Supporting Information

Contorted Polycyclic Aromatic Hydrocarbons with Cove regions and Zig-Zag Edges

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1. Materials and Methods.

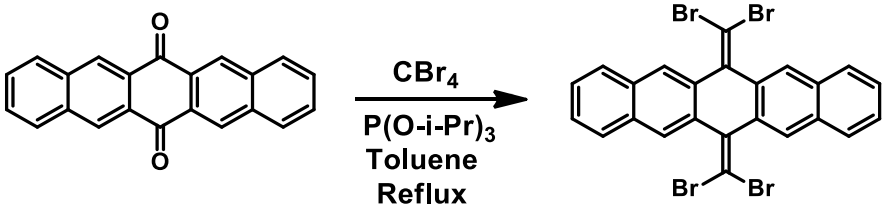
Unless otherwise stated, all starting materials and reagents were purchased from Aldrich or Acros and used without further purification. Pentacene-6,13-dione,[S1] 4, 4, 5, 5-tetramethyl-2-pyren-2-yl-[1, 3, 2] dioxaborolane **2a**,[S2] 2-(7-*tert*-butylpyren-2-yl)-4, 4, 5, 5-tetramethyl-[1, 3, 2] dioxaborolane **2b**,[S2] and 2-hydroxypyrene[S2] were prepared according to literature procedures. Dichloromethane (CH_2Cl_2) was distilled under Ar over CaH_2 prior to use. All reactions were performed under argon atmosphere unless otherwise specified, and monitored by TLC using silica gel 60 F254 pre-coated aluminum plates. All glassware was oven dried before use. The DFT calculations were carried out with Gaussian 09, B3LYP hybrid functions and 6-31g and 6-31g(d) basis sets. The predicted optical transitions were calculated by time dependent DFT TD-scf single energy calculations with number of states n=10.[S3] The optical spectra were calculated with TDDFT for the optimized structures.

2. Characterization.

^{1}H NMR and ^{13}C NMR spectra were recorded in deuterated solvents on a Bruker AVANCE 250, Bruker AVANCE III 500 and Bruker AVANCE III 700. The 2D and temperature-dependent ^{1}H-NMR experiments were acquired with a 5 mm BBFO z-gradient probe on the 500 MHz Bruker AVANCE III system (TOPSPIN 3.1 software version). The spectra were obtained with π/2-pulse lengths of 10 μs (^{1}H) and mostly 32 number of scans were required for sufficient signal to noise ratio. The used temperature between 298 K and 423 K was approved with a standard ^{1}H ethylenglycol NMR sample. The assignment was accomplished by ^{1}H-^{1}H 2D-NOESY and -COSY. The spectroscopic widths of the homo-nuclear NOESY (COSY) experiments were typically 13600 Hz in both dimension (f1 and f2) and the relaxation delay 2s. The mixing time used in the 2D NOESY was kept at 250 ms. The 2D ^{1}H,^{13}C-HSQC experiments was recorded with 2048 points in f2 and 256 points in f1 dimension. MALDI-TOF mass spectra were recorded on a Bruker Reflex II-TOF Spectrometer using a 337 nm nitrogen laser with TCNQ as matrix. ESI-HRMS spectra were recorded on a Bruker maXis ESI-Q-TOF spectrometer. Elemental analysis was performed with Exeter Analytical, Inc. CE–440F. UV-vis absorption spectra were obtained on a Perkin-Elmer Lambda 9 spectrophotometer. PL measurements were performed on a SPEX-Fluorolog II (F212) steady-state fluorometer at room temperature. CV measurements were carried out on a computer-controlled GSTAT12 in a three-electrode cell in a dichloromethane solution of Bu_4NPF_6 (0.1 M) with a scan rate of 50 mV/s at room temperature. A Pt wire, a silver wire, and a glassy carbon electrode were used as the counter electrode, the reference electrode, and the working electrode, respectively. Thermogravimetric analysis (TGA) was carried out with Rigaku DSC8230L under nitrogen atmosphere. Differential scanning calorimetry (DSC) measurements were carried out on a Mettler DSC 30 instrument, under a nitrogen atmosphere at a heating rate of 10 ºC/min. GIWAXS experiments were performed by means of a solid anode X-ray tube (Siemens Kristalloflex X-ray source, copper anode X-ray tube operated at 30 kV and 20 mA). Osmicconfocal MaxFlux optics, X-ray beam with pinhole collimation and a MAR345 image plate detector. Thin films were deposited by drop-casting 2 mg / mL 1,2 dichlorobenzene solution on silicon dioxide substrate. All

GIWAXS studies were performed at 30 ºC. Data analysis was performed using the Datasqueeze software. The hexagonal lattice parameters for **TPCa** were extracted from fitting the diffraction peaks. Figure S12 shows the in-plane integration of the GIWAXS pattern for **TPCa** with reflections assigned by Miller indices hk0 to fit the intercolumnar hexagonal unit cell with 1.75 nm. The organization in the stacks is derived from the distribution of the two out-of-plane reflections assigned to the π-stacking distance of 0.35 nm and the helical pitch length of 1.05 nm. From this data, it is concluded that one complete helix turn consists of four **TPCa** molecules which are rotated by 60° towards each other.

3. Synthetic Procedures.



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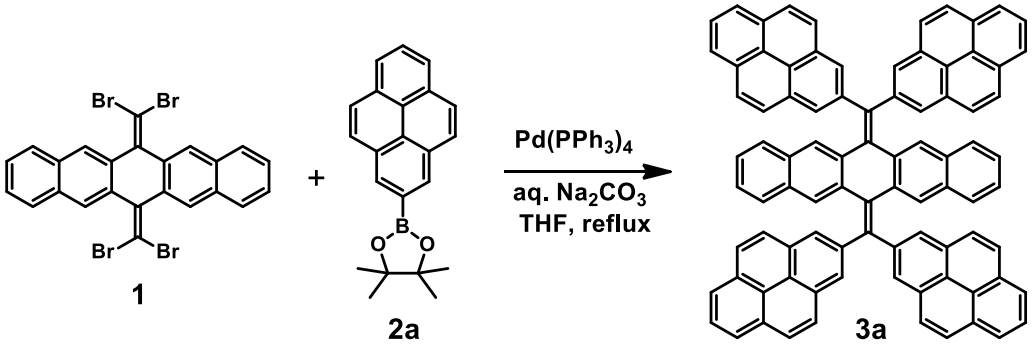
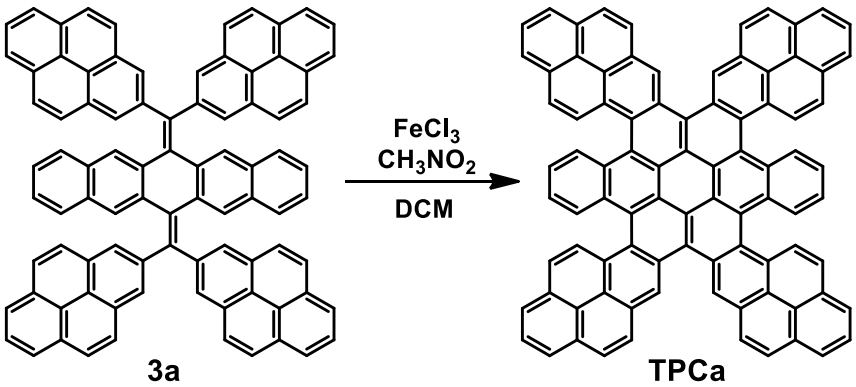
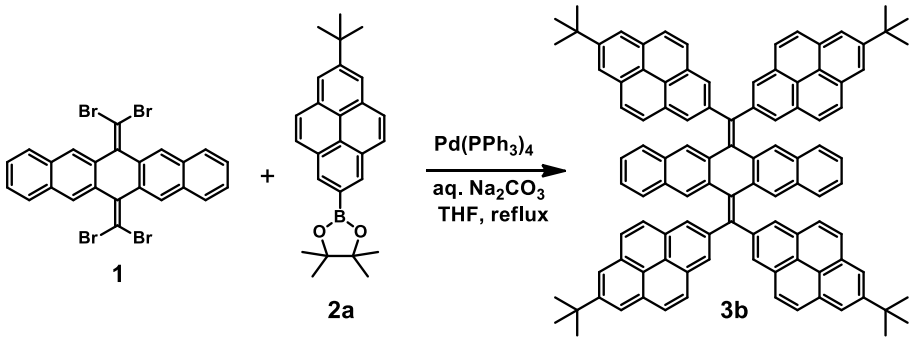
6,13-Bis(dibromomethylene)-6,13-dihydropentacene (1). An oven-dried 500 mL two-necked round bottom flask with a condenser were charged with tetrabromomethane (13.89 g, 41.88 mmol), pentacene-6,13-dione (2.152 g, 6.98 mmol), and 300 mL of anhydrous toluene. The mixture was stirred at 0 ºC for 5 minutes before adding triisopropyl phosphite (12.6 mL) dropwise. The reaction mixture was refluxed under Ar overnight. After cooling down, the reaction mixture was evaporated, and the residue was purified by silica gel chromatography (hexane/dichoromethane = 1/1 as eluent), affording compound **1** as an off-white solid (3.9 g, 90%). ^{1}H NMR (250 MHz, CD_2Cl_2, 298 K, ppm): δ 8.25 (s, 4H), 7.87 (m, 4H), 7.54 (m, 4H); ^{13}C NMR (62.5 MHz, CD_2Cl_2, 298 K, ppm): δ 140.03, 133.56, 132.14, 128.43, 128.15, 127.61, 127.51, 90.88. FD-MS (8 KV): m/z 618.8, calcd.: 619.97.



6,13-Dihydro-6,13-bis(di(pyren-2-yl)methylene)pentacene (3a). A mixture of **1** (1.064 g, 1.72 mmol), **2a** (2.632 g, 8.02 mmol), Na_2CO_3 (1.46 g, 13.77 mmol), THF (80 mL), and H_2O (30 mL) was carefully degassed before and after $Pd(PPh_3)_4$ (400 mg) was added. The mixture was heated to reflux and stirred under Ar for 24 h. The reaction mixture was extracted with CH_2Cl_2 (2 × 100 mL), and the combined organic layers were dried over anhydrous Na_2SO_4. After the removal of solvent, the residue was purified by silica gel chromatography (hexane/dichoromethane = 2/1 as eluent) to give compound **3a** as a light yellow solid (1.73 g, 91.2%). ^{1}H NMR (250 MHz, CD_2Cl_2, 298 K, ppm): δ 8.68 (s, 8H), 8.21-8.09 (m, 24H), 8.03-7.97 (m, 4H), 7.84 (s, 4H), 7.16 (m, 4H), 6.95 (m, 4H); ^{13}C NMR (62.5 MHz, CD_2Cl_2, 298 K, ppm): δ 140.77, 136.90, 131.75, 131.54, 131.52, 128.12, 127.77, 127.71, 127.44, 127.40, 126.38, 125.96, 125.54, 124.81, 123.88. MALDI-TOF-MS (TCNQ as matrix): m/z 1105.32, cacld.: 1105.09. Anal. Calcd for $C_{88}H_{48}$: C, 95.62; H, 4.38. Found: C, 95.17; H, 4.00.

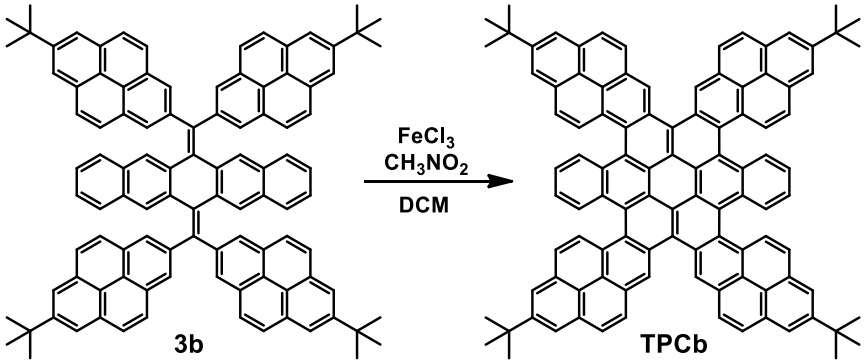


TPCa. Compound **3a** (100 mg, 0.09 mmol) was dissovled in anhydrous CH_2Cl_2 (150 mL) and bubbled with argon for 20 minutes. Then a solution of $FeCl_3$ (147 mg, 0.91 mmol) in CH_3NO_2 (2.0 mL) was added dropwise. The reaction mixture was further stirred at room temperature with argon bubbling for 40 min. Methanol (10 mL) was added to terminate the reaction. The reaction mixture was added with H_2O (100 mL) and extracted with $CHCl_3$ (2 x 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4. After the removal of most of solvent, the residue was precipitated into methanol, and the resulted precipitate was collected by filtration and dried under vacuum to give compound **TPCa** as a dark red solid (83 mg, 83.6 %). ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 413 K, ppm): δ 9.98 (s, 2H), 9.90 (s, 2H), 9.61 (d, 2H), 9.33 (dd, 4H), 8.78 (br, 2H), 8.42-8.05 (m, 24H), 7.68 (br, 2H), 7.46 (br, 2H); MALDI-TOF-MS (TCNQ as matrix): m/z 1096.32, calcd.: 1097.26. Anal. Calcd for $C_{88}H_{40}$: C, 96.33; H, 3.67. Found: C, 96.05; H, 3.68.

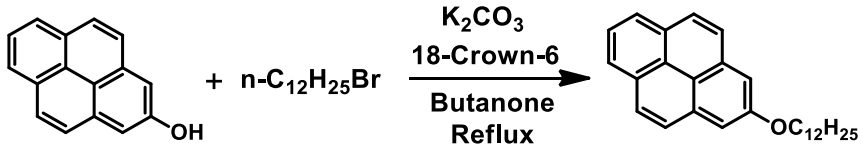


6,13-Bis(bis(2-tert-butylpyren-7-yl)methylene)-6,13-dihydropentacene (3b). Compound **3b** was synthesized using identical condition with that of **3a**. Compound **1** (0.62 g, 1.0 mmol), **2b** (1.73 g, 4.5 mmol), Na_2CO_3 (0.85 g, 8.0 mmol), THF (40 mL), H_2O (15 mL) and $Pd(PPh_3)_4$ (230 mg) were used. The crude product was purified by silica gel chromatography (hexane/dichoromethane = 2/1 as eluent) to afford **3b** as a light yellow solid (1.24 g, 93%). ^{1}H NMR (250 MHz, CD_2Cl_2, 298 K, ppm): δ 8.65 (s, 8H), 8.27-8.24 (m, 8H), 8.14-8.08 (m, 16H), 7.84 (s, 4H), 7.14 (m, 4H), 6.94 (m, 4H), 1.57 (s, 36H); ^{13}C NMR (62.5 MHz, CD_2Cl_2, 298 K, ppm): δ 149.67, 142.28, 140.48, 137.58, 136.96, 131.74, 131.36, 131.33, 128.28, 127.67, 127.39, 127.25, 125.90, 123.80, 123.03,

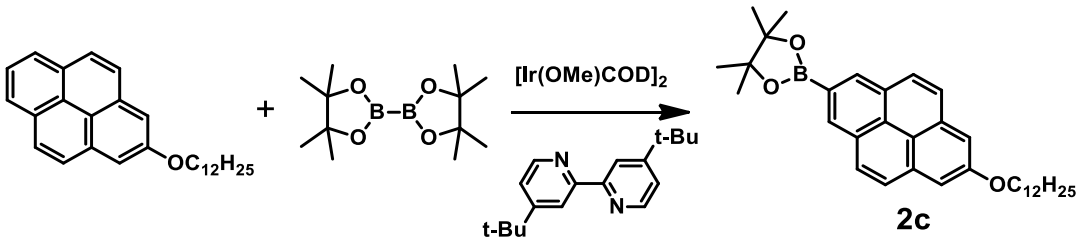
122.88, 35.55, 32.03. MALDI-TOF-MS (TCNQ as matrix): m/z 1329.75, calcd.: 1330.02. Anal. Calcd for $C_{104}H_{80}$: C, 93.94; H, 6.06. Found: C, 93.50; H, 6.09.



TPCb. Compound **TPCb** was synthesized using identical condition with that of **TPCa**. **3b** (40 mg, 0.03 mmol), $FeCl_3$ (49 mg, 0.30mmol), CH_3NO_2 (2.0 mL) and CH_2Cl_2 (100 mL) were used. The crude product was purified by silica gel chromatography and gel permeation chromatography (Bio-Beads S-X1 gel) (dichoromethane as eluent), followed with precipitation into MeOH to afford **TPCb** as a dark red solid (30 mg, 75%). ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 393 K, ppm): δ 10.00 (s, 2H), 9.90 (s, 2H), 9.58 (d, 2H), 9.34 (dd, 4H), 8.80 (br, 2H), 8.44-8.33 (m, 14H), 8.21 (dd, 4H), 8.07 (br, 2H), 7.68 (m, 2H), 7.45 (m, 2H), 1.79-1.74 (d, 36H); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 373 K, ppm): δ 149.87, 149.78, 139.24, 136.17, 132.92, 132.06, 131.99, 131.48, 131.22, 131.08, 130.93, 130.87, 129.75, 129.18, 128.78, 128.35, 128.32, 128.23, 127.85, 127.59, 127.26, 127.22, 127.15, 126.99, 126.95, 126.86, 126.22, 125.58, 124.49, 124.07, 123.67, 123.01, 122.75, 121.75, 35.20, 31.93, 31.90. MALDI-TOF-MS (TCNQ as matrix): m/z 1322.01, calcd.: 1321.68. Anal. Calcd for $C_{104}H_{72}$: C, 94.51; H, 5.49. Found: C, 94.32; H, 5.51.



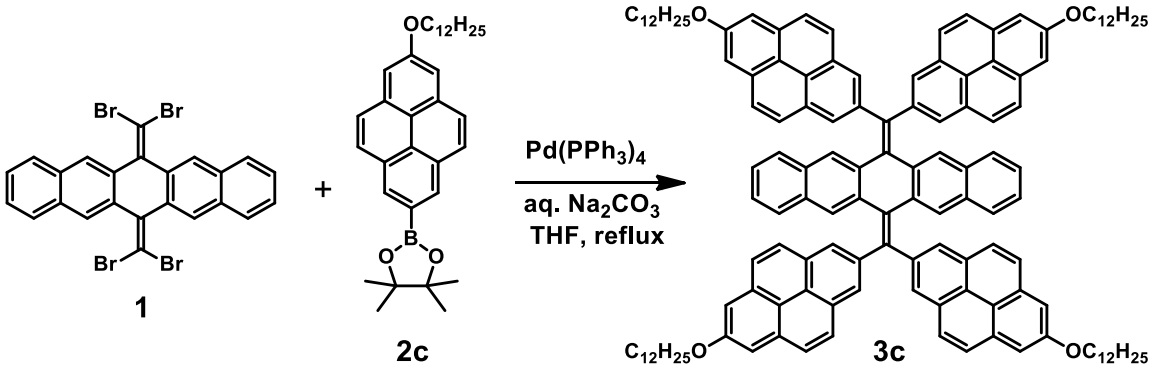
2-(Dodecyloxy)pyrene. A mixture of pyren-2-ol (1.1 g, 5.0 mmol), 1-bromododecane (1.38 g, 5.5 mmol), 18-crown-6 (0.5 g, 0.46 mmol), K_2CO_3 (1.4 g, 10 mmol) and butanone (150 mL) was stirred and heated to reflux under Ar overnight; H_2O (100 mL) were added; the mixture was extracted with ethyl acetate (2 x 50 mL). The combined organic layer was dried over anhydrous Na_2SO_4. After the removal of the solvent, the residue was purified by silica gel chromatography (hexane/dichoromethane = 3/1 as eluent) to afford 2-(dodecyloxy)pyrene as a colorless solid (1.7 g, 87.2%). ^{1}H NMR (250 MHz, CD_2Cl_2, 298 K, ppm): δ 8.16 (d, 2H), 8.08-7.90 (m, 5H), 7.72 (s, 2H), 4.26 (t, 2H), 1.93 (m, 2H), 1.60-1.26 (m, 18H), 0.88 (t, 3H); ^{13}C NMR (62.5 MHz, CD_2Cl_2, 298 K, ppm): δ 157.95, 132.99, 130.52, 128.28, 127.18, 125.55, 125.27, 124.94, 120.17, 111.31, 68.97, 32.34, 30.10, 30.07, 30.05, 29.87, 29.84, 29.78, 26.54, 23.11, 14.30. ESI-HRMS: m/z, 387.2702, cacld.: 386.57. Anal. Calcd for $C_{28}H_{34}O$: C, 87.00; H, 8.87. Found: C, 86.68; H, 9.02.



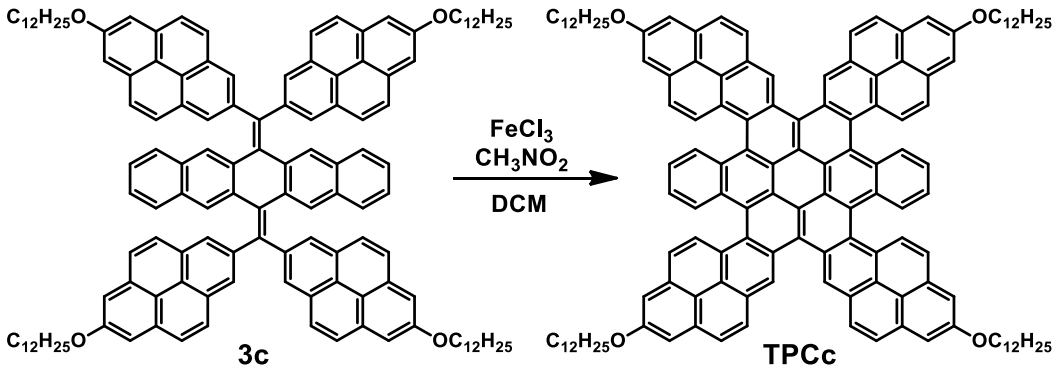
2c

2-(2-(Dodecyloxy)pyren-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2c). A mixture of [{Ir(μ-OMe)cod}$_2$] (22 mg, 0.033 mmol), dtbpy (18 mg, 0.067 mmol), B_2pin_2 (33 mg, 0.13 mmol), and hexane (15 mL) was carefully degassed before and after 2-(dodecyloxy)pyrene (1.0 g, 2.59 mmol) and B_2pin_2 (0.83 g, 3.27 mmol) were added. The mixture was stirred at 80 ºC under Ar for 16 h. The solvent was then removed under reduced pressure. Purification of the residue by silica gel chromatography (hexane/ethyl acetate = 4/1 as eluent) and subsequent recrystallization from hexane afforded **2c** (0.44 g, 33.2%) as a colorless solid. ^{1}H NMR (250 MHz, CD_2Cl_2, 298 K, ppm): δ 8.55 (s, 2H), 8.08 (d, 2H), 7.98 (d, 2H), 7.71 (s, 2H), 4.26 (t, 2H), 1.92 (m, 2H), 1.43 (s, 12H), 1.37-1.28 (m, 18H), 0.88 (t, 3H); ^{13}C NMR (62.5 MHz, CD_2Cl_2, 298 K, ppm): δ 158.38, 133.53, 131.89, 129.77, 128.66, 127.08, 126.59, 120.10, 111.23, 84.46, 68.97, 32.33,

30.09, 30.06, 30.03, 29.86, 29.81, 29.77, 26.52, 25.20, 23.10, 14.29. ESI-HRMS: m/z, 513.3455, calcd.: 512.53. Anal. Calcd for $C_{34}H_{45}BO_3$: C, 79.68; H, 8.85. Found: C, 80.19; H, 9.25.



6,13-Bis(bis(2-(dodecyloxy)pyren-7-yl)methylene)-6,13-dihydropentacene (3c). Compound **3c** was synthesized using identical condition with that of **3a**. Compound **1** (0.184 g, 0.29 mmol), **2c** (0.7 g, 1.36 mmol), Na_2CO_3 (0.26 g, 2.45 mmol), THF (20 mL), H_2O (7 mL) and $Pd(PPh_3)_4$ (270 mg) were used. The crude product was purified by silica gel chromatography (hexane/dichoromethane = 2/1 as eluent) to afford **3c** as a light yellow solid (0.44 g, 80.3%). ^{1}H NMR (250 MHz, CD_2Cl_2, 298 K, ppm): δ 8.61 (s, 8H), 8.06-7.95 (q, 16H), 7.84 (s, 4H), 7.70 (s, 8H), 7.17 (m, 4H), 6.96 (m, 4H), 4.32 (t, 8H), 1.90 (m, 8H), 1.58-1.28 (m, 72H), 0.88 (t, 12H); ^{13}C NMR (62.5 MHz, CD_2Cl_2, 298 K, ppm): δ 158.01, 142.15, 139.81, 137.52, 137.09, 133.01, 131.76, 130.48, 128.37, 127.73, 127.54, 127.34, 125.91, 123.89, 120.08, 111.50, 68.96, 32.34, 30.09, 30.06, 30.04, 29.87, 29.82, 29.77, 26.53, 23.11, 14.30. MALDI-TOF-MS (TCNQ as matrix): m/z 1841.24, calcd.: 1842.60. Anal. Calcd for $C_{136}H_{144}O_4$: C, 88.65; H, 7.88. Found: C, 88.66; H, 8.16.



TPCc. Compound **TPCc** was synthesized using identical condition with that of **TPCa**. **3c** (20 mg, 0.011 mmol), $FeCl_3$ (14.1 mg, 0.30mmol), CH_3NO_2 (2.0 mL) and CH_2Cl_2 (150 mL) were used. The crude product was purified by silica gel chromatography and gel permeation chromatography (Bio-Beads S-X1 gel) (dichoromethane as eluent), followed with precipitation into MeOH to afford **TPCc** as a dark red solid (16 mg, 80.3%). ^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 413 K, ppm): δ 10.60 (s, 2H), 9.48 (d, 2H), 8.84 (br, 4H), 8.58 (d, 4H), 8.36-7.61 (m, 24H), 4.47 (t, 8H), 2.11-0.86 (m, 92H); MALDI-TOF-MS (TCNQ as matrix): m/z, 1833.69, calcd.: 1834.53. Anal. Calcd for $C_{136}H_{136}O_4$: C, 89.04; H, 7.47; O, 3.49. Found: C, 88.68; H, 7.50; O, 3.50.

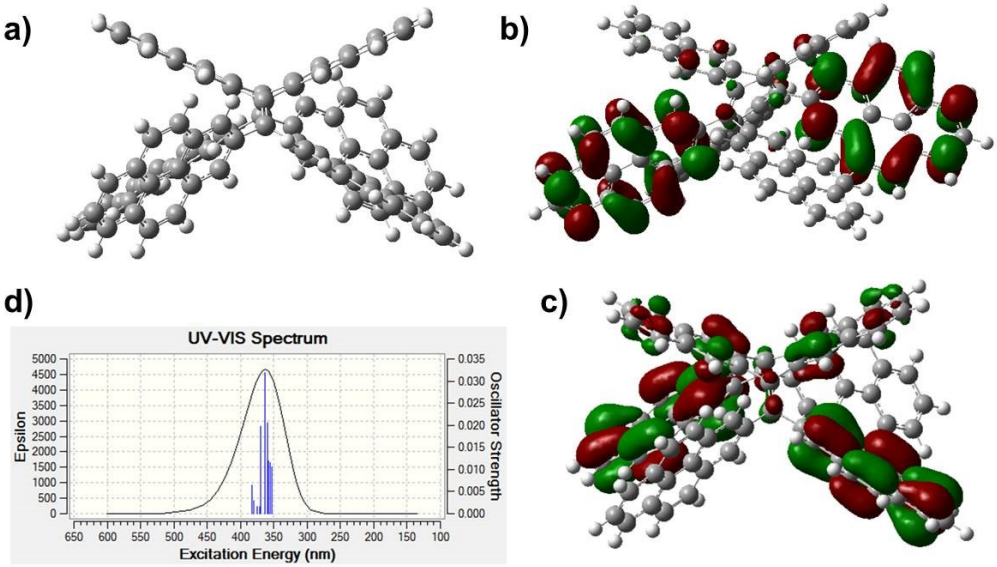


Figure S1. a) Calculated molecular structure of **3a**; b) LUMO and c) HOMO molecular orbitals of **3a**; d) simulated UV-vis spectrum of **3a** with λ_{max} at 383 nm.

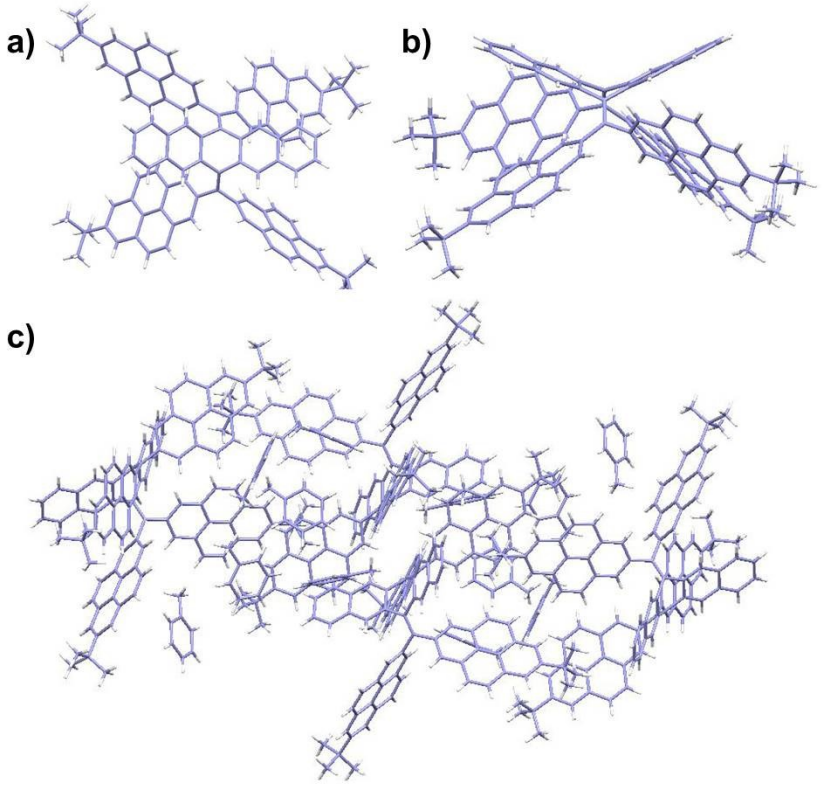
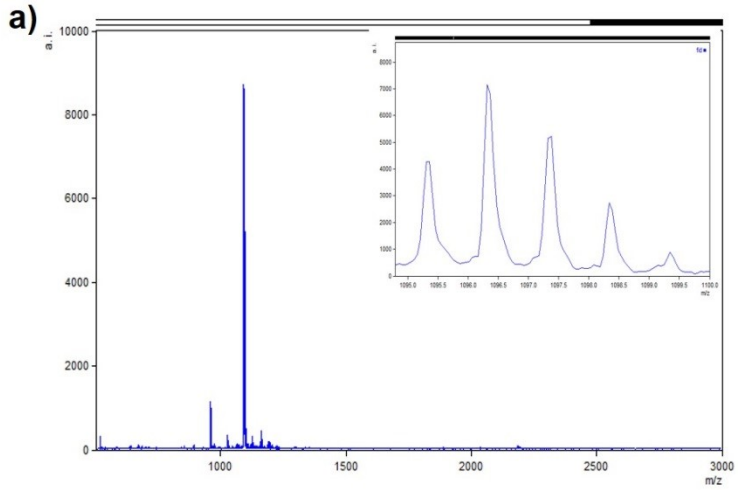


Figure S2. Crystal structures of **3b** from toluene/MeOH (CCDC 1517013). a) top view of **3b**; b) side view of **3b**; c) crystal packing of **3b** along *b* axis.



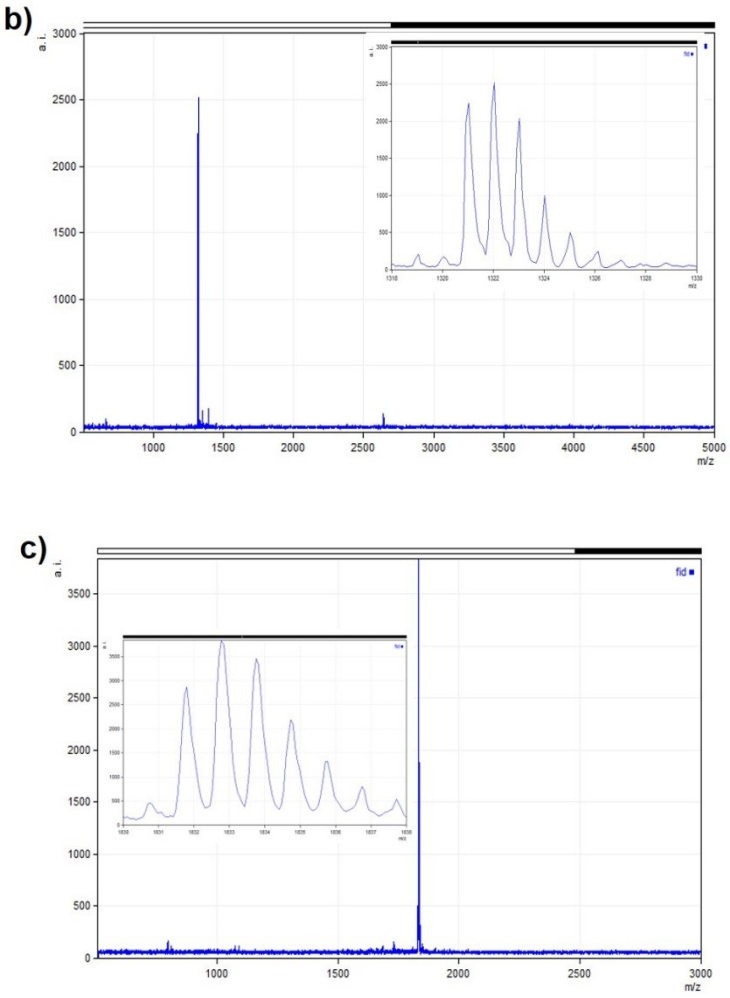


Figure S3. MALDI-TOF mass spectra of (a) **TPCa**; (b) **TPCb**; (c) **TPCc**.

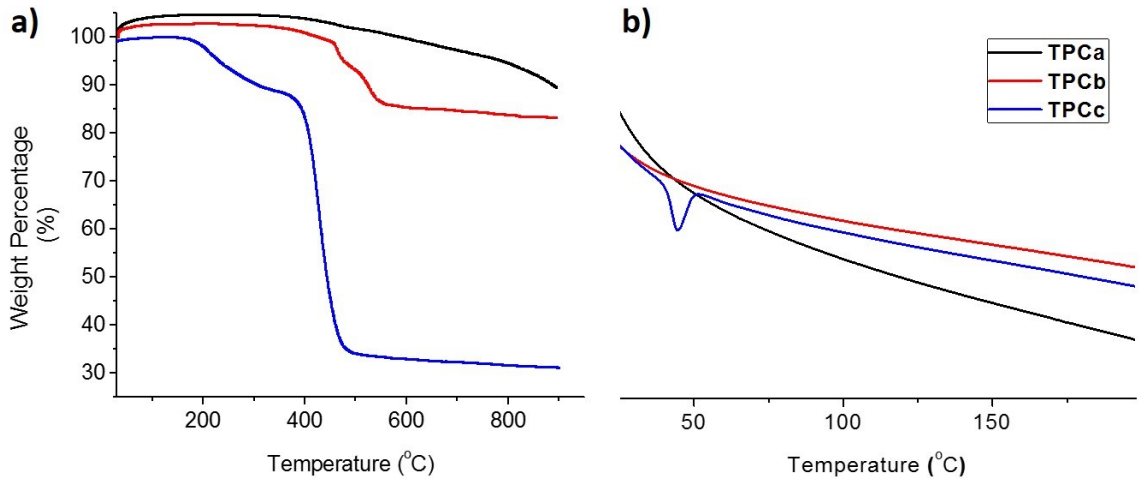


Figure S4. (a) TGA; (b) DSC curves of **TPCa-c**.

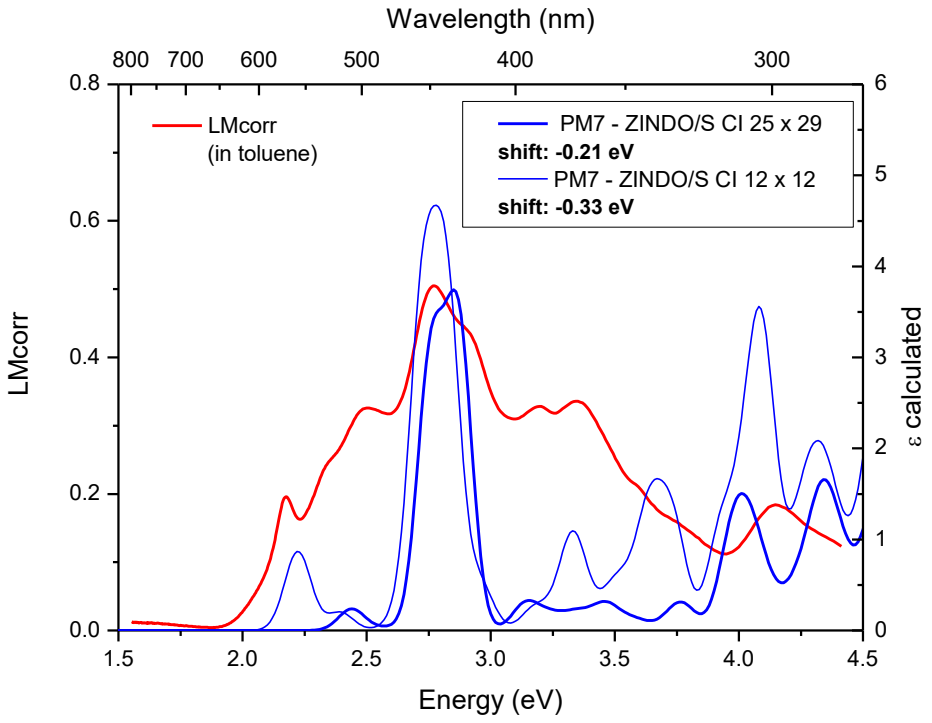


Figure S5. Excitation spectra of **TPCa** (red: experimental data; blue: calculated data).

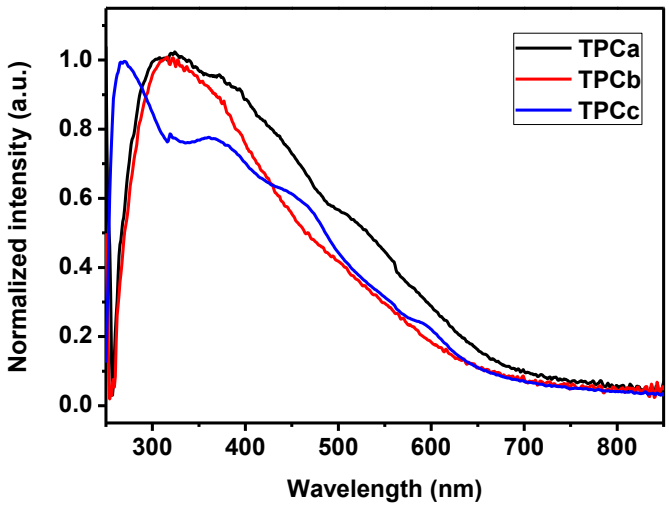


Figure S6. UV-vis spectra of **TPCa-c** in film.

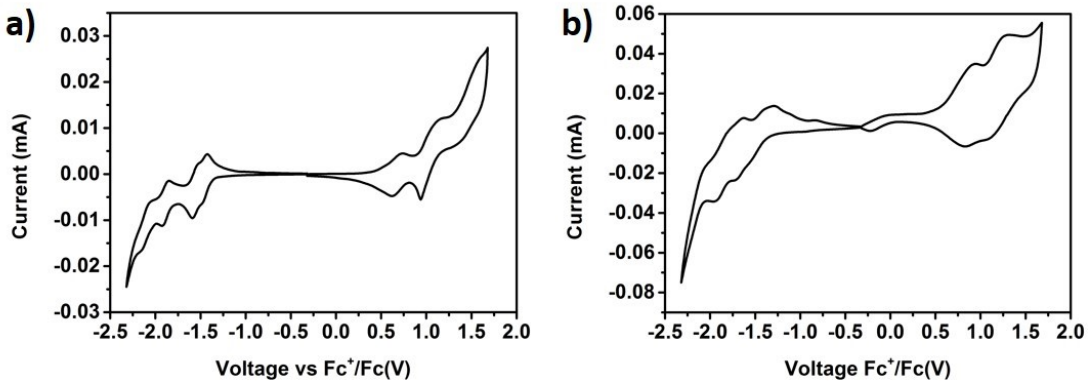


Figure S7. Cyclic voltammetric curves of a) **TPCa** and b) **TPCc** in DCM (0.5 mM) containing 0.1 M Bu_4NPF_6. Potentials are reported *vs* the Fc/Fc^+ redox couple as a standard, scan rate = 50 mV/s.

Table S1. Summary of UV-vis absorption and PL maxima (λ), energy gaps (ΔE), HOMO and LUMO levels of **TPCa-c**.

	λ_{abs}(nm) (ε (10^5 $M^{-1}cm^{-1}$))[a]	λ_{PL} (nm)[a]	ΔE (eV)[b/c]	HOMO (eV)[c]	LUMO (eV)[c]
TPCa	368 (0.53), 447 (0.59), 570(0.222)	584, 634, 693	1.92/1.80	-5.23	-3.43
TPCb	370 (1.247), 452 (1.287), 574 (0.528)	584, 634, 693	1.90/1.80	-5.17	-3.37
TPCc	350 (0.886), 456 (0.989), 596 (0.254)	571, 617, 670	1.89/1.88	-5.33	-3.45

[a] Measured in toluene. [b] Estimated from absorption onset. [c] Estimated from cyclic voltammetry.

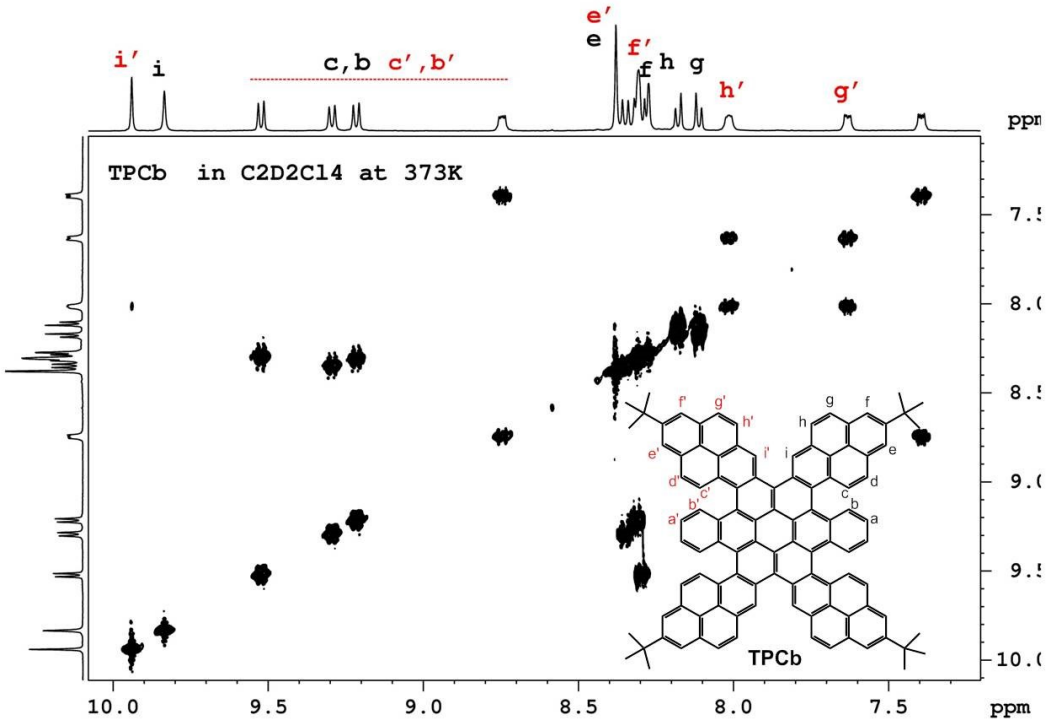
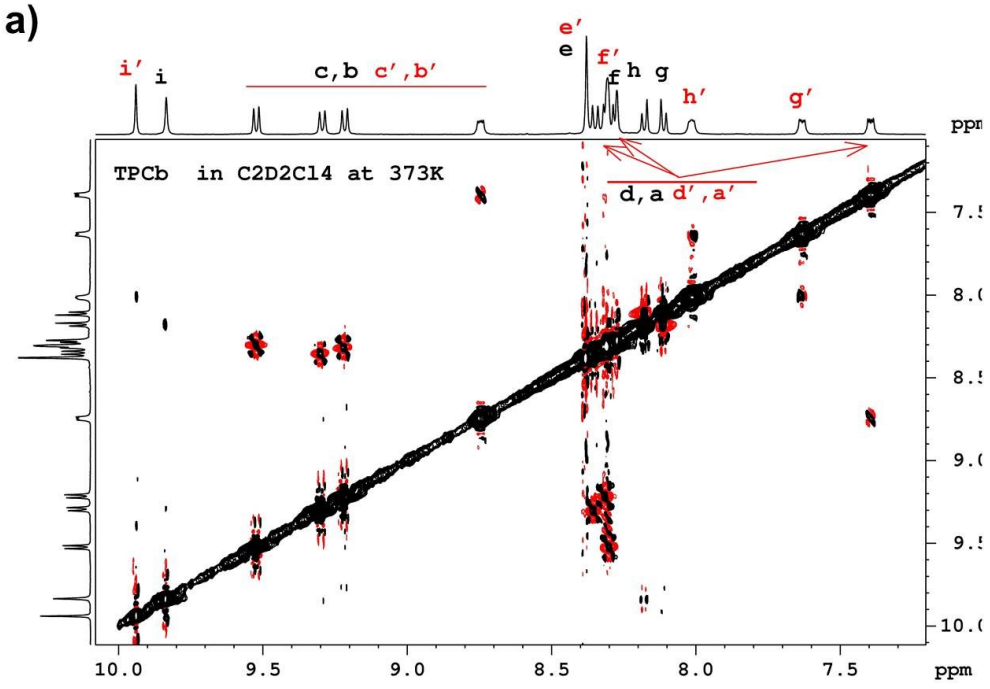


Figure S8. ^{1}H-^{1}H COSY 2D NMR spectra of **TPCb** at 373K (500 MHz).



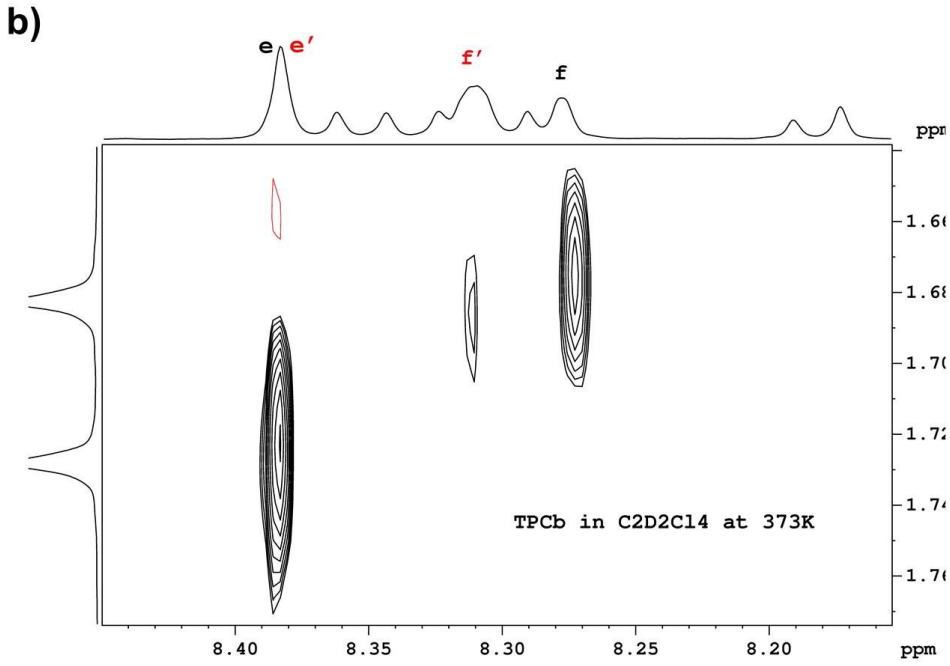
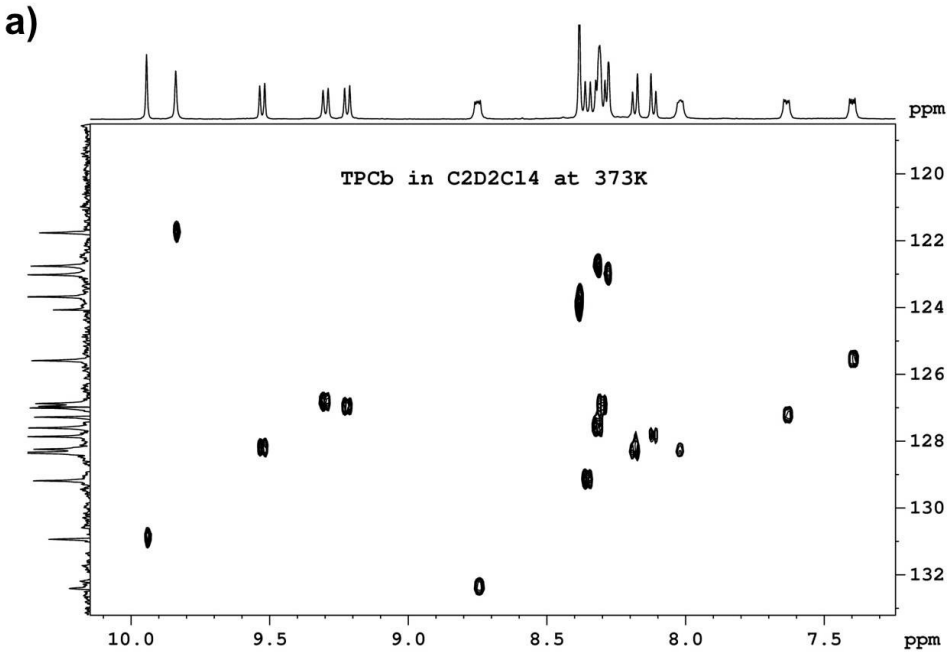


Figure S9. ^{1}H-^{1}H NOESY 2D NMR spectra of **TPCb** at 373K (500 MHz) shown in a) aromatic region and b) aliphatic region.



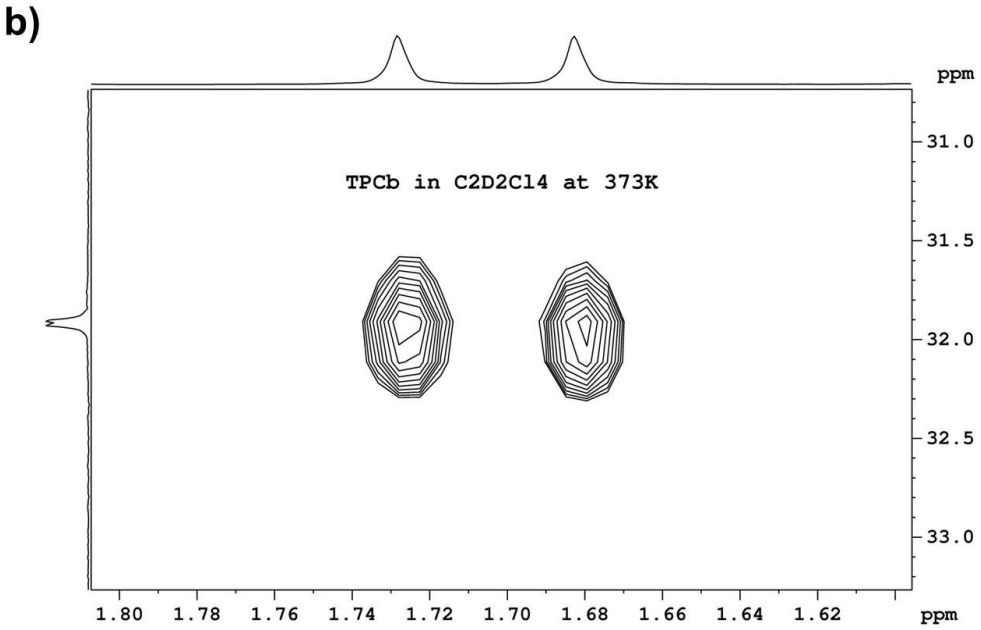
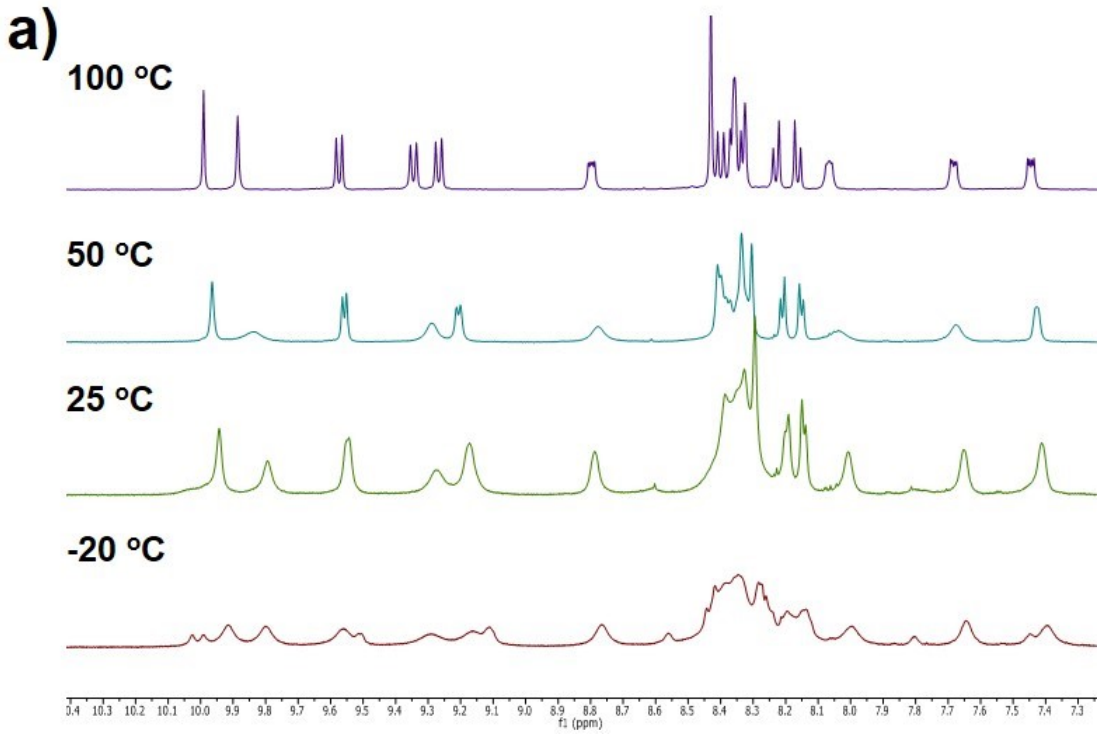
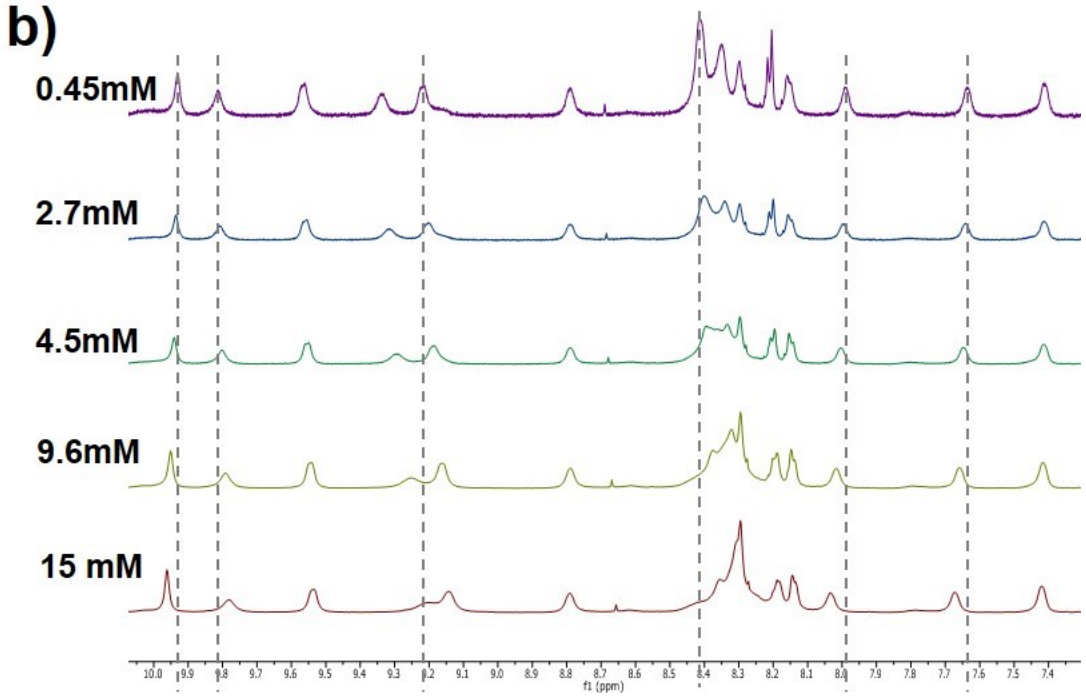
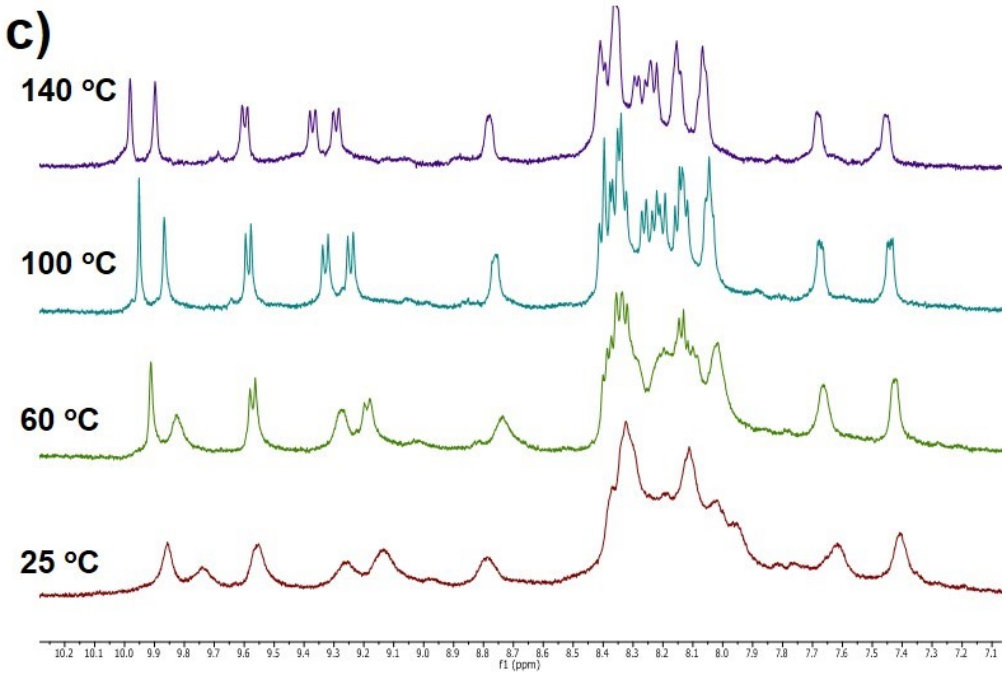


Figure S10. ^{1}H-^{13}C HSQC 2D NMR spectra of **TPCb** at 373K (500 MHz) shown in a) aromatic region and b) aliphatic region.




b)
0.45mM
2.7mM
4.5mM
9.6mM
15 mM
f1 (ppm)


c)
140 °C
100 °C
60 °C
25 °C
f1 (ppm)

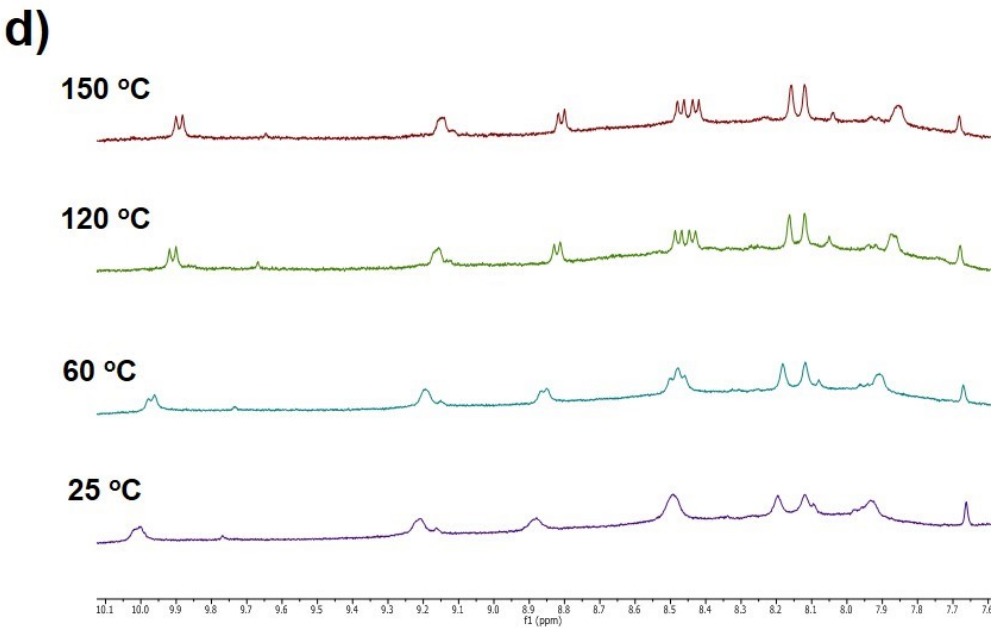


Figure S11. (a) Temperature-dependent ^{1}H NMR (500 MHz) spectra of **TPCb** (4 mM, $C_2D_2Cl_4$); (b) concentration-dependent ^{1}H NMR (500 MHz) spectra of **TPCb** (25 °C, $C_2D_2Cl_4$); (c) temperature-dependent ^{1}H NMR (500 MHz) spectra of **TPCa** (3 mM, $C_2D_2Cl_4$); (d) temperature-dependent ^{1}H NMR (500 MHz) spectra of **TPCc** (3 mM, d_4-*o*-dichlorobenzene).

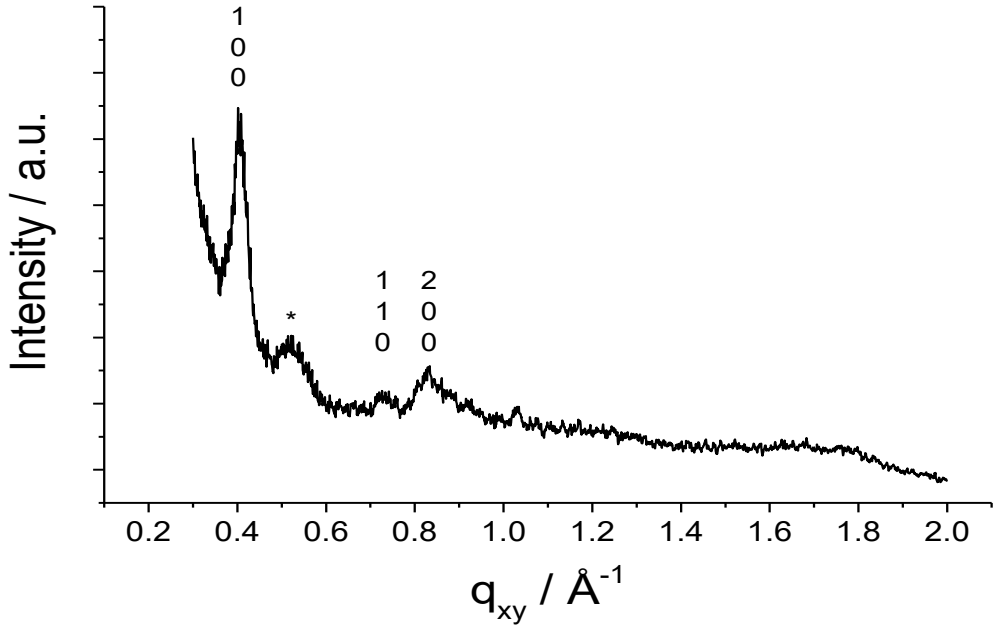


Figure S12. An in-plane integration of the GIWAXS pattern obtained for **TPCa** with reflections assigned by Miller indices hk0. Peaks indicated by the asterisk are assigned to the out-of-plane.

4. The calculation details of Cartesian coordinates and energies

TPC-updown

B3LYP, 6-31g

HF=-3376.9528339 a.u.

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	-2.83739	2.48281	-0.08827
C	-1.42066	2.44348	-0.34815
C	-2.86391	-0.00007	0.00012
C	-0.72242	1.22627	-0.20886
C	-3.56863	1.25945	-0.18568
C	-1.45164	-0.00004	0.00007
C	0.72233	1.2263	-0.20891
C	1.45161	0.00002	-0.00002

C	2.86388	0.00006	-0.00007
C	0.7224	-1.22629	0.20891
C	-0.72235	-1.22632	0.20896
C	3.56861	-1.25946	0.18564
C	2.83738	-2.48282	0.08831
C	1.42066	-2.44349	0.34822
C	-3.56325	3.68818	0.22071
C	-4.96737	3.7261	0.0253
C	-5.64029	2.55916	-0.46236
C	-4.94135	1.35937	-0.51993
H	-5.47041	0.48173	-0.86653
C	4.9414	-1.35931	0.51963
H	5.47051	-0.48162	0.86603
C	5.64035	-2.5591	0.46202
C	4.96738	-3.72608	-0.02543
C	3.56323	-3.6882	-0.22066
C	-1.42053	-2.44357	0.34829
C	3.56854	1.2596	-0.18579
C	2.83726	2.48293	-0.08839
C	1.42053	2.44354	-0.34825
C	0.71111	3.55167	-0.97165
C	-0.71133	3.55164	-0.97161
C	4.94131	1.35953	-0.51984
H	5.47044	0.48188	-0.8663
C	3.56307	3.68832	0.22065
C	5.64021	2.55934	-0.4622
C	-1.38815	4.53017	-1.74649
H	-2.46693	4.49544	-1.81619
C	-0.70301	5.48521	-2.46778
H	-1.25245	6.20478	-3.06848
C	0.7026	5.48524	-2.46783
H	1.25197	6.20484	-3.06857
C	-5.70967	4.91874	0.27529
C	-7.16682	7.27005	0.76998
C	-7.10638	4.97026	-0.02425
C	-7.81096	6.1547	0.22649
C	-5.80882	7.22847	1.0652
H	-8.87188	6.19992	-0.00737

H	-5.31263	8.09947	1.4863
H	-7.73324	8.17765	0.96044
C	5.70966	-4.91873	-0.27546
C	7.16678	-7.27005	-0.7702
C	5.05671	-6.0639	-0.81847
C	7.10642	-4.9702	0.02386
C	7.81098	-6.15464	-0.2269
C	5.80874	-7.22852	-1.06521
H	8.87194	-6.19983	0.00679
H	5.3125	-8.09955	-1.48617
H	7.73319	-8.17765	-0.96068
C	4.96721	3.72627	0.02536
C	5.70945	4.91893	0.27544
C	7.16651	7.27027	0.77029
C	7.1062	4.97048	-0.02395
C	5.05649	6.06403	0.81858
C	5.80848	7.22866	1.06536
C	7.81073	6.15493	0.22687
H	5.31223	8.09964	1.48642
H	8.87167	6.20018	-0.00687
H	7.73289	8.17788	0.9608
C	2.94109	4.84519	0.80047
H	1.88327	4.80838	1.03224
C	3.65576	5.96936	1.09968
H	3.16071	6.81869	1.56431
H	8.79492	3.85317	-0.82528
C	7.73609	3.80107	-0.58337
C	7.03813	2.65298	-0.79302
H	7.53263	1.77206	-1.19556
C	3.65596	-5.96931	-1.0995
H	3.16092	-6.8187	-1.56403
C	2.94126	-4.84515	-0.80034
H	1.88343	-4.8084	-1.03205
C	7.03829	-2.65265	0.79278
H	7.53277	-1.77169	1.19524
C	7.73629	-3.80072	0.58317
H	8.79513	-3.85277	0.82504
C	-7.03817	2.65277	-0.79335

H	-7.5326	1.77185	-1.19596
C	-7.73618	3.80084	-0.58376
H	-8.79498	3.85293	-0.8258
H	-1.88355	4.80829	1.03243
C	-2.94135	4.84507	0.80057
C	-5.05678	6.06386	0.81849
C	-3.65608	5.96923	1.09972
H	-3.16109	6.81857	1.56439
C	1.38784	4.53024	-1.74658
H	2.46661	4.49555	-1.81636
C	-0.7111	-3.55167	0.97177
C	-1.3878	-4.53016	1.74681
C	0.71133	-3.55164	0.9717
C	-0.70255	-5.48513	2.46808
H	-2.46657	-4.49545	1.81665
C	1.38818	-4.53015	1.74659
C	0.70306	-5.48514	2.46795
H	-1.25191	-6.20469	3.06889
H	2.46696	-4.49543	1.81623
H	1.25252	-6.2047	3.06866
C	-3.56855	-1.25964	0.18592
C	-2.83727	-2.48296	0.08842
C	-4.94126	-1.35964	0.52021
C	-5.64015	-2.55946	0.46256
C	-7.038	-2.65317	0.7936
C	-4.9672	-3.72632	-0.02525
C	-7.73598	-3.80124	0.58391
H	-8.79477	-3.85339	0.82598
C	-7.10616	-4.97056	0.02422
C	-5.70946	-4.91895	-0.27538
C	-3.56309	-3.68832	-0.22071
H	-7.53246	-1.77231	1.19633
H	-5.47035	-0.48206	0.86689
C	-7.81071	-6.15499	-0.22665
H	-8.87161	-6.20029	0.00725
C	-5.05656	-6.06396	-0.81877
C	-3.65588	-5.96923	-1.10009
C	-5.80857	-7.22857	-1.06561

C	-7.16655	-7.27024	-0.77032
H	-3.16089	-6.81848	-1.56492
H	-7.73295	-8.17784	-0.96088
H	-5.31237	-8.09948	-1.48686
C	-2.94118	-4.84509	-0.80081
H	-1.8834	-4.80823	-1.03275

Stoichiometry C88H40

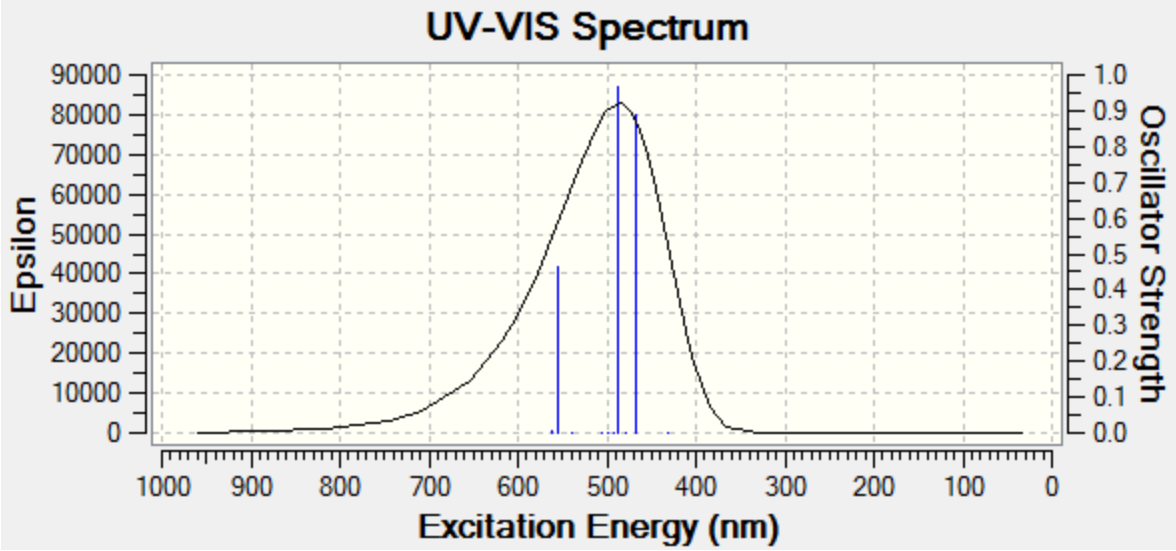
The energy difference between butterfly 1 and up/down conformation is □E= 0.1882 eV= 4.34 Kcal, so butterfly lower in energy and the two pyrenes on one side are asymmetric. (see .mol file)

TPC Up-down

TD-DFT results, n=10

λ_{max}= 555 nm, OS= 0.46

Excited State 1: Singlet-A 2.2065 eV 561.91 nm f=0.0046
282 ->285 -0.46494
284 ->287 0.51552
Excited State 2: Singlet-A **2.2343 eV 554.92 nm f=0.4619**
282 ->287 0.21189
284 ->285 0.66952 p-band
Excited State 3: Singlet-A 2.3023 eV 538.52 nm f=0.0000
283 ->285 0.44664 □□-band
284 ->286 0.53387
Excited State 7: Singlet-A 2.5399 eV 488.14 nm f=0.9680
282 ->285 0.52296 □-band
284 ->287 0.46862



TPC butterfly conformation
Pybenzcoron2 B3LYP / 6-31g(d)
6-31g no d pybenzcoron3

TPCbutteriso1, B3LYP / 6-31g
HF= -3376.95974421 a.u.
Symbolic Z-matrix:
Charge = 0 Multiplicity = 1

C	-2.85456	-2.51476	0.16537
C	-1.43068	-2.53072	0.41158
C	-2.84366	-0.03659	0.37162
C	-0.72186	-1.31362	0.43806
C	-3.5684	-1.29391	0.38641
C	-1.44109	-0.06554	0.43087
C	0.72182	-1.31364	0.43805
C	1.44109	-0.06558	0.43087
C	2.84366	-0.03666	0.37161
C	0.7178	1.15351	0.6674
C	-0.71777	1.15353	0.66739
C	3.48846	1.25691	0.16089
C	2.7688	2.47032	0.43377
C	1.41686	2.34568	0.93325
C	-3.60749	-3.66068	-0.27897

C	-5.01587	-3.6854	-0.1035
C	-5.6762	-2.5555	0.48113
C	-4.95256	-1.38394	0.66497
H	-5.46892	-0.5171	1.06001
C	4.76825	1.34857	-0.42178
H	5.27522	0.44729	-0.73872
C	5.40135	2.55925	-0.67097
C	4.68955	3.77765	-0.44219
C	3.35348	3.73375	0.0511
C	0.71275	3.31074	1.75639
C	-0.71268	3.31075	1.75638
C	-1.41681	2.34571	0.93324
C	-2.76873	2.4704	0.43375
C	-3.48843	1.257	0.16089
C	3.56836	-1.29401	0.3864
C	2.85448	-2.51484	0.16536
C	1.4306	-2.53076	0.41157
C	0.71291	-3.71109	0.87897
C	-0.71301	-3.71107	0.87898
C	-3.35337	3.73384	0.05105
C	-4.68943	3.77777	-0.44224
C	-5.40128	2.55939	-0.67099
C	-4.76822	1.3487	-0.42178
H	-5.27523	0.44743	-0.73871
C	1.39506	4.1509	2.67196
H	2.47916	4.12499	2.69639
C	0.70452	4.95857	3.55284
H	1.24952	5.57351	4.2637
H	-2.47908	4.12504	2.69639
C	-1.39498	4.15092	2.67195
H	-1.24942	5.57353	4.2637
C	-0.70443	4.95858	3.55284
C	4.95252	-1.38408	0.66495
H	5.46891	-0.51726	1.06
C	3.60738	-3.66078	-0.279
C	5.67613	-2.55566	0.4811
C	-1.38706	-4.7813	1.52388
H	-2.4656	-4.75538	1.59935

C	-0.70262	-5.82212	2.11566
H	-1.25265	-6.61274	2.61855
C	0.70246	-5.82214	2.11566
H	1.25247	-6.61277	2.61855
C	-5.78091	-4.82862	-0.48545
C	-7.28211	-7.08389	-1.23749
C	-7.18376	-4.87745	-0.21468
C	-7.90987	-6.01408	-0.59306
C	-5.91957	-7.04274	-1.51053
H	-8.97537	-6.0569	-0.38056
H	-5.43597	-7.87639	-2.01384
H	-7.865	-7.95428	-1.52642
C	-5.31283	5.01878	-0.78581
C	-6.54458	7.47135	-1.42074
C	-6.6585	5.04432	-1.26873
C	-4.58814	6.24018	-0.67181
C	-5.22302	7.45523	-0.98935
C	-7.25458	6.27733	-1.56637
H	-4.66308	8.38306	-0.90111
H	-8.28113	6.29481	-1.92438
H	-7.02473	8.41635	-1.66001
C	5.31299	5.01864	-0.78574
C	6.54483	7.47118	-1.42063
C	4.58835	6.24007	-0.67171
C	6.65866	5.04414	-1.26867
C	7.25479	6.27714	-1.56628
C	5.22328	7.4551	-0.98923
H	8.28133	6.29458	-1.9243
H	4.66338	8.38295	-0.90096
H	7.02502	8.41616	-1.65988
C	5.01576	-3.68554	-0.10354
C	5.78077	-4.82877	-0.48551
C	7.2819	-7.08408	-1.23757
C	7.18362	-4.87765	-0.21474
C	5.14644	-5.92675	-1.13719
C	5.91936	-7.04289	-1.51061
C	7.90969	-6.0143	-0.59314
H	5.43573	-7.87652	-2.01391

H	8.97519	-6.05715	-0.38063
H	7.86476	-7.95449	-1.52651
C	3.00741	-4.76204	-0.97875
H	1.94809	-4.72301	-1.20178
C	3.74208	-5.83323	-1.39833
H	3.26091	-6.63869	-1.94789
H	8.86445	-3.8047	0.66018
C	7.80009	-3.75382	0.44363
C	7.08284	-2.64671	0.77282
H	7.56637	-1.79614	1.24742
C	3.21349	6.16204	-0.28805
H	2.62296	7.07515	-0.28264
C	2.62541	4.97487	0.03598
H	1.5724	4.97233	0.27447
C	6.73988	2.61106	-1.19756
H	7.26014	1.67152	-1.36738
C	7.34974	3.79626	-1.45989
H	8.36854	3.82222	-1.8389
C	-6.73981	2.61124	-1.19757
H	-7.26011	1.67172	-1.36737
H	-8.36843	3.82245	-1.83893
C	-7.34963	3.79646	-1.45992
H	-2.62271	7.07519	-0.28278
C	-3.21328	6.16211	-0.28817
H	-1.57223	4.97234	0.27436
C	-2.62524	4.97492	0.03589
C	-7.08292	-2.64651	0.77286
H	-7.56642	-1.79592	1.24745
C	-7.8002	-3.7536	0.44368
H	-8.86456	-3.80445	0.66024
H	-1.94823	-4.72297	-1.20175
C	-3.00755	-4.76197	-0.97871
C	-5.14662	-5.92662	-1.13714
C	-3.74226	-5.83314	-1.39828
H	-3.26112	-6.63862	-1.94783
C	1.38692	-4.78133	1.52387
H	2.46546	-4.75544	1.59934

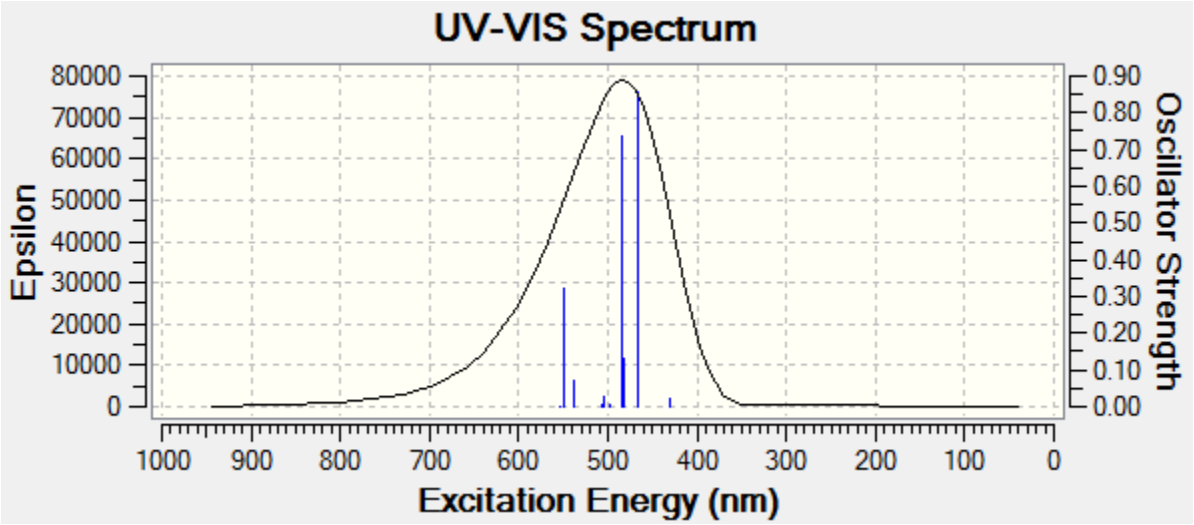
Stoichiometry C88H40

TPCbutterconformation1

TD-DFT, n=10

λ_{max}= 550 nm, OS= 0.32

Excited State 1: Singlet-A 2.2374 eV 554.14 nm f=0.0003
282 -> 285 -0.47686
284 -> 287 0.49392
Excited State 2: Singlet-A **2.2536 eV 550.15 nm f=0.3237**
282 -> 287 0.18967
284 -> 285 0.66321 HOMO – LUMO p-band
Excited State 7: Singlet-A 2.5587 eV 484.56 nm f=0.7383
282 -> 285 0.43426
282 -> 286 -0.11511
283 -> 287 0.33851
284 -> 287 0.41384



Another conformer of TPC butterfly with central bent pentacene was found with opposite twist of the pyrenes, with even lower energy

TPCButterflyiso2

B3LYP, 6-31g

HF=-3376.9645198 a.u.

Symbolic Z-matrix:

Charge = 0 Multiplicity = 1

C	1.95948281	-3.14078571	0.09652140
C	0.67903527	-2.75474460	-0.46555750
C	2.72948784	-0.80143617	-0.37054830

C	0.33933747	-1.38815570	-0.45992345
C	3.01213388	-2.16024347	0.09191548
C	1.38393921	-0.39457571	-0.40869959
C	-1.04161301	-0.99259200	-0.57453863
C	-1.38394549	0.39458161	-0.40868414
C	-2.72949320	0.80144407	-0.37051872
C	-0.33934450	1.38816028	-0.45993629
C	1.04160401	0.99259572	-0.57456710
C	-3.01213092	2.16025660	0.09193456
C	-1.95947831	3.14079769	0.09651674
C	-0.67904202	2.75474875	-0.46558495
C	-4.25658862	2.49987059	0.66714011
H	-5.02593286	1.74588530	0.75637499
C	-4.52489418	3.76017189	1.19556506
C	-3.47001639	4.72696702	1.26807612
C	-2.17372583	4.40019285	0.76733768
C	0.24335760	3.64612766	-1.14662160
C	1.60035641	3.23856444	-1.34280032
C	2.04790710	1.96207824	-0.78749777
C	3.43602408	1.57778615	-0.65258515
C	3.76245673	0.17782663	-0.65955338
C	-3.76246740	-0.17781950	-0.65950243
C	-3.43603538	-1.57777901	-0.65252898
C	-2.04792108	-1.96207560	-0.78744054
C	-1.60038515	-3.23858214	-1.34270553
C	-0.24338336	-3.64614203	-1.14654378
C	4.52613438	2.51552623	-0.49852654
C	5.85971689	2.09388603	-0.76471906
C	6.11524346	0.72866982	-1.13116215
C	5.08190412	-0.19661889	-1.01525160
H	5.29214186	-1.23537947	-1.23698462
C	-0.22215680	4.82491986	-1.79239749
H	-1.25947270	5.11035919	-1.67106574
C	0.60440435	5.57236502	-2.61091413
H	0.21879826	6.45493097	-3.11086102
H	3.41364045	3.67222242	-2.44344430
C	2.41141582	4.00999899	-2.21953364
H	2.57100134	5.70709154	-3.51506404

C	1.93226720	5.15326948	-2.83473339
C	-5.08191857	0.19662502	-1.01518834
H	-5.29215847	1.23538544	-1.23692005
C	-4.52614283	-2.51552228	-0.49847835
C	-6.11525876	-0.72866397	-1.13109116
C	6.95048022	3.01613167	-0.68183198
C	9.09378048	4.84111294	-0.52507730
C	8.27316558	2.60383403	-1.04802056
C	6.72450312	4.35348603	-0.23144995
C	7.81320482	5.24843832	-0.15586779
C	9.32381002	3.53232690	-0.96885752
H	7.64046131	6.26243046	0.19261193
H	10.32528362	3.22403369	-1.25454745
H	9.92072963	5.54162718	-0.46740738
C	-3.72006883	5.98613919	1.90449708
C	-4.21126769	8.48307384	3.12579922
C	-2.65727280	6.92394420	2.08246868
C	-5.03088065	6.30698587	2.38702857
C	-5.25417417	7.56061614	2.98127683
C	-2.92456598	8.16726086	2.69196624
H	-6.24998104	7.80567833	3.33894244
H	-2.11210344	8.87537003	2.82585202
H	-4.40436147	9.44492916	3.58993519
C	-5.85972737	-2.09388279	-0.76466053
C	-6.95048731	-3.01613284	-0.68177854
C	-9.09378127	-4.84112232	-0.52503356
C	-8.27317621	-2.60383425	-1.04795322
C	-6.72450285	-4.35349330	-0.23141770
C	-7.81320164	-5.24844961	-0.15584001
C	-9.32381758	-3.53233093	-0.96879467
H	-7.64045258	-6.26244655	0.19262307
H	-10.32529394	-3.22403688	-1.25447405
H	-9.92072804	-5.54163967	-0.46736759
C	-4.34404500	-3.84856250	0.01212760
H	-3.35438603	-4.15688373	0.32079331
C	-5.39124416	-4.71918982	0.14834982
H	-5.22249515	-5.71043451	0.55885228
H	-9.48100053	-0.94360925	-1.77626935

C	-8.47820372	-1.24408210	-1.48689169
C	-7.45063215	-0.34891628	-1.52103530
H	-7.62262909	0.67838489	-1.82915629
C	-1.34182889	6.52974980	1.67179879
H	-0.51276791	7.20130140	1.87552710
C	-1.11038438	5.32823884	1.06194991
H	-0.09614175	5.06251900	0.80470233
C	-5.82552342	4.09612179	1.72048714
H	-6.61052638	3.34813423	1.65793374
C	-6.07381328	5.31822648	2.26922267
H	-7.06209444	5.56455283	2.64624123
C	7.45061331	0.34892265	-1.52111889
H	7.62260618	-0.67837645	-1.82924909
H	9.48098111	0.94361382	-1.77636214
C	8.47818684	1.24408620	-1.48697515
H	5.22250692	5.71041594	0.55886093
C	5.39124919	4.71917870	0.14833770
H	3.35439270	4.15687444	0.32079428
C	4.34404650	3.84855663	0.01210977
C	4.25659928	-2.49985120	0.66710864
C	2.17374362	-4.40017951	0.76733866
C	4.52491407	-3.76014902	1.19553795
H	5.02594294	-1.74586368	0.75632965
C	3.47004069	-4.72694802	1.26806292
C	1.11040957	-5.32823264	1.06195370
C	5.82554993	-4.09609304	1.72044745
C	3.72010441	-5.98611866	1.90448207
C	1.34186521	-6.52974245	1.67180075
H	0.09616415	-5.06251914	0.80470902
C	6.07384963	-5.31819547	2.26918375
H	6.61054972	-3.34810300	1.65788377
C	2.65731419	-6.92392870	2.08246289
C	5.03092217	-6.30695904	2.38700153
H	0.51280977	-7.20129981	1.87553272
H	7.06213561	-5.56451738	2.64619267
C	2.92461864	-8.16724366	2.69195901
C	5.25422659	-7.56058767	2.98124902
C	4.21132552	-8.48304997	3.12578149

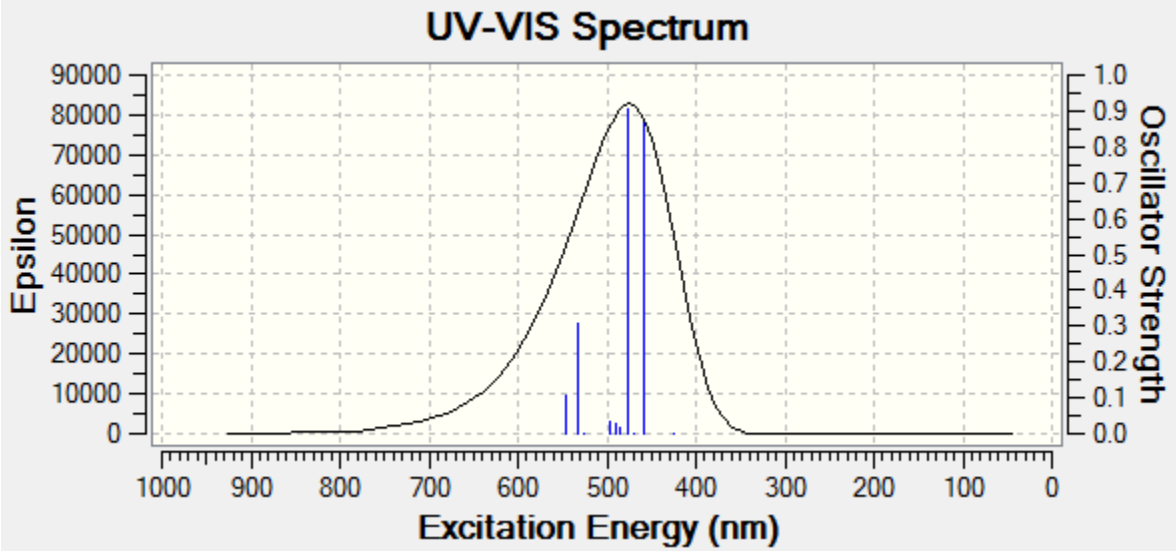
H	2.11216081	-8.87535696	2.82585155
H	6.25003787	-7.80564526	3.33890558
H	4.40442793	-9.44490413	3.58991627
C	0.22210918	-4.82496477	-1.79227894
C	-2.41147390	-4.01005458	-2.21937757
H	-3.41370688	-3.67228794	-2.44326796
C	-1.93234547	-5.15335327	-2.83454098
H	-2.57110141	-5.70720547	-3.51482663
C	-0.60447695	-5.57244207	-2.61074147
H	-0.21888826	-6.45503251	-3.11065851
H	1.25942630	-5.11040496	-1.67095812

This butterfly isomer 2 is even lower in energy

□E= 0.12995 eV =3.0 Kcal between butterfly first and second
□E= 0.317989 eV= 7.33 Kcal between butterfly2nd up/down

TPCbutterconformation2
TD-DFT, n=10
λ_{max}= 546 nm, OS= 0.11

Excited State 1: Singlet-A 2.2699 eV 546.20 nm f=0.1066 <S**2>=0.000
282 ->285 -0.38740
282 ->287 0.15645
284 ->285 0.41064
284 ->287 0.37500
Excited State 2: Singlet-A 2.3306 eV 531.98 nm f=0.3055 <S**2>=0.000
282 ->285 0.31475
282 ->287 0.15061
284 ->285 0.52696
284 ->287 -0.30029
Excited State 3: Singlet-A 2.3554 eV 526.38 nm f=0.0013 <S**2>=0.000
283 ->285 0.36205
284 ->286 0.59026
Excited State 7: Singlet-A 2.6074 eV 475.50 nm f=0.9050 <S**2>=0.000
282 ->285 0.48949
284 ->287 0.50061



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