963
61	1	0	-0.205177	-6.041780	1.971625
62	1	0	3.872477	-5.419205	0.257526
63	6	0	-3.270010	-0.140239	-1.025401
64	6	0	-3.720761	-1.423653	-0.681406
65	6	0	-5.471011	-0.267700	-1.545741
66	6	0	-2.036516	0.378495	-0.757853
67	6	0	-2.988874	-2.395389	-0.056250
68	6	0	-4.350182	0.565195	-1.572799
69	6	0	-5.081786	-1.498297	-1.009015
70	6	0	-3.827318	-3.581262	0.163408
71	1	0	-3.405870	-4.493683	0.562641
72	6	0	-1.945653	1.755967	-1.246112
73	1	0	-1.002413	2.283046	-1.209338
74	6	0	-4.357395	1.889449	-1.921785
75	6	0	-6.756240	0.109104	-1.837421
76	6	0	-5.928309	-2.536653	-0.724932
77	6	0	-5.692021	2.337465	-2.298937
78	1	0	-5.845927	3.367614	-2.612220
79	6	0	-3.030916	2.467140	-1.772224
80	1	0	-2.845534	3.494724	-2.076054
81	6	0	-5.197302	-3.639769	-0.127998
82	1	0	-5.709606	-4.569550	0.109080
83	6	0	-6.818233	1.504333	-2.255528
84	1	0	-7.773831	1.941937	-2.535513
85	6	0	-7.698558	-0.974820	-1.582918
86	1	0	-8.757337	-0.827605	-1.783979
87	6	0	-7.309367	-2.216942	-1.065809
88	1	0	-8.089964	-2.956064	-0.900673

Optimized S0 geometry of **M-1** (at the B3LYP/6-31G(d)/PCM level)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.573832	1.499239	0.274452
2	6	0	0.815734	1.117117	-0.123065
3	6	0	3.434932	2.119159	-0.542140
4	6	0	1.709676	-1.149585	0.155160
5	6	0	1.001478	2.539507	-0.292411
6	6	0	3.266373	0.726985	-0.314158
7	6	0	-1.342279	2.904321	0.312043
8	6	0	-0.103716	3.440525	-0.264522
9	6	0	-2.083835	-1.319830	0.096163
10	6	0	2.868934	-1.974313	0.489250
11	6	0	-4.693557	-2.267198	0.418403
12	6	0	-3.634174	-3.157676	0.081313
13	6	0	1.928959	0.234342	-0.089394
14	6	0	2.728895	-3.219674	1.131163
15	1	0	1.740724	-3.640261	1.282694
16	6	0	0.093180	4.793546	-0.725101
17	6	0	-0.719027	-0.804618	0.069735
18	6	0	-3.143948	-0.426127	0.434411
19	6	0	0.400987	-1.638908	0.187619
20	1	0	0.238899	-2.692033	0.369389
21	6	0	3.870692	4.894722	-0.858773
22	1	0	4.019875	5.964909	-0.979457
23	6	0	-0.498366	0.598955	0.007694
24	6	0	4.931479	4.036579	-0.908482
25	1	0	5.938799	4.412070	-1.071165
26	6	0	1.409086	5.236617	-0.821288
27	1	0	1.602907	6.271066	-1.083601
28	6	0	2.323281	3.014015	-0.510644
29	6	0	-2.825501	0.974689	0.701977
30	6	0	4.380594	-0.160562	-0.352726
31	6	0	4.182550	-1.460777	0.302542
32	6	0	2.535308	4.403144	-0.692237
33	6	0	4.737709	2.623076	-0.782867

34	6	0	-5.620426	-4.196487	-0.413265
35	6	0	-4.541363	-0.892749	0.447010
36	6	0	-2.363234	-2.723782	-0.247069
37	6	0	-2.242518	3.692448	1.040992
38	1	0	-1.997377	4.735626	1.189081
39	6	0	5.772494	1.696739	-1.010743
40	1	0	6.723418	2.103310	-1.339541
41	6	0	-5.915267	-2.910359	0.101015
42	6	0	-3.690220	1.821093	1.418653
43	1	0	-4.573030	1.388630	1.866582
44	6	0	5.613978	0.316076	-0.928770
45	6	0	-4.212099	-4.340913	-0.440052
46	6	0	5.253907	-2.146694	0.912963
47	1	0	6.228059	-1.677839	0.879523
48	6	0	-1.625887	-3.659876	-1.074221
49	1	0	-0.624801	-3.412454	-1.407933
50	6	0	-5.782890	-0.169410	0.244915
51	1	0	-5.778763	0.913893	0.225430
52	6	0	-2.310794	5.083665	-1.720652
53	1	0	-2.114385	4.207346	-2.348840
54	1	0	-2.900817	5.791700	-2.313352
55	1	0	-2.933023	4.762960	-0.887674
56	6	0	5.110612	-3.355077	1.595273
57	6	0	-7.078349	-2.229002	-0.223426
58	6	0	-6.469500	-4.886749	-1.263000
59	6	0	-3.566942	-5.177268	-1.338058
60	6	0	-0.991211	5.769695	-1.296190
61	6	0	3.815372	-3.902637	1.653224
62	1	0	3.637415	-4.845385	2.157395
63	6	0	-8.065818	-3.020015	-0.927439
64	1	0	-9.033407	-2.581243	-1.159627
65	6	0	-6.984604	-0.801106	-0.058372
66	1	0	-7.848778	-0.177966	-0.276847
67	6	0	-3.393665	3.167361	1.647116
68	6	0	-2.190630	-4.826748	-1.579355

69	1	0	-1.594848	-5.430285	-2.260194
70	6	0	6.718024	-0.536052	-1.640996
71	6	0	-0.443770	6.392945	-2.615671
72	1	0	0.423556	7.039977	-2.463376
73	1	0	-1.225206	7.010027	-3.072957
74	1	0	-0.163931	5.613439	-3.332815
75	6	0	-1.276714	6.937893	-0.323523
76	1	0	-1.723480	6.604852	0.618093
77	1	0	-1.971127	7.650996	-0.784570
78	1	0	-0.355710	7.478256	-0.077468
79	6	0	-7.777509	-4.285961	-1.419442
80	1	0	-8.530579	-4.793809	-2.017554
81	6	0	-5.825119	-5.925313	-2.039290
82	1	0	-6.426856	-6.560404	-2.685348
83	6	0	6.284095	-1.976055	-1.999414
84	1	0	6.206095	-2.643562	-1.143741
85	1	0	7.024812	-2.406919	-2.682622
86	1	0	5.316650	-1.977469	-2.514291
87	6	0	-4.277478	4.069801	2.530451
88	6	0	-4.443826	-6.061181	-2.077313
89	1	0	-4.012910	-6.796099	-2.753234
90	6	0	6.325428	-4.021904	2.270404
91	6	0	8.041429	-0.551113	-0.841094
92	1	0	8.402850	0.466819	-0.656984
93	1	0	8.816136	-1.083803	-1.405850
94	1	0	7.943373	-1.044617	0.130571
95	6	0	7.017963	0.127397	-3.019089
96	1	0	6.107268	0.206232	-3.623010
97	1	0	7.737125	-0.490778	-3.568423
98	1	0	7.452924	1.126066	-2.932341
99	6	0	5.935497	-5.301403	3.036134
100	1	0	5.207138	-5.096376	3.828893
101	1	0	6.826399	-5.730956	3.507547
102	1	0	5.514219	-6.064624	2.372029
103	6	0	7.372737	-4.407294	1.199009

104	1	0	6.949152	-5.107911	0.469953
105	1	0	8.238415	-4.890034	1.668962
106	1	0	7.738055	-3.532875	0.650720
107	6	0	6.962855	-3.038023	3.280033
108	1	0	7.309348	-2.118816	2.796411
109	1	0	7.828361	-3.503579	3.766963
110	1	0	6.244957	-2.757091	4.058996
111	6	0	-5.438464	3.295084	3.183929
112	1	0	-6.121061	2.870465	2.439170
113	1	0	-6.022599	3.975729	3.813164
114	1	0	-5.077090	2.480804	3.822158
115	6	0	-3.420667	4.685547	3.662629
116	1	0	-2.980310	3.902990	4.290894
117	1	0	-4.042629	5.324600	4.301067
118	1	0	-2.603844	5.301725	3.272959
119	6	0	-4.882757	5.205076	1.671011
120	1	0	-4.108701	5.826027	1.208100
121	1	0	-5.506948	5.859574	2.291586
122	1	0	-5.510431	4.797594	0.869883

Optimized S0 geometry of **P-2** (at the B3LYP/6-31G(d)/PCM level)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.323284	3.578516	-0.556256
2	6	0	-1.846927	-0.540147	0.398853
3	6	0	1.539778	1.958885	0.169008
4	6	0	-1.013095	3.064357	-0.362427
5	6	0	-0.561381	-1.077658	0.681114
6	6	0	-3.349043	1.362241	-0.114235
7	6	0	0.583345	-0.306627	0.314727
8	6	0	-0.881502	1.660790	-0.053971
9	6	0	1.371414	3.369349	0.079357
10	6	0	0.129595	3.907639	-0.488565
11	6	0	-2.483251	4.944017	-0.899487

12	6	0	4.422790	-0.486794	0.100654
13	6	0	0.409357	1.084504	0.077087
14	6	0	-0.527741	-2.395993	1.327294
15	6	0	2.118268	-2.233269	-0.342529
16	6	0	2.801237	1.425474	0.550046
17	6	0	-3.802504	5.484911	-1.035486
18	1	0	-3.910231	6.533805	-1.300570
19	6	0	3.867879	-3.860660	-0.931038
20	6	0	3.411181	-2.707995	-0.246792
21	6	0	-1.330880	5.695115	-1.193195
22	1	0	-1.494005	6.696874	-1.574647
23	6	0	1.352170	-1.852136	2.925330
24	1	0	1.259247	-0.797470	2.700383
25	6	0	3.050952	0.008436	0.301169
26	6	0	1.928021	-0.854368	0.127362
27	6	0	4.533632	-1.861747	-0.018585
28	6	0	3.511265	3.659033	1.265144
29	6	0	5.268131	-3.747138	-1.106586
30	6	0	3.068990	-4.612918	-1.778560
31	6	0	2.346726	4.177917	0.679637
32	1	0	2.154982	5.240868	0.738463
33	6	0	1.068909	6.062542	-1.811416
34	6	0	-3.474030	2.751171	-0.387231
35	6	0	-2.980932	-1.414953	0.295458
36	6	0	0.480465	-2.780388	2.294080
37	6	0	5.675969	-2.506338	-0.556960
38	6	0	-2.019388	0.825567	0.045806
39	6	0	-0.030845	5.206036	-1.095844
40	6	0	0.554599	-4.144959	2.720715
41	6	0	-2.780734	-2.821912	0.369890
42	6	0	-1.572285	-3.297704	1.044208
43	6	0	-1.475265	-4.647307	1.496177
44	1	0	-2.263362	-5.350165	1.250235
45	6	0	2.292050	-2.259796	3.849727
46	1	0	2.934685	-1.521530	4.321586

47	6	0	-4.259669	-0.905534	-0.053828
48	6	0	1.682249	-4.217282	-1.783267
49	1	0	0.973275	-4.757053	-2.406821
50	6	0	1.235464	-3.085009	-1.112126
51	1	0	0.200754	-2.795301	-1.251082
52	6	0	-4.903384	4.701500	-0.841166
53	1	0	-5.902678	5.120381	-0.930911
54	6	0	6.796446	-1.827872	-1.011551
55	6	0	-4.504043	0.538156	0.028413
56	6	0	5.641798	0.222986	-0.240057
57	1	0	5.666245	1.304954	-0.197342
58	6	0	-5.790259	1.171358	0.185508
59	6	0	-0.421606	-5.070635	2.257239
60	1	0	-0.356886	-6.107188	2.578604
61	6	0	-4.768444	3.315578	-0.505691
62	6	0	5.958856	-4.392026	-2.120181
63	6	0	3.744742	2.286559	1.134617
64	1	0	4.645927	1.854723	1.546951
65	6	0	2.417088	-3.622911	4.197071
66	1	0	3.171572	-3.935688	4.913529
67	6	0	0.490612	6.585317	-3.160756
68	1	0	0.132335	5.758181	-3.783416
69	1	0	1.281107	7.106750	-3.711594
70	1	0	-0.330253	7.295821	-3.035644
71	6	0	1.551502	-4.543199	3.648263
72	1	0	1.600825	-5.590247	3.937574
73	6	0	5.173125	-5.355206	-2.861503
74	1	0	5.651172	-5.953480	-3.633814
75	6	0	2.330310	5.266931	-2.221815
76	1	0	2.974176	4.993694	-1.388233
77	1	0	2.927288	5.880838	-2.905745
78	1	0	2.058996	4.346786	-2.751707
79	6	0	3.797323	-5.456949	-2.701550
80	1	0	3.247866	-6.129581	-3.356246
81	6	0	6.769491	-0.411925	-0.749088

82	1	0	7.610874	0.206356	-1.053613
83	6	0	-5.875968	2.512408	-0.179096
84	1	0	-6.839806	3.009076	-0.152773
85	6	0	1.458752	7.302827	-0.973131
86	1	0	0.579844	7.918477	-0.751016
87	1	0	2.171480	7.923935	-1.529389
88	1	0	1.924753	7.040294	-0.018688
89	6	0	-3.772061	-3.670942	-0.130689
90	1	0	-3.597487	-4.740558	-0.132567
91	6	0	7.644339	-2.587901	-1.906103
92	1	0	8.579431	-2.153103	-2.251641
93	6	0	-5.195598	-1.802298	-0.601305
94	1	0	-6.109270	-1.390019	-1.004170
95	6	0	7.247382	-3.809893	-2.431499
96	1	0	7.886744	-4.290235	-3.168655
97	6	0	4.482378	4.598056	2.007473
98	6	0	-4.963033	-3.178143	-0.684540
99	6	0	-7.064410	0.581389	0.880935
100	6	0	-8.181688	0.284836	-0.146609
101	1	0	-8.439125	1.183114	-0.719215
102	1	0	-9.088333	-0.054761	0.369242
103	1	0	-7.898112	-0.491699	-0.862959
104	6	0	-6.802030	-0.661079	1.763834
105	1	0	-6.614716	-1.573260	1.200784
106	1	0	-7.684399	-0.840298	2.388420
107	1	0	-5.949137	-0.497929	2.432174
108	6	0	-7.617451	1.646953	1.874676
109	1	0	-6.852018	1.941854	2.600775
110	1	0	-8.461885	1.219457	2.426548
111	1	0	-7.983819	2.550953	1.382242
112	6	0	-5.955614	-4.157986	-1.339500
113	6	0	5.657829	3.836360	2.649758
114	1	0	5.312919	3.089989	3.374322
115	1	0	6.303156	4.542855	3.183529
116	1	0	6.277007	3.327844	1.902094

117	6	0	3.723007	5.340213	3.133390
118	1	0	2.896151	5.942934	2.743729
119	1	0	4.403781	6.014862	3.666257
120	1	0	3.308313	4.632176	3.859960
121	6	0	5.064348	5.632589	1.015213
122	1	0	5.617946	5.135895	0.209879
123	1	0	5.754350	6.309384	1.533597
124	1	0	4.281042	6.244715	0.556299
125	6	0	-7.177972	-3.443634	-1.946523
126	1	0	-6.886437	-2.714969	-2.711631
127	1	0	-7.770600	-2.925167	-1.184777
128	1	0	-7.832627	-4.180542	-2.424944
129	6	0	-6.462330	-5.165461	-0.279370
130	1	0	-5.641842	-5.738243	0.165444
131	1	0	-7.157361	-5.879716	-0.737330
132	1	0	-6.990311	-4.650127	0.531365
133	6	0	-5.241223	-4.929030	-2.475809
134	1	0	-4.874464	-4.241238	-3.246368
135	1	0	-5.936110	-5.632411	-2.950228
136	1	0	-4.386326	-5.504642	-2.106127

Optimized S0 geometry of **M-2** (at the B3LYP/6-31G(d)/PCM level)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.334129	3.562129	-0.554942
2	6	0	1.839802	-0.555063	0.400063
3	6	0	-1.535893	1.959274	0.169821
4	6	0	1.022003	3.053279	-0.361345
5	6	0	0.551604	-1.086778	0.681078
6	6	0	3.351867	1.341992	-0.110229
7	6	0	-0.589907	-0.309928	0.314871
8	6	0	0.884897	1.650276	-0.052166
9	6	0	-1.361318	3.368831	0.080262
10	6	0	-0.117153	3.901189	-0.488342

11	6	0	2.499410	4.926864	-0.899040
12	6	0	-4.430057	-0.473246	0.101265
13	6	0	-0.409216	1.079870	0.078368
14	6	0	0.510991	-2.405144	1.324427
15	6	0	-2.133139	-2.229235	-0.344805
16	6	0	-2.799730	1.431562	0.550677
17	6	0	3.820705	5.463216	-1.033733
18	1	0	3.932364	6.511484	-1.299653
19	6	0	-3.890084	-3.848536	-0.933582
20	6	0	-3.428012	-2.698362	-0.248805
21	6	0	1.350328	5.682150	-1.194139
22	1	0	1.517522	6.683063	-1.576063
23	6	0	-1.367747	-1.856946	2.922306
24	1	0	-1.269019	-0.802019	2.700945
25	6	0	-3.055929	0.015964	0.301209
26	6	0	-1.936713	-0.851594	0.126405
27	6	0	-4.546741	-1.847597	-0.019025
28	6	0	-3.499504	3.668168	1.266430
29	6	0	-5.289971	-3.729047	-1.107885
30	6	0	-3.095003	-4.603692	-1.782072
31	6	0	-2.332605	4.181856	0.680672
32	1	0	-2.136173	5.243969	0.739190
33	6	0	-1.048059	6.058571	-1.812778
34	6	0	3.481575	2.730553	-0.383739
35	6	0	2.969979	-1.435006	0.299599
36	6	0	-0.500468	-2.787652	2.288781
37	6	0	-5.692184	-2.487001	-0.556956
38	6	0	2.018984	0.810335	0.048050
39	6	0	0.048329	5.198199	-1.096730
40	6	0	-0.582040	-4.153077	2.710764
41	6	0	2.763970	-2.838540	0.371613
42	6	0	1.552356	-3.310918	1.040138
43	6	0	1.446955	-4.662066	1.487033
44	1	0	2.231607	-5.368353	1.240130
45	6	0	-2.310733	-2.262752	3.844460

46	1	0	-2.949938	-1.522693	4.318165
47	6	0	4.254620	-0.929530	-0.045212
48	6	0	-1.706560	-4.214026	-1.787304
49	1	0	-1.000259	-4.756487	-2.411552
50	6	0	-1.254482	-3.084193	-1.115577
51	1	0	-0.218523	-2.799006	-1.254670
52	6	0	4.918341	4.676302	-0.836532
53	1	0	5.919325	5.091447	-0.924681
54	6	0	-6.810269	-1.803555	-1.009959
55	6	0	4.504146	0.514861	0.036600
56	6	0	-5.646411	0.241856	-0.237797
57	1	0	-5.666397	1.323876	-0.194115
58	6	0	5.792136	1.144739	0.195116
59	6	0	0.390073	-5.082263	2.245048
60	1	0	0.319460	-6.119569	2.562748
61	6	0	4.777827	3.291116	-0.499883
62	6	0	-5.984267	-4.370404	-2.121276
63	6	0	-3.739269	2.296945	1.135648
64	1	0	-4.642243	1.869052	1.548136
65	6	0	-2.443104	-3.626259	4.187195
66	1	0	-3.199785	-3.937521	4.901992
67	6	0	-0.467871	6.577732	-3.162670
68	1	0	-0.113062	5.748588	-3.784645
69	1	0	-1.256339	7.101875	-3.713858
70	1	0	0.355903	7.284996	-3.038301
71	6	0	-1.581687	-4.549220	3.636099
72	1	0	-1.636647	-5.596934	3.921969
73	6	0	-5.203148	-5.336418	-2.863787
74	1	0	-5.684297	-5.932318	-3.636008
75	6	0	-2.312883	5.267976	-2.222216
76	1	0	-2.957717	4.998138	-1.388273
77	1	0	-2.907375	5.883862	-2.906541
78	1	0	-2.045570	4.346257	-2.751416
79	6	0	-3.827648	-5.444071	-2.704979
80	1	0	-3.281611	-6.118732	-3.360445

81	6	0	-6.777198	-0.387962	-0.746337
82	1	0	-7.616315	0.234063	-1.049491
83	6	0	5.882066	2.485419	-0.169902
84	1	0	6.846770	2.979796	-0.141639
85	6	0	-1.432550	7.301169	-0.975458
86	1	0	-0.551021	7.913271	-0.753923
87	1	0	-2.142714	7.924846	-1.532119
88	1	0	-1.899540	7.041304	-0.020763
89	6	0	3.752437	-3.697590	-0.130487
90	1	0	3.563061	-4.762453	-0.138250
91	6	0	-7.662081	-2.559432	-1.904326
92	1	0	-8.595700	-2.120553	-2.248673
93	6	0	5.185352	-1.831617	-0.580889
94	1	0	6.109332	-1.430224	-0.974885
95	6	0	-7.270655	-3.782673	-2.430982
96	1	0	-7.912731	-4.259824	-3.167850
97	6	0	4.946159	-3.210705	-0.671538
98	6	0	7.063558	0.549666	0.891394
99	6	0	8.168047	0.206486	-0.136089
100	1	0	8.430704	1.084262	-0.737442
101	1	0	9.074805	-0.127737	0.382963
102	1	0	7.872769	-0.587632	-0.827962
103	6	0	6.777584	-0.661612	1.809318
104	1	0	6.531704	-1.576506	1.274651
105	1	0	7.670113	-0.865921	2.411337
106	1	0	5.953813	-0.444148	2.498708
107	6	0	7.652787	1.626810	1.851208
108	1	0	6.897841	1.976388	2.563750
109	1	0	8.478657	1.186094	2.420377
110	1	0	8.056742	2.497791	1.329227
111	6	0	5.985425	-4.130468	-1.342391
112	6	0	7.315563	-4.081208	-0.553854
113	1	0	8.061862	-4.729466	-1.028846
114	1	0	7.731932	-3.069464	-0.515133
115	1	0	7.173967	-4.426287	0.476977

116	6	0	5.519545	-5.598299	-1.399052
117	1	0	5.371955	-6.020877	-0.398708
118	1	0	4.584693	-5.708110	-1.960383
119	1	0	6.281353	-6.204309	-1.901886
120	6	0	6.232411	-3.651794	-2.793288
121	1	0	5.306884	-3.684404	-3.379368
122	1	0	6.615792	-2.626749	-2.827996
123	1	0	6.969188	-4.298981	-3.284274
124	6	0	-4.466207	4.611547	2.008969
125	6	0	-5.644310	3.855034	2.652513
126	1	0	-6.266191	3.348690	1.905627
127	1	0	-5.301873	3.107614	3.377200
128	1	0	-6.286300	4.564444	3.186434
129	6	0	-3.703050	5.351198	3.134000
130	1	0	-3.290395	4.641872	3.860461
131	1	0	-2.874323	5.950719	2.743393
132	1	0	-4.380820	6.028600	3.667204
133	6	0	-5.044494	5.647921	1.016506
134	1	0	-5.731104	6.328130	1.534919
135	1	0	-4.258866	6.256245	0.556494
136	1	0	-5.600925	5.153082	0.211960

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9 Reference

(S1) Xu, Q.; Wang, C.; Zhao, Y.; Zheng, D.; Shao, C.; Guo, W.; Deng, X.; Wang, Y.; Chen, X.; Zhu, J.; Jiang, H. Tuning the Properties of Corannulene-Based Polycyclic Aromatic Hydrocarbons by Varying the Fusing Positions of Corannulene. *Org. Lett.* **2020**, 22, 7397-7402.

(S2) Mack, J.; Vogel, P.; Jones, D.; Kaval, N.; Sutton, A. The development of corannulene-based blue emitters. *Org. Biomol. Chem.* **2007**, 5, 2448-2452.

(S3) Zhao, H.-J.; Zhou, Z.-Z.; Zhang, Y.; Su, X.; Chen, X.-M.; Liang, Y.-M. Visible-light-mediated borylation of aryl and alkyl halides with a palladium complex. *Org. Biomol. Chem.* **2020**, 18, 4390-4394.

(S4) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J; Howard, J. A. K.; Puschmann, H. J. *Appl. Cryst.* **2009**, 42, 339-341.

(S5) Sheldrick, G. M. *Acta Cryst.* **2015**, A71, 3-8.

(S6) Sheldrick, G. M. *Acta Cryst.* **2015**, C71, 3-8.

(S7) Spek, A. L. *Acta Cryst.* **2015**, C71, 9-18.

(S8) Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, M. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision D.01; Gaussian, Inc.: Wallingford, CT, 2013.

(S9) (a) Herges, R.; Geuenich, D. *J. Phy. Chem. A.* **2001**, 105, 3214-3220. (b) Geuenich, D.; Hess, K.; Kohler, F.; Herges, R. *Chem. Rev.* **2005**, 105, 3758-3772.

(S10) (a) Steiner, E.; Fowler, P. W.; Jenneskens, L. W. *Angew. Chem. Int. Ed.* **2001**, 40, 362-366. (b) Morita, Y.; Ueda, A.; Nishida, S.; Fukui, K.; Ise, T.; Shiomi, D.; Sato, K.; Takui, T.; Nakasuji, K. *Angew. Chem. Int. Ed.* **2008**, 47, 2035-2038. (c) Spisak, S. N.; Li, J.; Rogachev, A. Y.; Wei, Z.; Papaianina, O.; Amsharov, K.; Rybalchenko, A. V.; Goryunkov, A. A.; Petrukhina, M. A. *Organometallics.* **2016**, 35, 3105-3111. (d) Dickens, T. K.; Mallion, R. B. *J. Phy. Chem. A.* **2018**, 122, 7666-7678.