Supporting information

New synthetic approaches for hexacene and its application in thin-film transistors

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Table of Content

1. General information

Unless otherwise specified, the chemicals (AR grade) were obtained from commercial sources and were used without further purification. 1,2,3,4-tetraphenyl-1,4-carbonyl-9,10-oxido-1,4,9,9a,10,10a-hexahydroanthracen (**Ⅲ**)[1], 2,3-bis(chloromethyl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalene (**Ⅳ**)[1], 2,3-dimethylene-1,2,3,4-tetrahydro-1,4-epoxynaphthalene (**2**)[1] was synthesized according to reported procedures. The progress of the reactions was monitored by TLC (silica gel, Polygram SILG/UV 254 plates). Column chromatography was performed on silica gel (200-300 mesh). ^{1}H and ^{13}C NMR spectra were recorded at 500 MHz and 125 MHz, respectively, and $CDCl_3$, was used as the solvent with TMS as the internal standard. The ^{13}C CP/MAS NMR spectra were acquired with a Bruker (Germany) AvanceIII 400MHz NMR spectrometer. UV-Vis absorbance spectra were recorded using Shimadzu UV-Vis Spectrophotometer model UV-2501PC. All FTIR spectra were obtained using a Nicolet FTIR IS10 Spectrometer. Spectrometer Elemental analysis of all new compounds was performed by using a Vario EL III CHN elemental analyzer. High resolution mass spectra (HRMS) were obtained on a Sciex Triple TOF 4600. Mass spectra were obtained using a Shimadzu LC/MS 2020 equipped with a Shimadzu C18 column (3 um, 50 x 4.6 mm) and a Shimadzu APCI ionization source. X-ray intensity data were collected on a Bruker D8 CMOS detector employing graphite-monochromated Mo-Kα radiation (λ=0.71073 Å). Yields refer to isolated yield of analytically pure material unless otherwise noted.

STM imaging

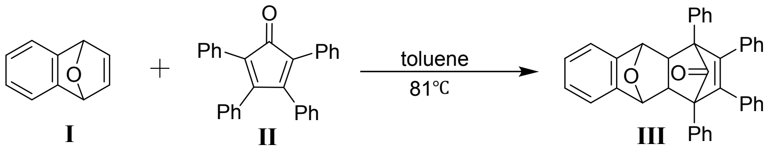
STM experiments were taken in an ultra-high vacuum (UHV) multichamber system (base pressure 2×10^{-10} mbar) equipped with the low-temperature JT-STM at -196℃, a molecular evaporator and other facilities for sample preparation. The Cu(110) substrate was prepared by several cycles of 1.5 keV Ar^+ sputtering followed by anneal at 527℃ for 10 min to obtain a clean and flat terraces. A tungsten tip was prepared as probes by electrochemical etching and then treated on a clean Cu(110) surface to get a better spatial resolution. The precursor molecule **6** were loaded into a quartz crucible in the molecular evaporator. After a thorough degassing, the precursor molecule **6** were sublimated at 130℃ onto the clean Cu(110) surface held at room temperature.[2] After molecule deposition the sample was put into the microscope at liquid nitrogen (-196℃) temperature, and subsequently STM measurements were performed at constant-current mode. The bias voltage was applied to the sample during the STM observations. The STM images were analyzed using Gwyddion 2.491.[3]

Fabrication of OFETs

All organic field effect transistors were fabricated in bottom-gate and top-contact configuration. The heavily doped n-type Si substrate having 50 nm of thermally grown silica was sequentially washed with acetone, isopropanol and deionized water for 15 minutes in an ultrasonic bath, and dried at 120 °C for 30 minutes. For the polymer electret layers PS (PMMA), it was dissolved in toluene at a concentration of 3 mg/mL, and after it is completely dissolved, the solution was spun onto the cleaned substrates at 3000 rpm for 30 seconds. For OTS, it was dissolved in toluene at a concentration of 3 mg/mL, then the solution was placed onto clean substrates and the OTS was allowed to self-assemble on the substrates for 12 hours. Subsequently, the substrates were transferred in the oven to bake for 30 min at 80 °C in the air. Thereafter, hexacene was vapor-deposited onto the substrates having the dielectric layer by a thermal vapor deposition method at a deposition rate of 1 Å s^{-1} at a pressure of less than 5×10^{-6} Pa as semiconductor layer. Finally, Au was evaporated by a shadow mask to 50 nm as source and drain electrodes, the channel width (W) and length (L) of the devices were 1500 and 100 μm, respectively. The electrical characteristics of the devices were measured in air using a Keithley 4200 SCS semiconductor parameter analyzer.

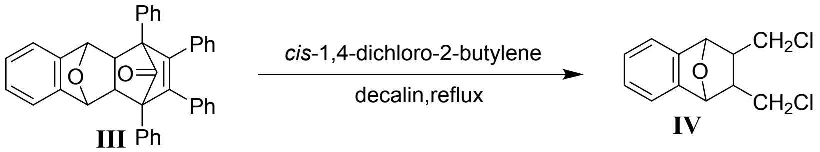
2. Synthetic details

1,2,3,4-tetraphenyl-1,4-carbonyl-9,10-oxido-1,4,9,9a,10,10a-hexahydro-anthracen (Ⅲ)[1]:



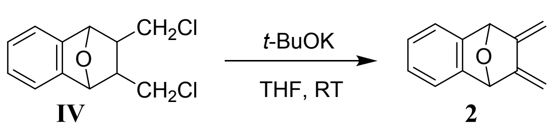
A solution of endoxide **I** (8.650 g, 60 mmol) and tetraphenylcyclopentadienone **Ⅱ** (23.049 g, 60 mmol) in toluenen (360 mL) was heated at 81 ºC until the purple color disappeared (20 h). Evaporation of solvents gave a white solid, and recrystallized from methylene chloride-methanol to give compound **Ⅲ** (30.114 g, 95%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm):3.12 (s, 1H), 5.85 (s, 1 H), 6.90-7.06 (m, 5H), 7.25-7.29 (m, 1H), 7.32 (t, J = 7.3 Hz, 1H), 7.40 (t, J = 7.6 Hz, 2H), 7.44-7.52 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 47.04, 64.68, 81.47 119.40, 127.04, 127.59, 127.69, 127.83 (overlapped peaks), 128.60, 129.92 (overlapped peaks), 130.25 (overlapped peaks), 135.49, 135.75, 138.87, 146.83, 179.07; mp: 184-185 ºC.

2,3-Bis(chloromethyl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalene(Ⅳ) [1]:



To a refluxing solution of *cis*-l,4-dichloro-2-butylene (36.0 mL) in decalin (180 mL) under nitrogen was added dropwise a solution of **Ⅲ** (12.68 g, 24 mmol) in decalin (720 mL) over 1.5 h. After reacting under reflux for additional 0.5 h, the solvent was removed by vacuum distillation and the residue was chromatographed over silica gel (petroleum ether/methylene chloride =8/1) to give compound **Ⅳ** (3.77 g, 65%).^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 2.53 (t, J = 10.9 Hz, 1H), 3.05 (dd, J = 10.0, 4.9 Hz, 1H), 3.27 (dd, J = 10.8, 5.2 Hz, 1H), 5.54 (d, J = 4.4 Hz, 1H), 7.30-7.34 (m, 1H), 7.48 (dd, J = 5.2, 3.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 42.58, 44.67, 82.61, 121.71, 127.66, 142.20; mp: 68-69 ºC.

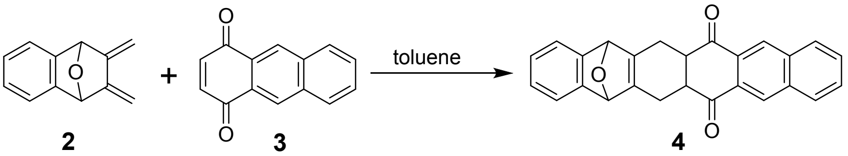
2,3-Dimethylene-1,2,3,4-tetrahydro-1,4-epoxynaphthalene (2)[1]:



To an ice-cold solution of **Ⅳ** (3.630 g, 15 mmol) in anhydrous tetrahydrofuran (600 mL) under argon was added, in small portions, 9.090 g (75 mmol) of solid potassium *tert*-butoxide. After completion of charging, the mixture was stirred at room temperature overnight. The mixture was poured into water (1000 mL) and extracted with methylene chloride (3 × 375 mL). Combined organic layers were washed with water, dried, and concentrated to give crude product. After recrystallization from petroleum ether, 2.373 g (93%) of compound **2** was obtained as a white solid. ^{1}H NMR (500 MHz,

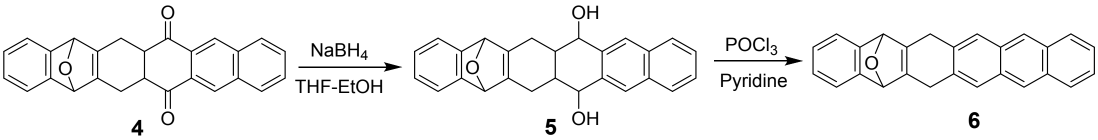
$CDCl_3$), δ (ppm): 5.26 (s, 1H), 5.36 (s, 1H), 5.64 (s, 1H), 5.54 (d, *J* = 4.4 Hz, 1H), 7.24 (dd, *J* = 5.3, 3.0 Hz, 1H), 7.37 (dd, *J* = 5.3, 3.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 83.98, 103.57, 120.00 (overlapped peaks), 127.59, 144.59; mp 73-74 ºC.

5,6,6a,14a,15,16-Hexahydro-5,16-epoxyhexacene-7,14-dione (4):



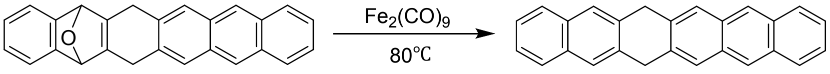
A mixture of **2** (1.701 g, 10 mmol) and anthracene-1,4-dione (**3)** (2.082 g, 10 mmol) in toluene (500 mL) was refluxed for 20 h under N_2. The mixture was concentrated in vacuum and purified by silica gel column chromatography eluting with (petroleum ether/methylene chloride =1/8) to give diketone derivative **4** (1.928 g, 51%) as yellow solid. ^1H NMR (500 MHz, $CDCl_3$), δ (ppm): 2.18 (dd, *J* = 15.7, 5.5 Hz, 2H), 2.99 (dd, *J* = 15.7, 5.5 Hz, 2H), 3.22 (t, *J* = 4.7 Hz, 2H), 5.48 (s, 2 H), 7.00 (dd, *J* = 4.7, 3.2 Hz, 2H), 7.25 (dd, *J* = 6.3, 3.3 Hz, 2H), 7.69 (dd, *J* = 6.3, 3.1 Hz, 2H), 8.07 (dd, *J* = 6.1, 3.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 22.86, 46.97, 84.17, 119.52, 125.16, 129.02, 129.44, 130.03 (overlapped peaks), 135.36, 146.14, 148.89, 197.09; IR (thin film, υ cm^{-1}): 2925, 1668, 1610, 1454, 1291, 838, 756, 643; APCI-MS: m/z [$(M+H)^+$]: 379.1; $C_{26}H_{18}O_3$ (378.43): C 82.52, H 4.79, O 12.68; found: C 82.51, H 4.82, O 12.66. mp 365-367 ºC.

5,6,15,16-Tetrahydro-5,16-epoxyhexacene (6):



To a solution of diketone derivative **4** (0.945 g, 2.5mmol) in EtOH (100 mL) and THF (150 mL) was added $NaBH_4$ (0.473 g, 12.5 mmol) at 0 ºC, then the reaction was stirred at room temperature. After 10 h, the reaction was quenched by water. The reaction mixture was extracted with ethyl acetate (3×125 mL), and the combined organic extracts were washed with brine, and dried with anhydrous Na_2SO_4. Evaporation of the solvents gave the diol intermediate **5**. To a solution of crude diol intermediate **5** in anhydrous pyridine (38 mL) was added dropwise $POCl_3$ (1.3 mL) at 0 ºC. The reaction was stirred at room temperature. After 15 h, the reaction was quenched by adding ice water. The reaction mixture was extracted with methylene chloride (3 × 50 mL), and the combined organic extracts were washed with 3N HCl and brine, dried with anhydrous Na_2SO_4. The mixture was concentrated in vacuum and was purified by silica gel column chromatography eluting with (petroleum ether/methylene chloride = 4/1) to give compound **6** (0.519 g, 60 %) as yellow solid. ^1H NMR (500 MHz, $CDCl_3$), δ (ppm): 3.52 (dd, *J* = 22.2, 5.0 Hz, 2H), 4.07 (dd, *J* = 22.2, 5.0 Hz, 2H), 5.66 (s, 2H), 6.99 (dd, *J* = 5.1, 2.9 Hz, 2H), 7.32 (dd, *J* = 4.8, 3.1 Hz, 2H), 7.41 (dd, *J* = 6.6, 3.1 Hz, 2H), 7.82 (s, 2H), 7.94 (dd, *J* = 6.4, 3.2 Hz, 1H), 8.30 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 28.34, 84.37, 119.51, 125.11 (overlapped peaks), 125.16 (overlapped peaks), 127.40, 128.12, 130.83, 131.62, 145.84, 148.99; IR (thin film, υ cm^{-1}): 2989, 1413, 960, 882, 746, 634; APCI-MS: m/z [$(M-H)^-$]: 345.0; C26 H18O (346.40): C 90.14, H 5.24, O 4.62; found: C 90.15, H 5.23, O 4.60. mp: 275-277 ºC.

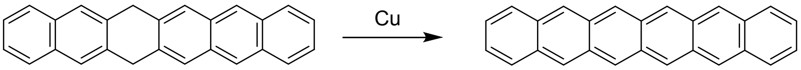
6,15-dihydrohexacene (7):



6 **7**

A mixture of **6** (0.346 g, 1 mmol) and $Fe_2(CO)_9$ (1.090 mg, 3 mmol) in toluene (100 mL) was heated at 80℃ for 20 h under N_2. The reaction mixture was filtered through celite and the solvent was concentrated in vacuum. The crude product was purified by silica gel column chromatography eluting with (petroleum ether/methylene chloride = 4/1) to give the dihydrohexacene **7** (0.214 mg, 65 %) as yellowish white solid. ^1H NMR (500 MHz, $CDCl_3$), δ (ppm): 4.30 (s, 4H), 7.43 (dd, *J* = 6.4, 3.3 Hz, 2H), 7.81 (dd, *J* = 6.4, 3.3 Hz, 2H), 7.82 (s, 2H), 7.95 (s, 2H), 7.98 (dd, *J* = 6.4, 3.3 Hz, 2H), 8.37 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 37.67, 124.82, 125.05, 125.20, 125.39 (overlapped peaks), 125.44, 127.31, 128.14, 131.14, 131.58, 132.59, 135.85; IR (thin film, υ cm^{-1}): 2925, 1448, 1258, 935, 866, 742; C_{26} H_{18} (330.14): C 90.51, H 5.49; found: C 90.53, H 5.47.

Hexacene (1):



7 **1**

A mixture of dihydrohexacene **7** (0.115 g, 0.5mmol) and copper powder was heated at 270℃ for 1 h under N_2. Then sublimation under vacuum gave hexacene **1** (90 mg, 55%). ^{13}C (CP-MAS) NMR, δ (ppm): 120-135. HR-MS m/z: calcd for $C_{26}H_{16}$, 329.1330 $[M+H]^+$; found: 329.1304.

3. Characterization of OTFTs

(1) Schematic illustration

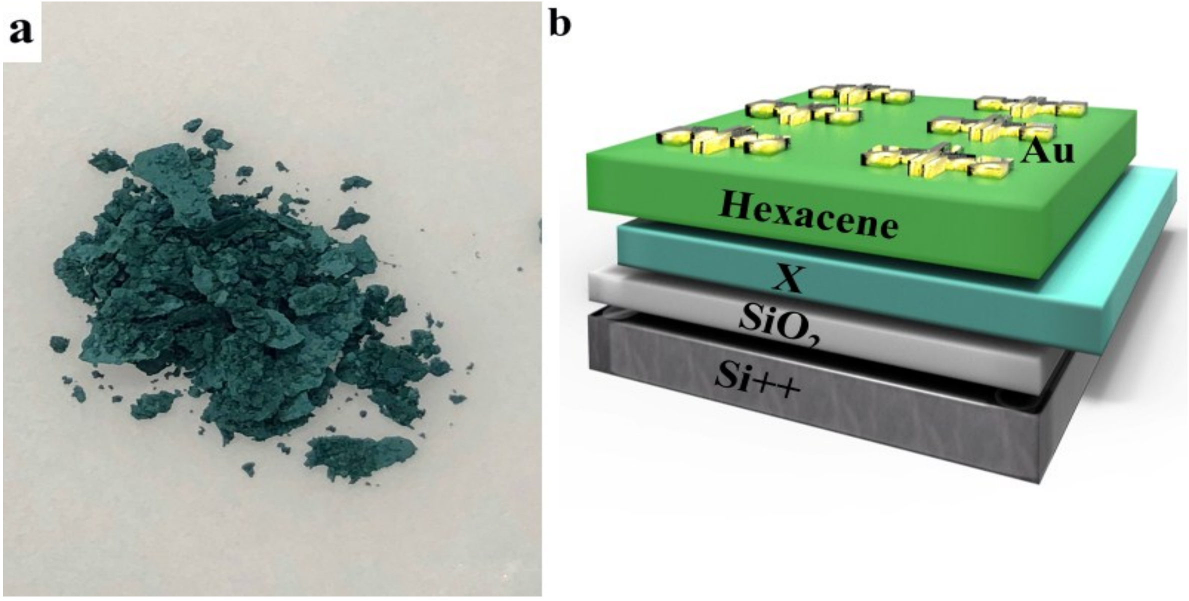


Figure S1 (a) Physical appearance of hexacene; (b) Schematic illustration of hexacene-based OFET device

(2) Electrical measurements

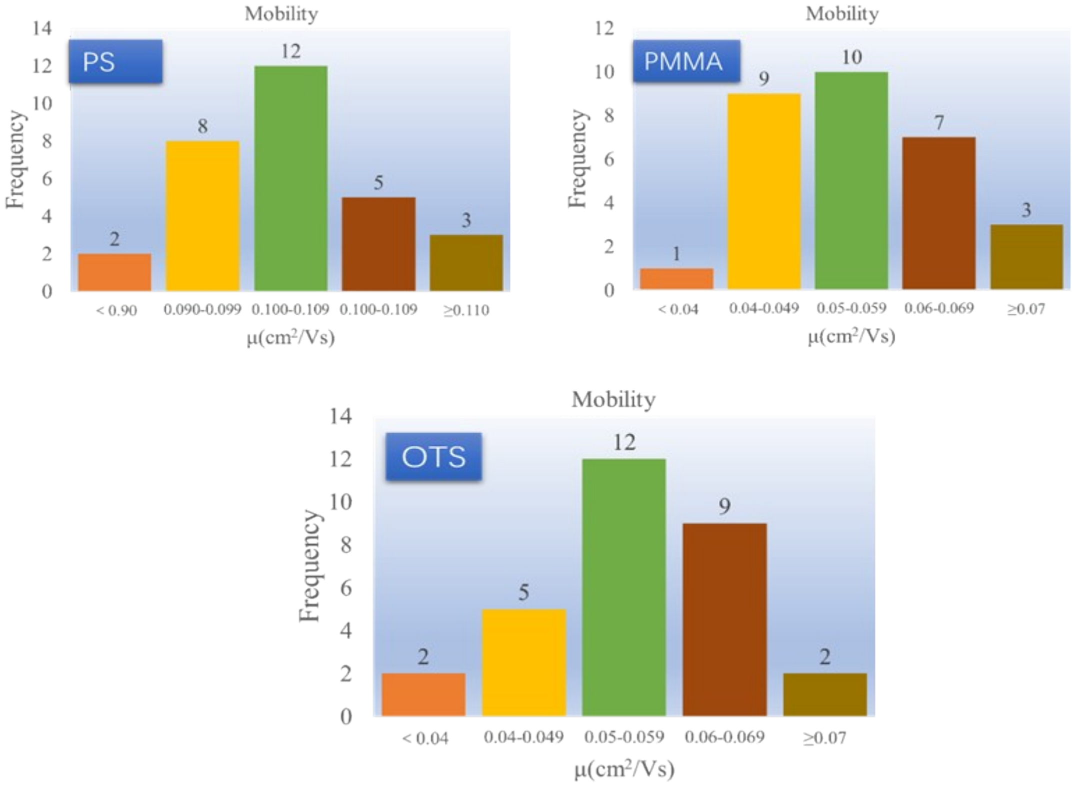


Figure S2 Statistic histograms for the field-effect hole mobilities of hexacene-based OFET devices

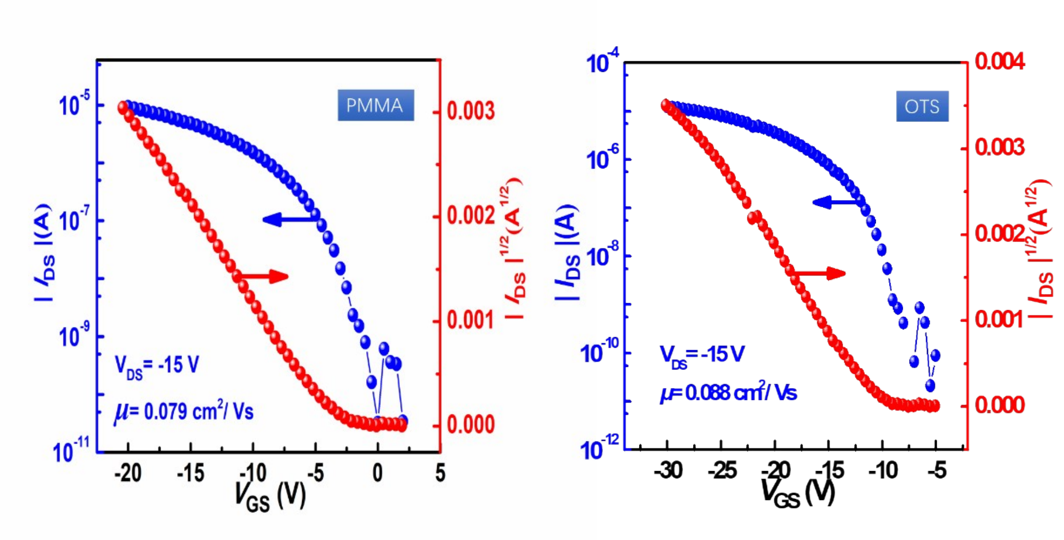


Figure S3 Transfer characteristics of the OFETs with different dielectric layers that exhibited the highest field effect mobility as measured in air at room temperature.

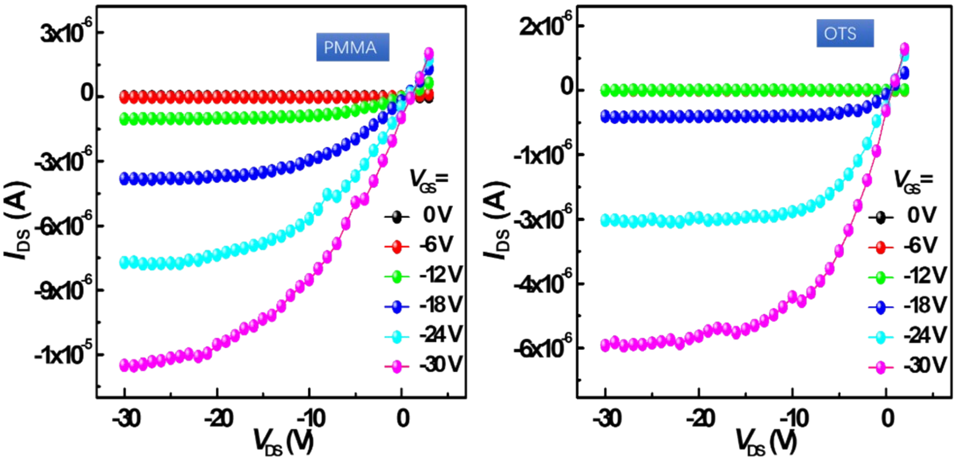


Figure S4 Output characteristics of the OFETs with different dielectric layers that measured in air at room temperature.

(3) Atomic force microscopy (AFM)

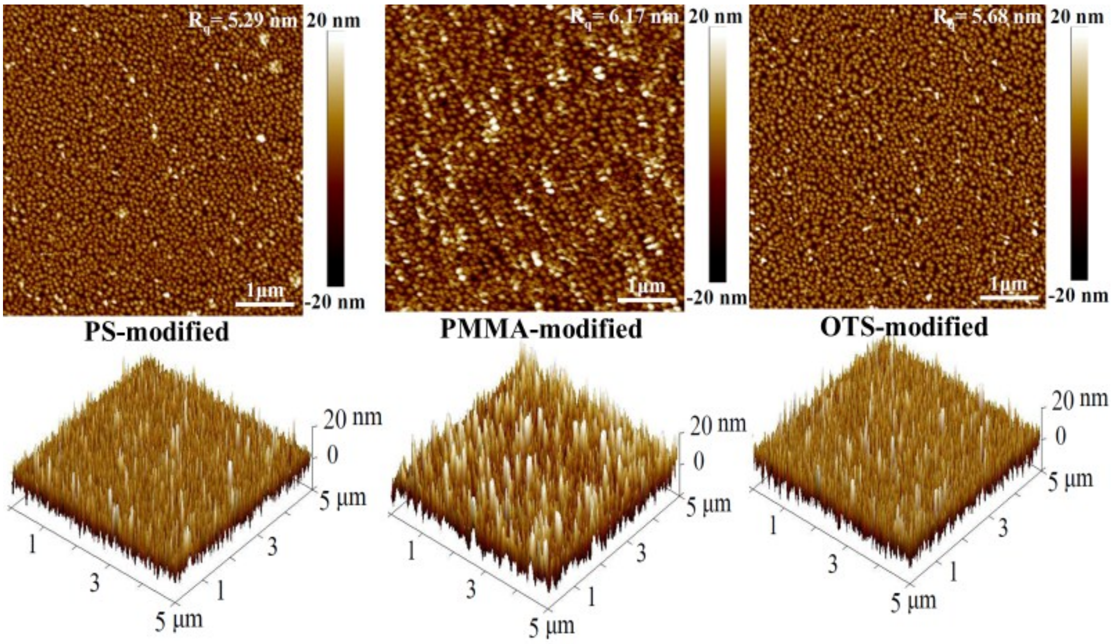


Figure S5 AFM images of hexacene deposited on PS, PMMA and OTS.

4. ^{1}H-NMR, ^{13}C-NMR and FT-IR Spectra of Compounds

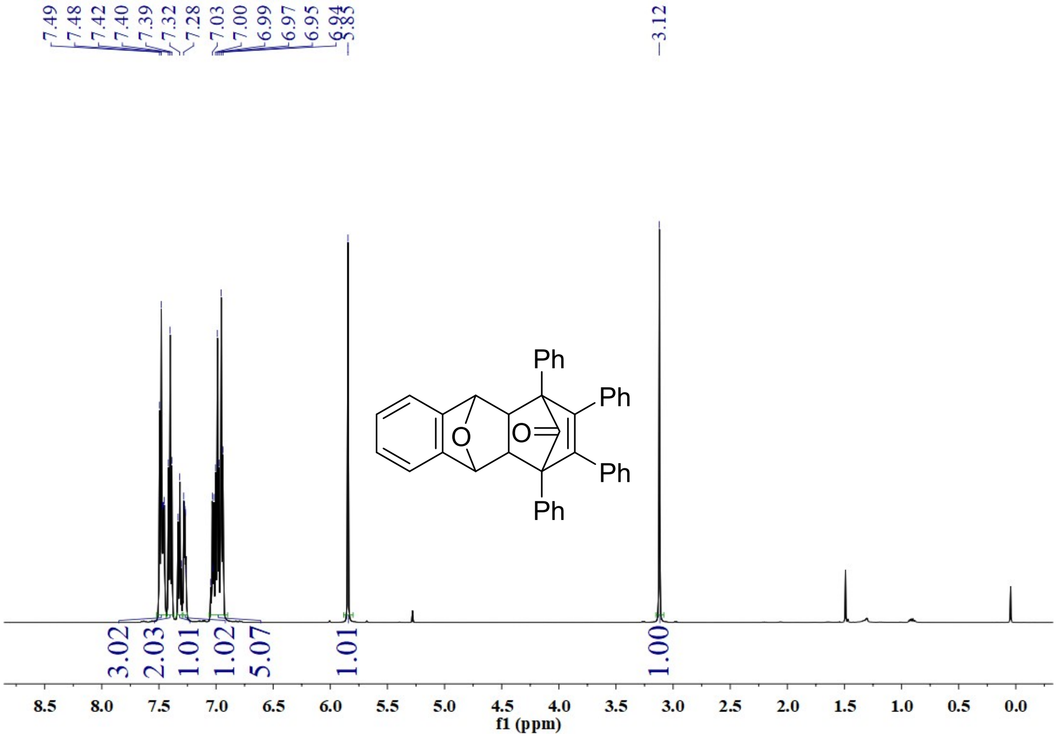


Figure S6 ^{1}H NMR spectrum of 1,2,3,4-tetraphenyl-1,4-carbonyl-9,10-oxido-1,4,9,9a,10,10a- hexahydro-anthracen ($CDCl_3$, 500 MHz)

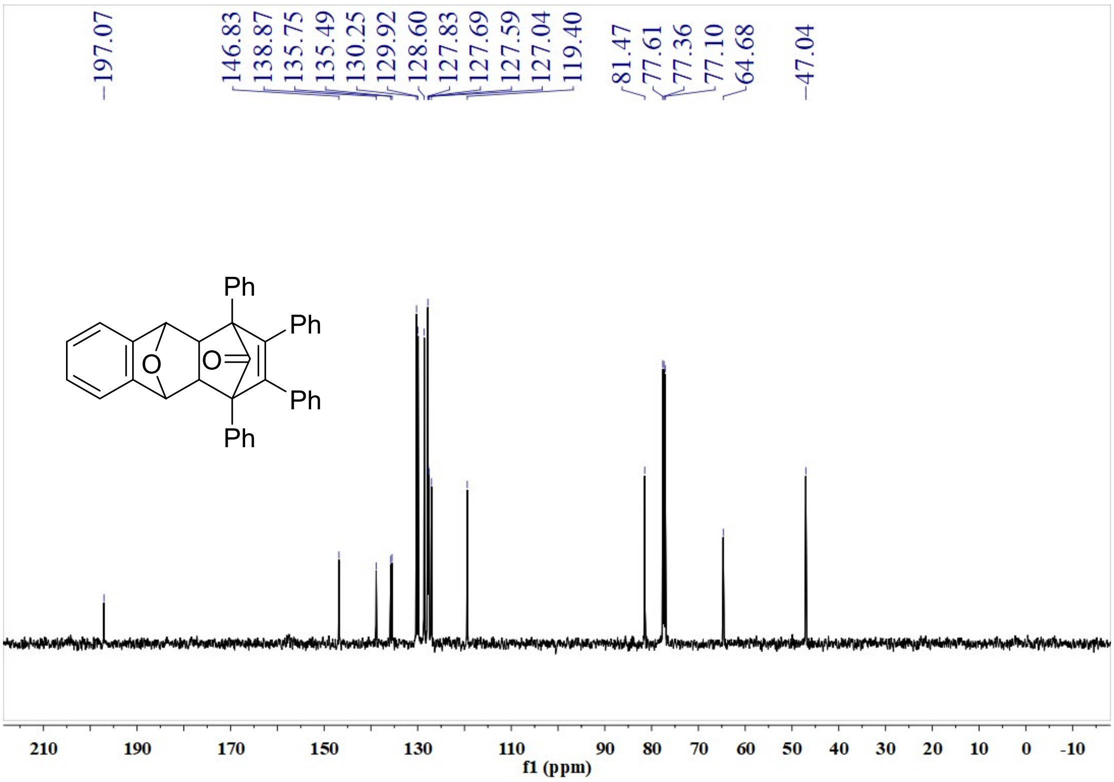


Figure S7 ^{13}C NMR spectrum of 1,2,3,4-tetraphenyl-1,4-carbonyl-9,10-oxido-1,4,9,9a,10,10a hexahydro-anthracen ($CDCl_3$, 125 MHz)

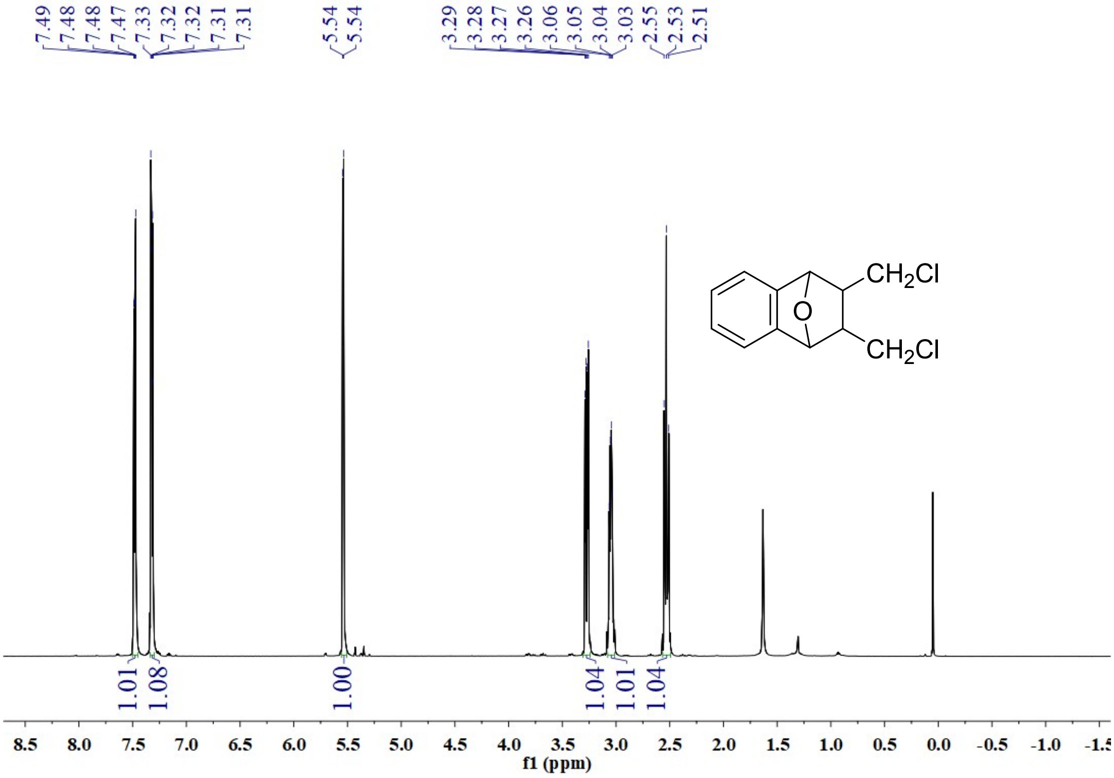


Figure S8 ^{1}H NMR spectrum of 2,3-bis(chloromethyl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalene (CDCl$_3$, 500 MHz)

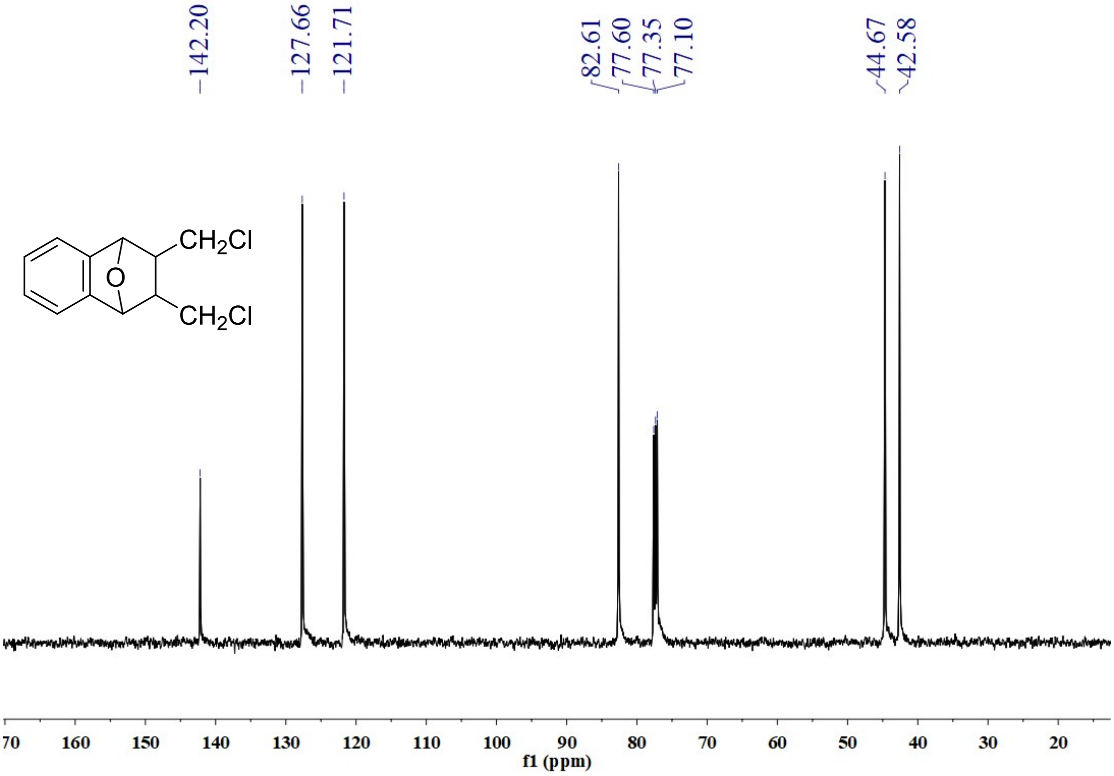


Figure S9 ^{13}C NMR spectrum of 2,3-bis(chloromethyl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalene (CDCl$_3$, 125 MHz)

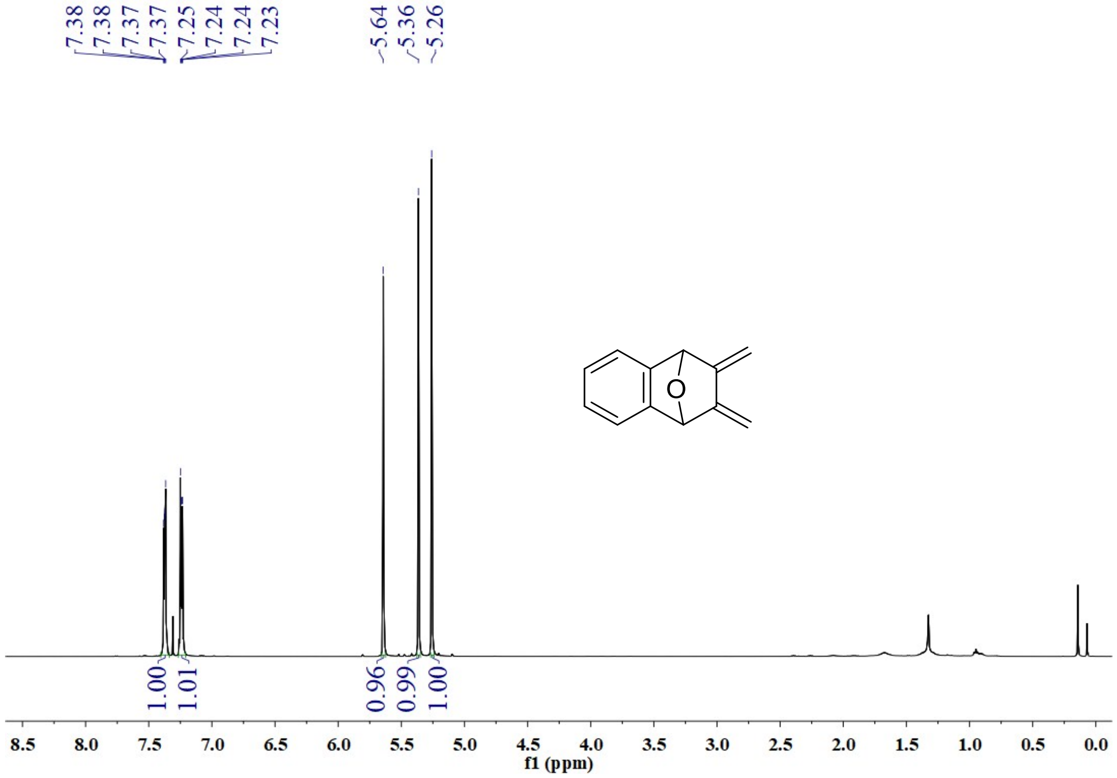


Figure S10 ^{1}H NMR spectrum of compound 2 ($CDCl_3$, 500 MHz)

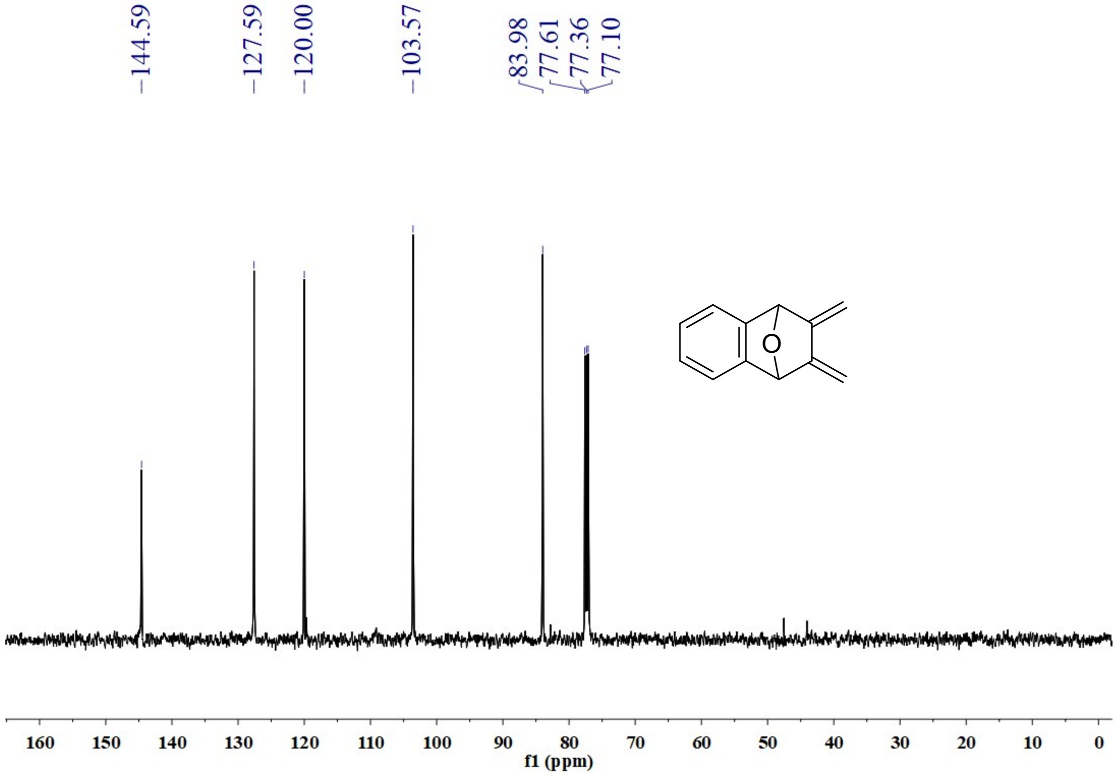


Figure S11 ^{13}C NMR spectrum of compound 2 ($CDCl_3$, 125 MHz)

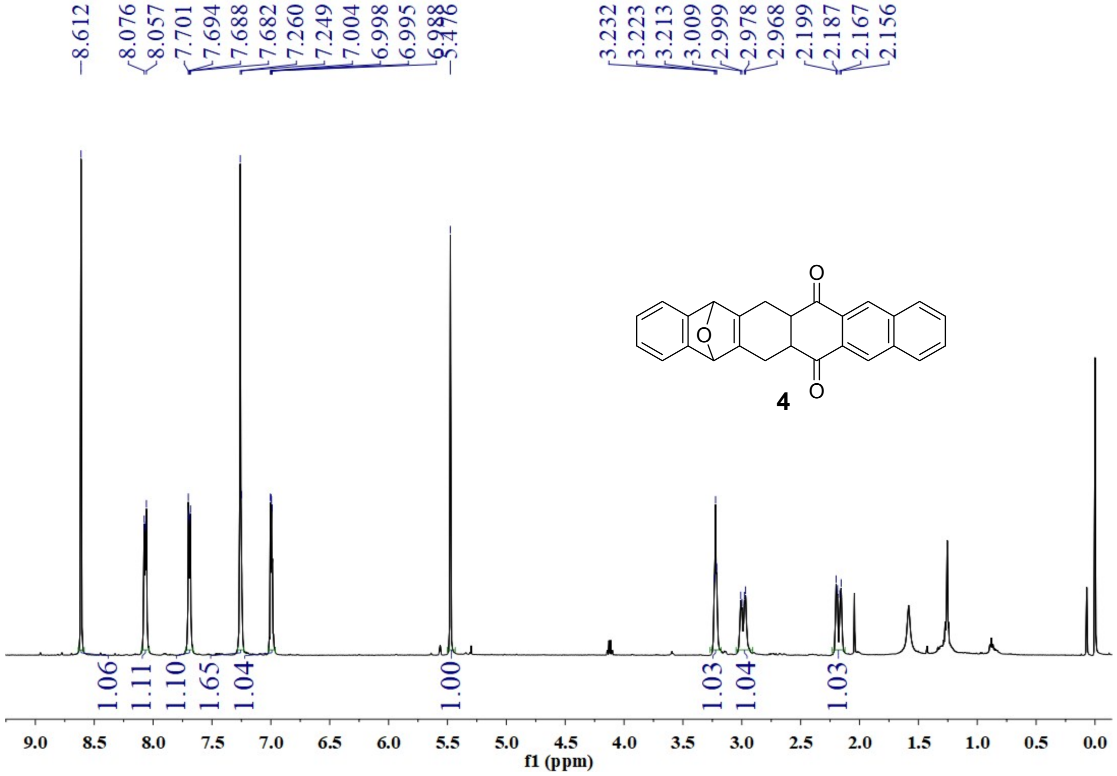


Figure S12 ^{1}H NMR spectrum of compound 4 ($CDCl_3$, 500 MHz)

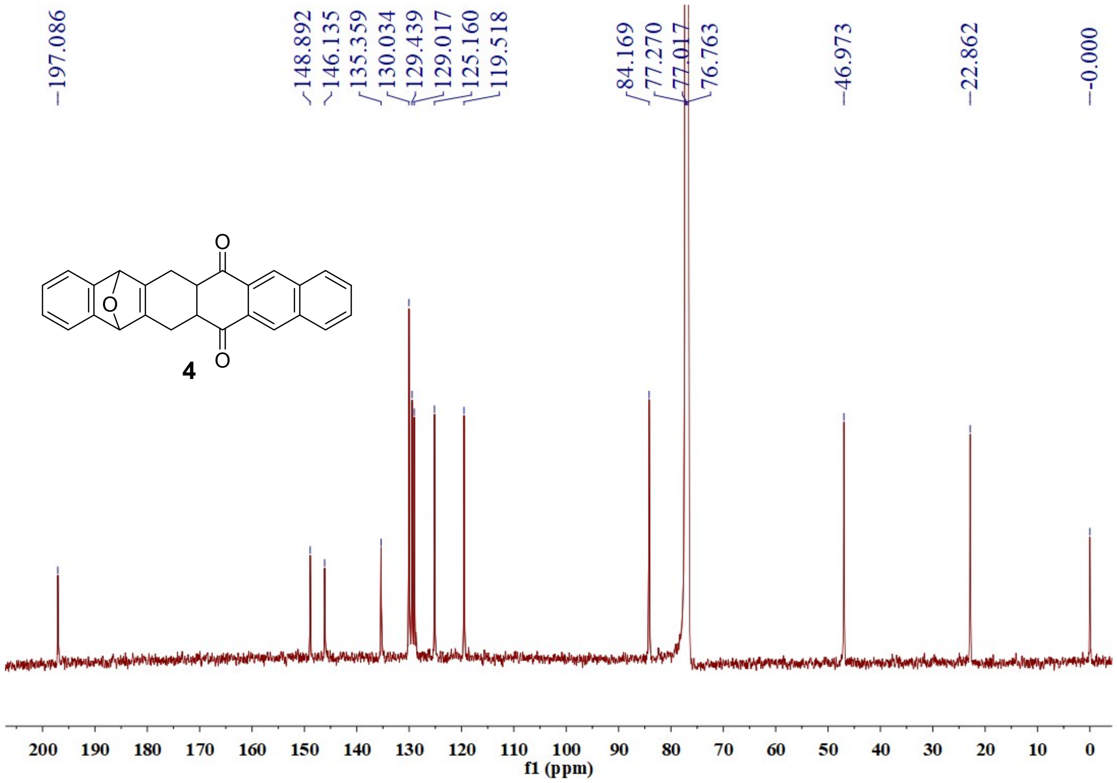


Figure S13 ^{13}C NMR spectrum of compound 4 ($CDCl_3$, 125 MHz)

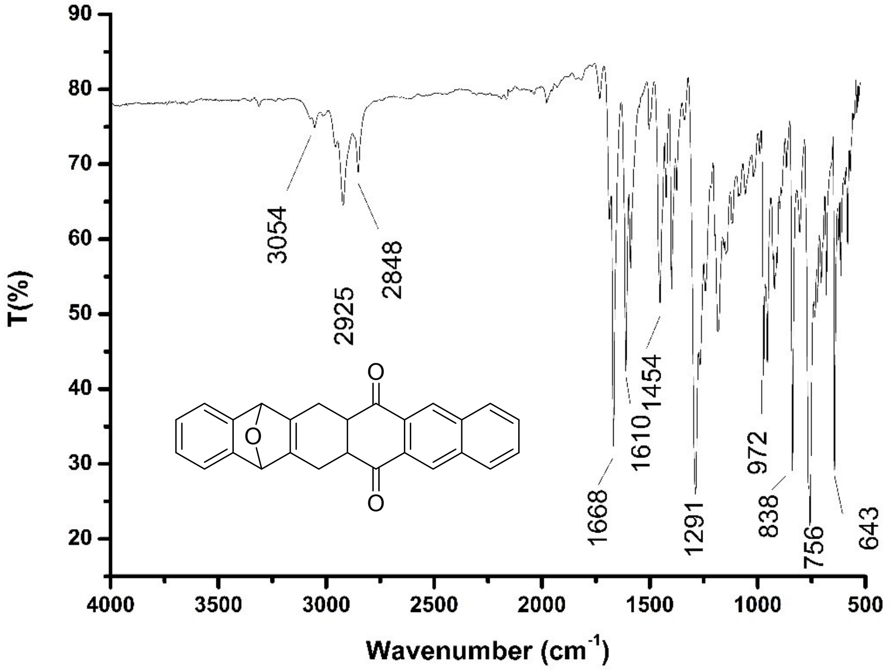


Figure S14 IR spectrum of compound 4

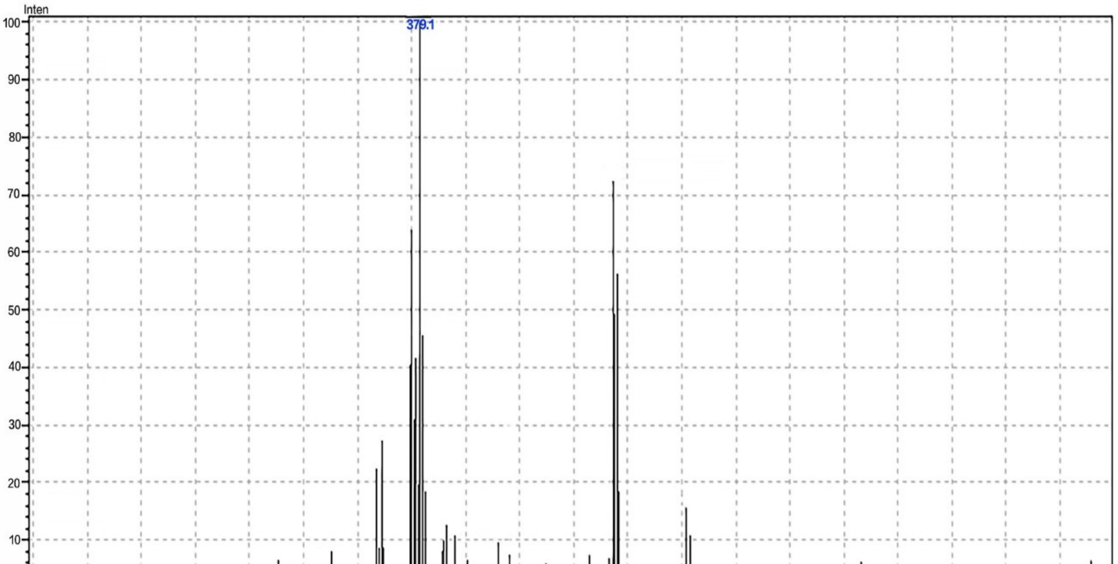


Figure S15 APCI Mass Spectrometry of compound 4

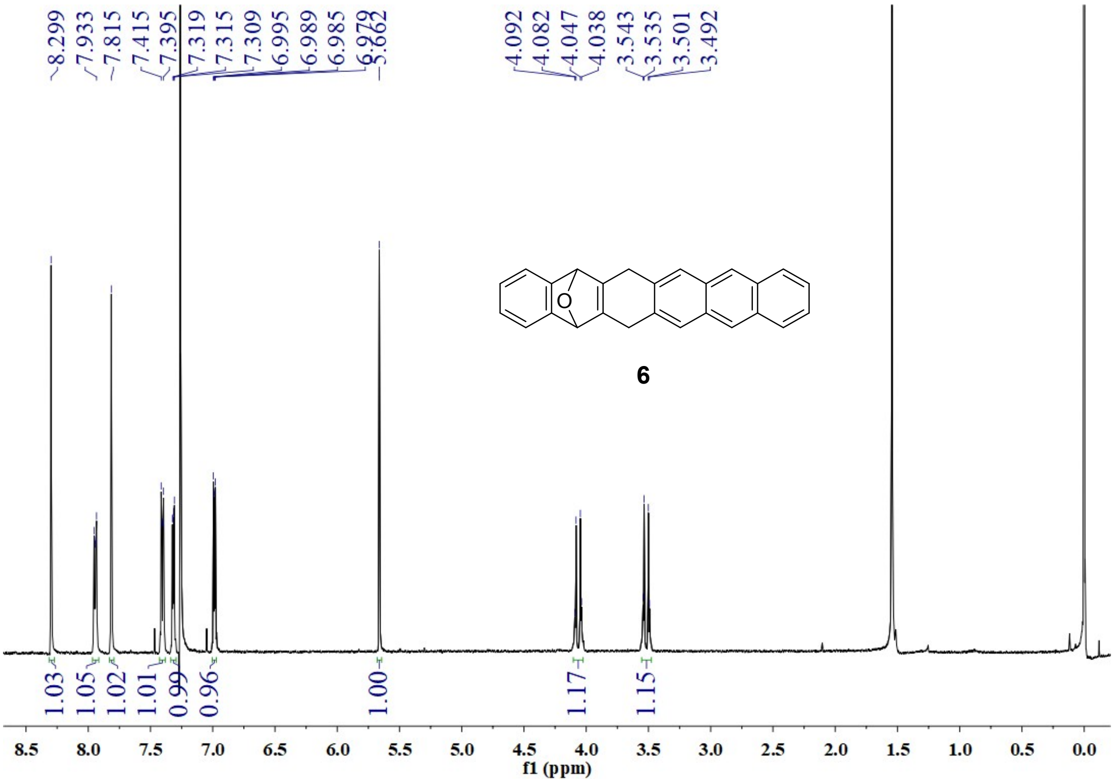


Figure S16 ^{1}H NMR spectrum of compound 6 ($CDCl_3$, 500 MHz)

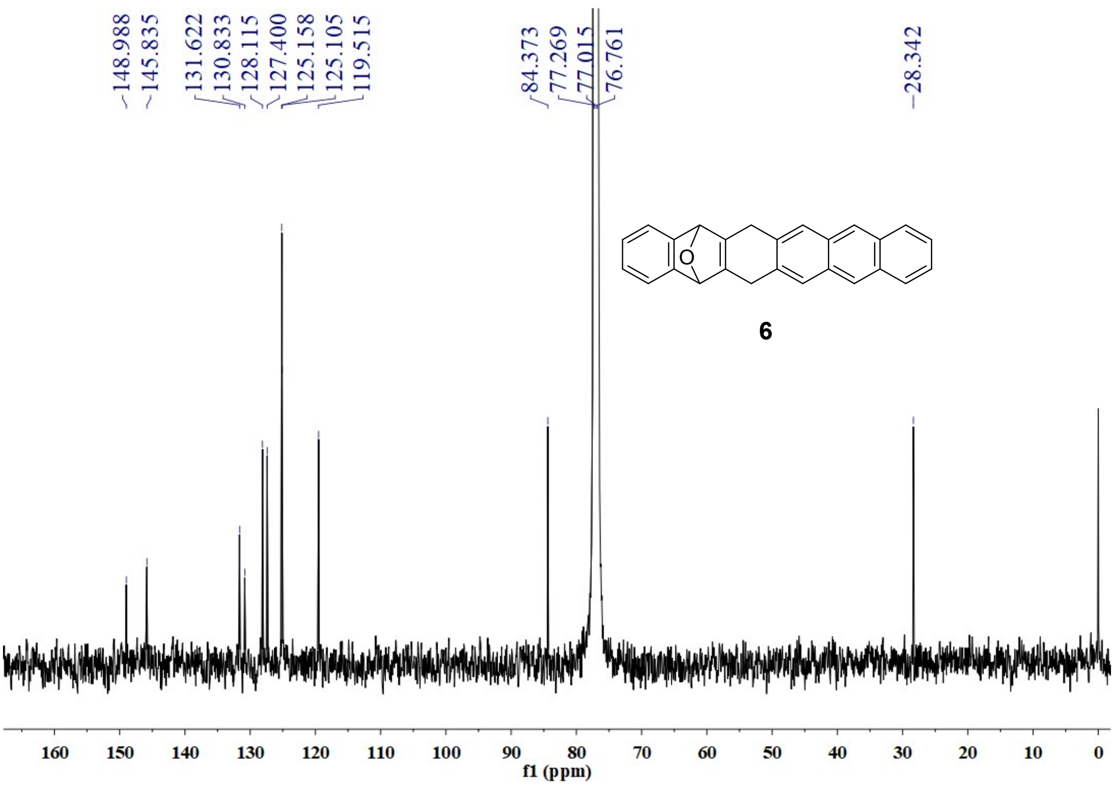


Figure S17 ^{13}C NMR spectrum of compound 6 ($CDCl_3$, 125 MHz)

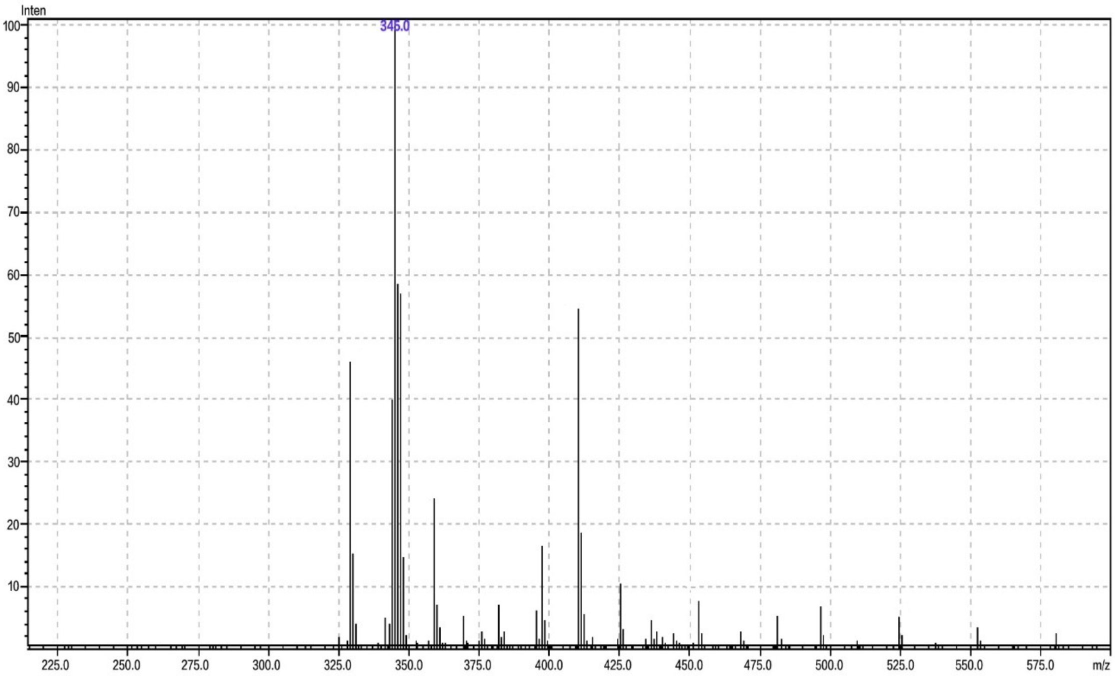


Figure S18 APCI Mass Spectrometry of compound 6

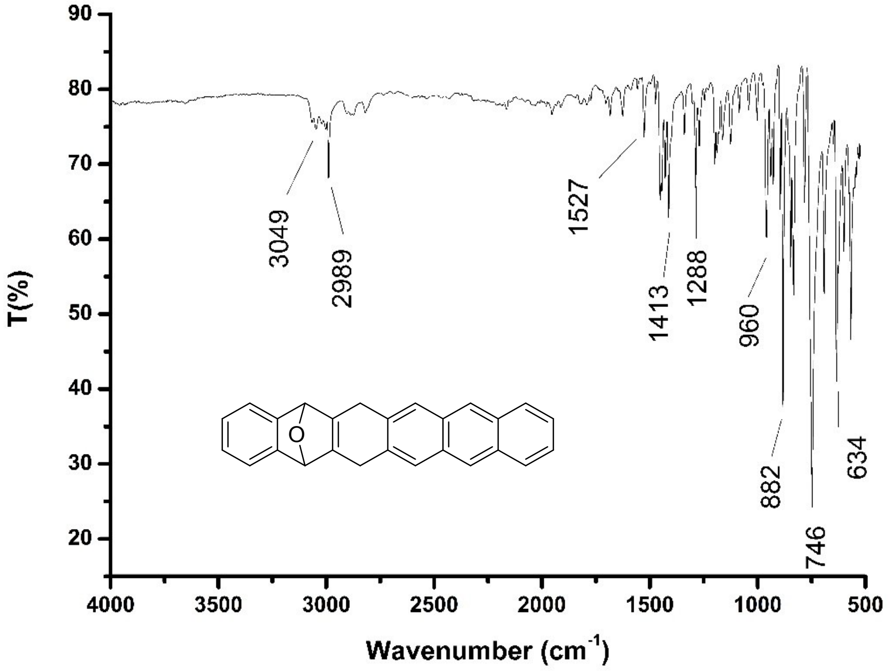


Figure S19 IR spectrum of compound 6

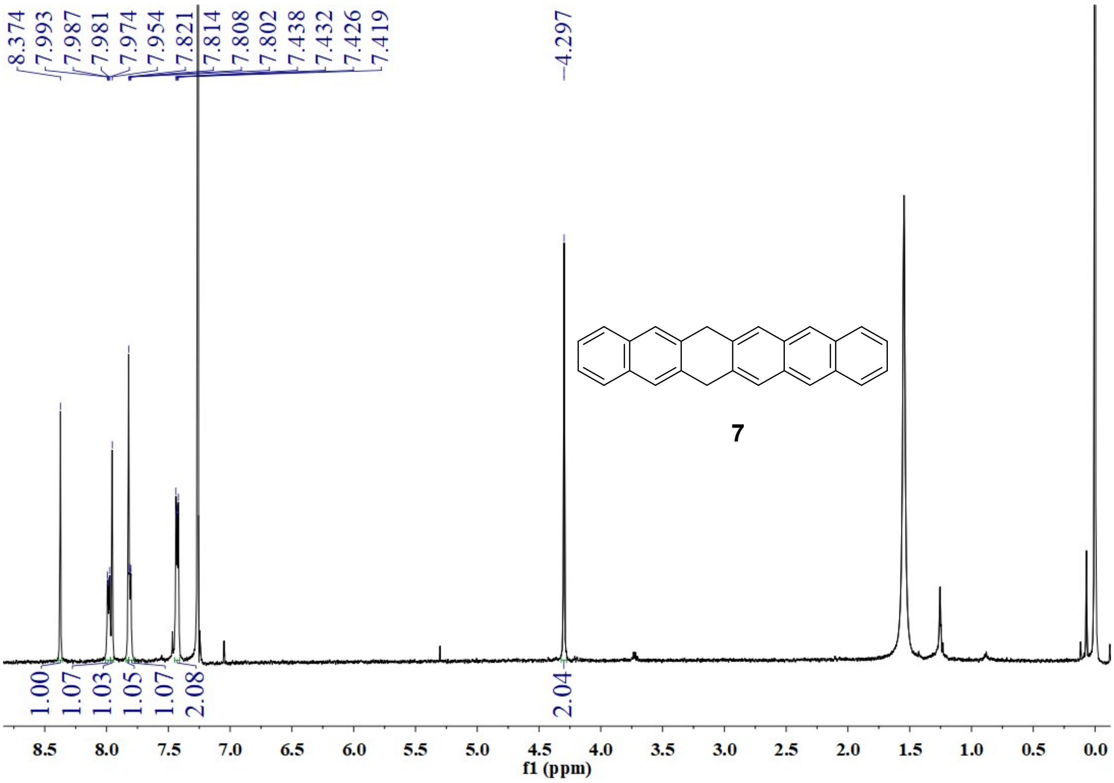


Figure S20 ^{1}H NMR spectrum of compound 7 ($CDCl_3$, 500 MHz)

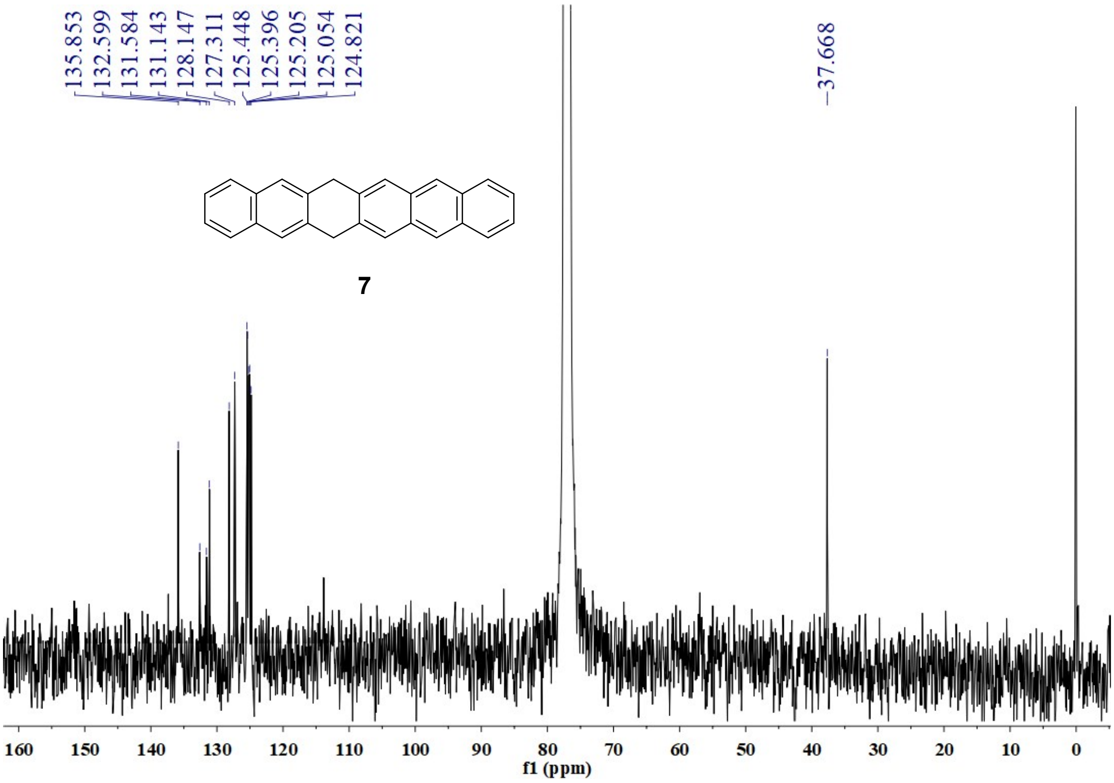


Figure S21 ^{13}C NMR spectrum of compound 7 ($CDCl_3$, 125 MHz)

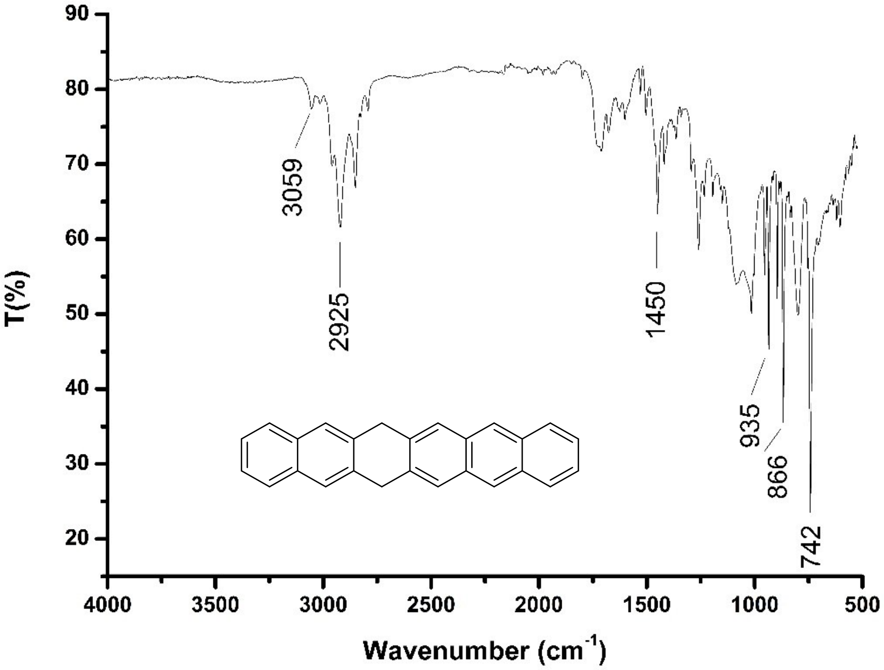


Figure S22 IR spectrum of compound 7

5. X-ray Crystal Structure and Data of Compound 6

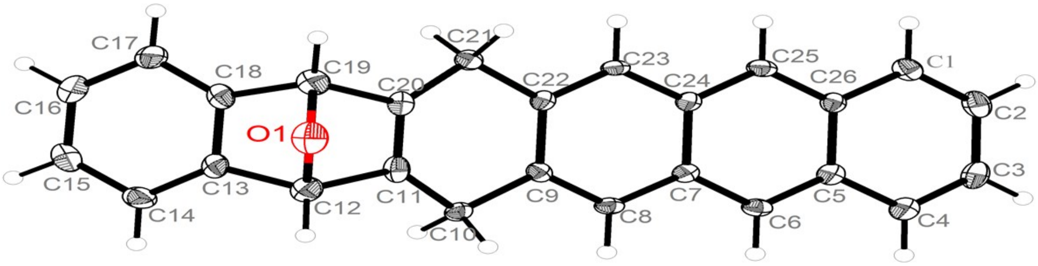


Figure S23 ORTEP diagram of 6 Color code: Carbon (grey), Oxygen (red), Nitrogen (blue)

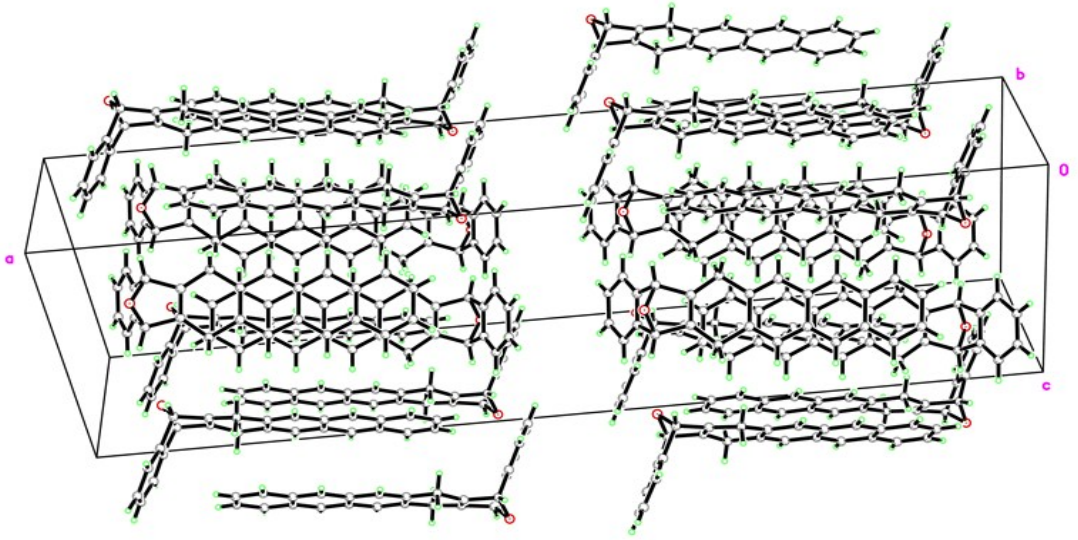


Figure S24 Crystal packing of 6

Table S1. Crystal data and structure refinement for **6**

Compound	6
Empirical formula	$C_{26} H_{18}O$
Formula weight	346.40
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C12/c1
Unit cell dimensions	a = 42.263(3) Å alpha = 90 deg.
	b = 7.4986(7) Å beta = 93.813(3) deg.
	c = 12.0012(10) Å gamma = 90 deg.
Volume	3794.92(60) $Å^3$
Z	8
Calculated density	1.21252 g/cm^3

Absorption coefficient	0.072 mm^{-1}
F(000)	1456
Crystal size	0.22 × 0.19 × 0.02 mm
Theta range for data collection	2.759 to 25.009 deg.
Limiting indices	-38≤h≤50， -8≤k≤8， -13≤l≤14
Data / restraints / parameters	3339/0/244
Goodness-of-fit on F^2	1.022
Final R indices [I>2sigma(I)]	R1 = 0.0784，wR2 = 0.1726
R indices (all data)	R1 = 0.0580，wR2 = 0.1579
Largest diff. peak and hole	0.388 and -0.478 e Å^{-3}

Table S2. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for **6**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	0.82390(7)	0.5026(4)	0.4815(2)	0.0184
C(2)	0.85382(7)	0.4514(4)	0.5170(2)	0.0209
C(3)	0.85901(7)	0.3476(4)	0.6158(2)	0.0207
C(4)	0.83419(6)	0.2971(4)	0.6755(2)	0.0185
C(5)	0.80246(6)	0.3488(4)	0.6414(2)	0.0140
C(6)	0.77655(6)	0.2980(4)	0.7003(2)	0.0155
C(7)	0.74571(6)	0.3496(4)	0.6661(2)	0.0130
C(8)	0.71897(6)	0.2977(4)	0.7241(2)	0.0143
C(9)	0.68872(6)	0.3479(4)	0.6904(2)	0.0141
C(10)	0.66165(6)	0.2792(4)	0.7553(2)	0.0172
C(11)	0.63099(6)	0.3644(4)	0.7184(2)	0.0192
C(12)	0.59807(7)	0.3298(4)	0.7608(3)	0.0227
C(13)	0.58022(6)	0.2110(4)	0.6730(2)	0.0195
C(14)	0.56950(7)	0.0389(4)	0.6722(3)	0.0234
C(15)	0.55334(7)	-0.0235(4)	0.5732(3)	0.0256
C(16)	0.54926(7)	0.0846(4)	0.4803(3)	0.0254
C(17)	0.56059(6)	0.2607(4)	0.4818(3)	0.0227
C(18)	0.57567(6)	0.3214(4)	0.5793(2)	0.0195
C(19)	0.59032(7)	0.4992(4)	0.6163(3)	0.0223
C(20)	0.62621(6)	0.4691(4)	0.6301(2)	0.0175
C(21)	0.65046(6)	0.5233(4)	0.5527(2)	0.0163
C(22)	0.68348(6)	0.4594(4)	0.5931(2)	0.0134
C(23)	0.70879(6)	0.5103(3)	0.5357(2)	0.0139
C(24)	0.74048(6)	0.4585(4)	0.5679(2)	0.0132
C(25)	0.76636(7)	0.5074(4)	0.5081(2)	0.0154
C(26)	0.79727(6)	0.4557(4)	0.5422(2)	0.0145
O(1)	0.58279(5)	0.5006(3)	0.73323(18)	0.0184

Table S3 Bond lengths [Å] and angles [deg] for **6**.

Bond	（Å）	Bond	（Å）
C(1)-C(2)	1.362(4)	C(12)-H(12)	0.9800
C(1)-C(26)	1.424(4)	C(13)-C(14)	1.367(4)
C(1)-H(1)	0.9300	C(13)-C(18)	1.399(4)
C2-C(3)	1.423(4)	C(14)-C(15)	1.410(4)
C(2)-H(2)	0.9300	C(14)-H(14)	0.9300
C(3)-C(4)	1.363(4)	C(15)-C(16)	1.380(4)
C(3)-H(3)	0.9300	C15-H(15)	0.9300
C(4)-C(5)	1.429(4)	C(16)-C(17)	1.404(5)
C(4)-H(4)	0.9300	C(16)-H(16)	0.9300
C(5)-C(6)	1.395(4)	C(17)-C(18)	1.372(4)
C(5)-C(26)	1.441(4)	C(17)-H(17)	0.9300
C(6)-C(7)	1.395(4)	C(18)-C(19)	1.524(4)
C(6)-H(6)	0.9300	C(19)-O(1)	1.459(4)
C(7)-C(8)	1.420(4)	C(19)-C(20)	1.531(4)
C(7)-C(24)	1.439(4)	C(19)-H(19)	0.9800
C(8)-C(9)	1.368(4)	C(20)-C(21)	1.486(4)
C(8)-H(8)	0.9300	C(21)-C(3)	1.524(4)
C(9)-C(22)	1.441(4)	C(21)-H(21A)	0.9700
C(9)-C(10)	1.516(4)	C(21)-H(21B)	0.9700
C(10)-C(11)	1.485(4)	C(22)-C(23)	1.365(4)
C(10)-H(10A)	0.9700	C(23)-C(24)	1.423(4)
C(10)-H(10B)	0.9700	C(23)-H(23)	0.9300
C(11)-C(20)	1.323(4)	C(24)-C(25)	1.397(4)
C(11)-C(12)	1.535(4)	C(25)-C(26)	1.398(4)
C(12)-O(1)	1.463(4)	C(25)-H(25)	0.9300
C(12)-C(3)	1.538(4)		

angles	（deg）	angles	（deg）
C(1)-O(1)-H(1)	104(2)	C(13)-C(8)-C(9)	119.3(3)
C(2)-C(1)-C(26)	121.3(3)	C(13)-C(14)-H(14)	121.300
C(2)-C(1)-H(1)	119.300	C(15)-C(14)-H(14)	121.300
C(26)-C(1)-H(1)	119.300	C(16)-C(15)-C(14)	120.9(3)
C(1)-C(2)-C(3)	120.2(3)	C(16)-C(15)-H(15)	119.600
C(1)-C(2)-H(2)	119.900	C(14)-C(15)-H(15)	119.600
C(3)-C(2)-H(2)	119.900	C(15)-C(16)-C(17)	121.2(3)
C(4)-C(3)-C(2)	120.6(3)	C(15)-C(16)-H(16)	119.400
C(4)-C(3)-H(3)	119.700	C(17)-C(16)-H(16)	119.400
C(2)-C(3)- H(3)	119.700	C(18)-C(17)-C(16)	117.5(3)
C(3)-C(4)-C(5)	121.0(3)	C(18)-C(17)-H(17)	121.300
C(3)-C(4)-H(4)	119.500	C(16)-C(17)-H(17)	121.300
C(5)-C(4)-H(4)	119.500	C(17)-C(18)-C(13)	121.4(3)

C(6)-C(5)-C(4)	122.3(3)	C(17)-C(18)-C(19)	134.0(3)
C(6)-C(5)-C(26)	119.3(2)	C(13)-C(18)-C(19)	104.6(3)
C(4)-C(5)-C(56)	118.4(2)	O(1)-C(19)-C(18)	100.1(2)
C(7)-C(6)-C(5)	121.6(3)	O(1)-C(19)-C(20)	100.1(2)
C(7)-C(6)-H(6)	119.200	C(1)-C(19)-C(20)	106.4(2)
C(5)-C(6)-H(6)	119.200	O1-C(19)-H(19)	116.000
C(6)-C(7)-C(8)	122.5(2)	C(18)-C(19)-H(19)	116.000
C(6)-C(7)-C(24)	119.2(2)	C(20)-C(19)-H(19)	116.000
C(8)-C(7)-C(24)	118.2(2)	C(11)-C(20)-C(21)	126.0(3)
C(9)-C(8)-C(7)	122.6(3)	C(11)-C(20)-C(19)	105.8(2)
C(10)-C(8)-H(8)	118.700	C(21)-C(20)-C(19)	127.7(3)
C(7)-C(8)-H(8)	118.700	C(20)-C(21)-C(22)	111.7(2)
C(8)-C(9)-C(22)	119.3(2)	C(20)-C(21)-H(21A)	109.300
C(8)-C(9)-C(10)	118.5(2)	C(22)-C(21)-H(21A)	109.300
C(22)-C(9)-C(10)	122.2(2)	C(20)-C(21)-H(21B)	109.300
C(11)-C(10)-C(9)	112.0(2)	C(22)-C(21)-H(21B)	109.300
C(11)-C(10)-H(10A)	109.200	H(21A)-C(21)-H(21B)	107.900
C(9)-C(10)-H(10A)	109.200	C(23)-C(22)-C(9)	119.2(2)
C(11)-C(10)-H(10B)	109.200	C(23)-C(22)-C(21)	118.9(2)
C(9)-C(10)-H(10B)	109.200	C(9)-C(22)-C(21)	121.9(2)
H(10A)-C(10)-H(10B)	107.900	C(22)-C(23)-C(24)	122.8(2)
C(20)-C(11)-C(10)	125.3(3)	C(22)-C(23)-H(23)	118.600
C(20)-C(11)-C(12)	105.8(2)	C(24)-C(23)-H(23)	118.600
C(10)-C(11)-C(12)	128.3(3)	C(25)-C(24)-C(23)	122.9(3)
O(1)-C(12)-C(11)	100.0(2)	C(25)-C(24)-C(7)	119.2(2)
O(1)-C(12)-C(13)	99.4(2)	C(23)-C(24)-C(7)	117.9(2)
C(11)-C(12)-C(13)	106.6(2)	C(24)-C(25)-C(26)	121.7(3)
O(1)-C(12)-H(12)	116.200	C(24)-C(25)-H(25)	119.100
C(11)-C(12)-H(12)	116.200	C(26)-C(25)-H(25)	119.100
C(13)-C(12)-H(12)	116.200	C(25)-C(26)-C(1)	122.5(3)
C(14)-C(13)-C(18)	121.7(3)	C(25)-C(26)-C(5)	119.0(2)
C(14)-C(13)-C(12)	134.3(3)	C(1)-C(26)-C(5)	118.5(2)
C(18)-C(13)-C(12)	104.0(3)	C(19)-O(1)-C(12)	95.2(2)
C(13)-C(14)-C(15)	117.4(3)		

Table S4 Anisotropic displacement parameters (Å^2) for B

Anisotropic displacement parameters (Å^2) for **6**.

	U11	U22	U33	U12	U13	U23
C(1)	0.0202(15)	0.0177(15)	0.0176(15)	-0.0021(12)	0.0047(11)	-0.0020(12)
C(2)	0.0178(15)	0.0220(16)	0.0238(16)	-0.0035(12)	0.0081(12)	-0.0052(13)
C(3)	0.0133(14)	0.0213(16)	0.0272(16)	0.0022(12)	-0.0002(12)	-0.0071(13)
C(4)	0.0182(15)	0.0168(14)	0.0204(15)	0.0011(11)	-0.0002(12)	-0.0023(12)
C(5)	0.0163(14)	0.0122(14)	0.0159(14)	0.0013(11)	0.0010(11)	-0.0044(11)
C(6)	0.0195(14)	0.0123(13)	0.0145(14)	0.0010(11)	0.0009(11)	0.0015(11)

C(7)	0.0149(13)	0.0112(13)	0.0127(13)	0.0011(10)	0.0001(10)	-0.0027(11)
C(8)	0.0188(14)	0.0137(14)	0.0103(13)	0.0005(11)	0.0007(11)	0.0003(11)
C(9)	0.0176(14)	0.0120(14)	0.0127(14)	-0.0032(11)	0.0021(11)	-0.0033(11)
C(10)	0.0155(14)	0.0246(15)	0.0112(13)	-0.0027(12)	0.0000(11)	0.0013(12)
C(11)	0.0149(14)	0.0220(15)	0.0211(15)	-0.0035(12)	0.0046(11)	-0.0080(13)
C(12)	0.0157(15)	0.0336(18)	0.0193(15)	-0.0004(13)	0.0044(12)	-0.0018(13)
C(13)	0.0078(13)	0.0286(16)	0.0226(15)	-0.0005(12)	0.0046(11)	0.0000(13)
C(14)	0.0181(15)	0.0269(17)	0.0255(17)	0.0005(13)	0.0040(12)	0.0082(13)
C(15)	0.0202(15)	0.0211(16)	0.0361(19)	-0.0040(13)	0.0055(13)	-0.0003(14)
C(16)	0.0191(15)	0.0307(18)	0.0258(17)	-0.0020(13)	-0.0022(12)	-0.0054(14)
C(17)	0.0144(14)	0.0294(17)	0.0244(16)	0.0022(13)	0.0007(12)	0.0042(14)
C(18)	0.0087(13)	0.0227(15)	0.0276(16)	0.0012(11)	0.0059(11)	0.0004(13)
C(19)	0.0176(15)	0.0207(15)	0.0291(17)	0.0031(12)	0.0041(12)	0.0000(13)
C(20)	0.0138(14)	0.0154(14)	0.0233(16)	0.0000(11)	0.0008(11)	-0.0037(12)
C(21)	0.0173(14)	0.0113(14)	0.0200(15)	0.0001(11)	-0.0010(11)	0.0002(11)
C(22)	0.0144(14)	0.0113(13)	0.0143(14)	-0.0004(11)	-0.0001(11)	-0.0036(11)
C(23)	0.0214(15)	0.0101(13)	0.0096(13)	-0.0008(11)	-0.0023(11)	0.0006(11)
C(24)	0.0156(14)	0.0118(13)	0.0121(14)	-0.0010(11)	0.0003(10)	-0.0029(11)
C(25)	0.0217(15)	0.0129(13)	0.0115(14)	-0.0013(11)	0.0009(11)	0.0006(11)
C(26)	0.0166(14)	0.0125(13)	0.0143(14)	-0.0021(11)	0.0003(11)	-0.0023(11)
O(1)	0.0188(11)	0.0316(13)	0.0352(13)	0.0031(9)	0.0091(9)	-0.0099(10

Table S5 Hydrogen coordinates and isotropic displacement parameters (Å^2) for **6**

	x	y	z	U(eq)
H(1)	0.82081	0.56945	0.41646	0.0220
H(2)	0.87091	0.48445	0.47654	0.0250
H(3)	0.87952	0.31398	0.63986	0.0250
H(4)	0.83795	0.22794	0.73938	0.0220
H(6)	0.77992	0.22795	0.76398	0.0190
H(8)	0.72215	0.22680	0.78745	0.0170
H(10A)	0.65985	0.15116	0.74541	0.0210
H(10B)	0.66629	0.30262	0.83419	0.0210
H(12)	0.59765	0.29080	0.83863	0.0270
H(14)	0.57273	-0.03410	0.73458	0.0280
H(15)	0.54534	-0.13907	0.57054	0.0310
H(16)	0.53882	0.04008	0.41556	0.0300
H(17)	0.55796	0.33349	0.41915	0.0270
H(19)	0.58331	0.60347	0.57209	0.0270
H(21A)	0.65056	0.65228	0.54618	0.0200
H(21B)	0.64493	0.47417	0.47918	0.0200
H(23)	0.70517	0.58184	0.47282	0.0170
H(25)	0.76293	0.57616	0.44392	0.0180

Accession Codes

CCDC 1887661 (**6**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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