Supplementary Information for

Synthesis, electrochemical properties, and crystal packing of perfluororubrene

Zhuoran Zhang,[a] William A. Ogden,[a,b] Victor G. Young, Jr.[b] and Christopher J. Douglas[a]

Department of Chemistry, University of Minnesota – Twin Cities,
207 Pleasant St. SE, Minneapolis, MN 55455
cdouglas@umn.edu
(612) 625-0922

Contents

Part I: General Methods

Chemicals were used as received unless otherwise noted. All oxygen or moisture sensitive reactions were performed under nitrogen atmosphere following standard Schlenk techniques. Anhydrous diethyl ether was purchased from Sigma-Aldrich (ACS reagent, ≥ 99.0%) and used without further purification. Dichloromethane was distilled from CaH_2 prior to use. Bromopentafluorobenzene (99%) was purchased from Synquest Labs, Inc. Methanesulfonic acid (≥99.5%) was purchased from Sigma-Aldrich.

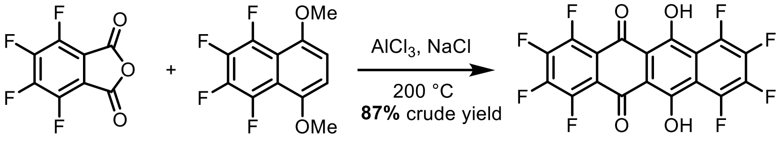
Analytical thin layer chromatography (TLC) was performed using 0.25 mm silica plates from Silicycle. Flash chromatography was performed using 230–400 mesh (particle size 0.04–0.063 mm) silica gel purchased from Silicycle.

^{1}H–NMR (400 or 500 MHz) and ^{13}C–NMR (100 or 125 MHz) spectra were recorded on Bruker FT NMR instruments. ^{19}F–NMR (282 MHz) were recorded on a Varian Inova NMR instrument. All NMR spectra were reported as δ values in ppm referenced to chloroform (7.26 ppm) or tetramethylsilane (TMS, 0.00 ppm) for ^{1}H, chloroform (77.00 ppm) for ^{13}C, and hexafluorobenzene (-163.00 ppm) for ^{19}F NMR. ^{13}C–NMR spectra were obtained using a triple resonance probe with simultaneous ^{1}H and ^{19}F decoupling. In the cases where all fluorine nuclei could not be decoupled simultaneously (the spectral width between the most upfield and downfield resonances was greater than 20 ppm) two ^{13}C spectra were collected with the decoupling frequencies in the ^{19}F set at optimal values to maximize the number of fluorine resonances decoupled.

High-resolution mass spectra (HRMS) in ESI experiments were performed on a Bruker BioTOF II instrument. Low-resolution mass spectra (LRMS) in EI were performed on a MAT 95 (GC/MS) instrument.

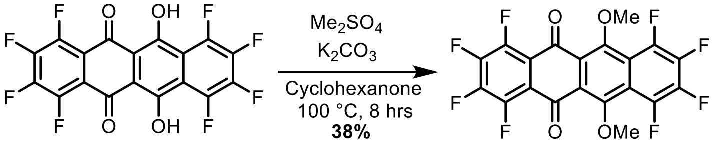
Elemental analysis was performed by Atlantic Microlab, Inc., 6180 Atlantic Blvd, Suite M, Norcross, GA, 30071.

Part II: Experimental procedures for newly synthesized compounds



Synthesis of 1,2,3,4,7,8,9,10-octafluoro-6,11-dihydroxy-5,12-naphthacenedione (**5**)

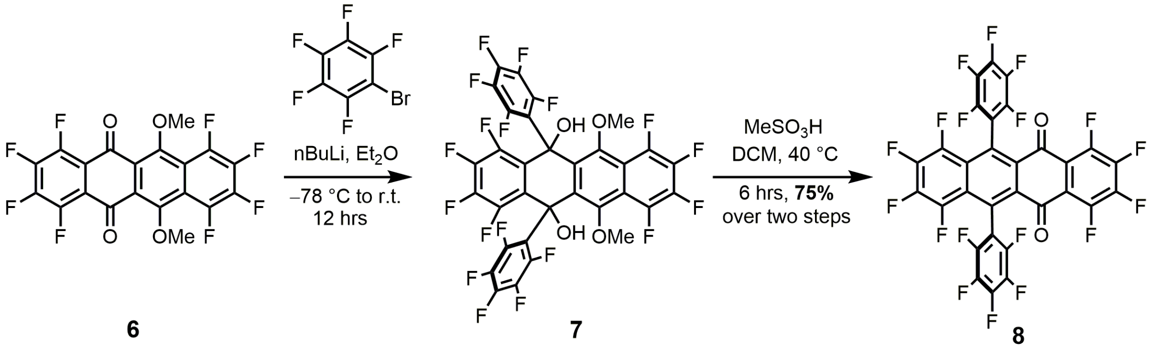
Aluminum trichloride (20.5 g, 154 mmol) and sodium chloride (3.60 g, 61.6 mmol) were mixed in a 250 mL round-bottom flask and heated to 200 °C until molten. A mixture of 1,2,3,4-tetrafluoro-5,8-dimethoxynaphthalene **4** (4.00 g, 15.4 mmol) and tetrafluorophthalic anhydride **3** (4.06 g, 18.4 mmol) were added to the stirred molten salt in small portions. After complete addition of the starting materials, the round-bottom flask was loosely capped and heated with vigorous stirring at 200 °C for one hour. Upon cooling, the reaction mixture was carefully poured into 150 mL ice-cold 1M aqueous HCl. The reaction flask was further rinsed with 50 mL of 1M HCl. All the acidic aqueous solutions were combined and heated to 100 °C for half an hour, until the aqueous phase became light yellow and the formation of red solids ceased. The crude product was collected by vacuum filtration and washed with water and then methanol. The red solid (5.79 g, 87 %) was dried under vacuum and used for the next step without further purification.



Synthesis of 1,2,3,4,7,8,9,10-octafluoro-6,11-methoxy-5,12-naphthacenedione (**6**)

To a 100 mL round-bottom flask was added **5** (5.048 g, 11.63 mmol), K_2CO_3 (16.04 g, 116.3 mmol) and cyclohexanone (100 mL) under nitrogen atmosphere. Dimethyl sulfate (14.67 g, 116.3 mmol) was then transferred to the solution via syringe. The resulting mixture was heated to 100 °C and heating was maintained for 8 hours. Another 11 mL of dimethyl sulfate was added to the reaction mixture in three portions during the course of heating. After the reaction was complete as determined by a color change from dark purple to yellow, the mixture was cooled to room temperature and filtered through celite to remove potassium carbonate. The filtrate was concentrated *in vacuo*. The resulting mixture was then dissolved in 100 mL diethyl ether, followed by slow addition of 15 mL triethylamine. After stirring at room temperature for half an hour, 40 mL 1M HCl was added. The organic layer was separated and washed with sat. aq. NH_4Cl (30 mL), brine (30 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The product was then purified by column chromatography on silica gel (hexane/ethyl acetate = 10/1, v/v) to give **6** as a yellow solid: 2.68 g (38 %).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.12 (s, 6H).
^{13}C-NMR (125 MHz, $CDCl_3$) δ 177.7, 153.1, 146.0, 144.4, 144.2, 141.3, 123.5, 119.9, 119.5, 64.9.
^{19}F-NMR (470 MHz, $CDCl_3$) δ -139.94 to -140.07 (m, 2F), -142.58 to -142.68 (m, 2F), -145.73 to -145.86 (m, 2F), -150.85 to -150.95 (m, 2F).
HRMS (ESI) calcd for $C_{20}H_6F_8O_4$ [M+Na$^+$] *m/z* 485.0031, found [M+Na$^+$] 485.0035.
IR (neat) 2957, 1681, 1648, 1619, 1514 cm^{-1}.
Melting point: 182–184 °C.

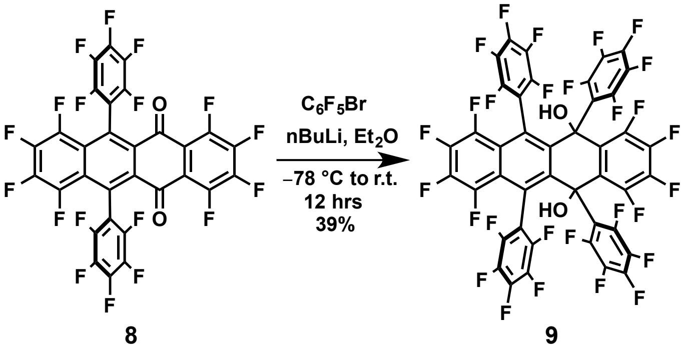


Synthesis of 1,2,3,4,7,8,9,10-octafluoro-6,11-bis(perfluorophenyl)-tetracene-5,12-dione (**8**)

Bromopentafluorobenzene (4.89 g, 19.8 mmol) and 30 mL diethyl ether were added to a flame-dried 250 mL round-bottom flask under nitrogen atmosphere. With stirring, the solution was cooled to –78 °C in a dry ice/acetone cooling bath. *n*-Butyl lithium 2.5 M solution in hexane (7.8 mL, 19.5 mmol) was then transferred dropwise into the solution via syringe. The solution was maintained at –78 °C for an hour before **6** (1.50 g, 3.2 mmol) was added as a solid. By removing the cooling bath, the reaction mixture was allowed to warm to room temperature over 5 hours. After maintaining the solution at room temperature overnight, the mixture was diluted with ethyl acetate (10 mL) and quenched by adding sat. aq. NH_4Cl (20 mL). The organic layer was separated and washed with brine (20 mL × 2). After drying over $MgSO_4$, the solvent was removed *in vacuo* to give crude product as a light yellow solid, which was used in the next step without further purification.

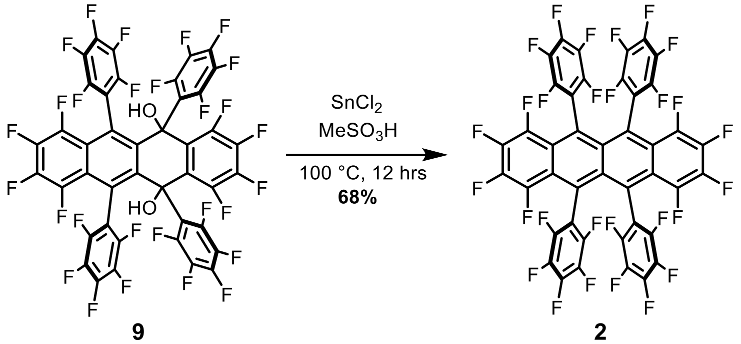
To a flame-dried, nitrogen flushed 100 mL round-bottom flask containing crude product from the previous step was added 20 mL dichloromethane. The flask was capped using a rubber septum with a needle connected to the nitrogen line. Methane sulfonic acid (3 mL) was then transferred into the flask dropwise via syringe, followed by stirring at 40 °C for 3 hours. After the reaction was complete as judged by TLC (hexanes/ethyl acetate = 10/1, $R_f = 0.57$), the solution was washed with water (20 mL × 2), sat. aq. $NaHCO_3$ (20 mL × 2) and brine (10 mL). The organic layer was collected and dried over $MgSO_4$. The solution was concentrated *in vacuo* to give a brown solid that was purified by column chromatography on silica gel (hexanes/DCM = 5/1 to 2/1, v/v) to give **8** as a yellow solid: 1.75 g (75% over two steps).

^{13}C-NMR (125 MHz, $CDCl_3$) δ 178.3, 146.3, 144.9, 144.8, 143.9, 142.0, 141.9, 137.8, 131.6, 125.0, 121.3, 118.9, 111.6.
^{19}F-NMR (282MHz, $CDCl_3$) δ -138.18 to -138.32 (m, 4F), -142.62 to -142.74 (m, 4F), -143.14 to -143.27 (m, 2F), -147.05 to -147.09 (m, 2F), -153.09 (t, $J_1 = J_2 = 19.7$ Hz, 2F), -162.64 to -162.81 (m, 4F).
LRMS (EI) calcd for $C_{30}F_{18}O_2$ [M^+] *m/z* 734.0, found [M^+] 734.0.
IR (neat) 1694, 1621, 1515, 1500, 1485 cm^{-1}.
Melting point: 178–180 °C.



Synthesis of 1,2,3,4,7,8,9,10-octafluoro-5,6,11,12-tetrakis(perfluorophenyl)-5,12-dihydrotetracene-5,12-diol (**9**)

Bromopentafluorobenzene (404 mg, 1.63 mmol) and diethyl ether (anhydrous, 10 mL) were added to a flame-dried 100 mL round-bottom flask under nitrogen atmosphere. The solution was cooled to –78 °C in a dry ice/acetone bath. *n*-Butyl lithium (1.66 mmol, 2.5 M in hexane solution) was then transferred dropwise into the solution via syringe. The resulting solution was maintained at –78 °C for a half an hour and **8** (200 mg, 0.27 mmol) was then added to the solution as a solid. The mixture was allowed to slowly warm to room temperature over 6.5 hours by allowing the cooling bath to expire and then the solution was maintained at room temperature for another 12 hours. After the reaction was complete as judged by TLC (hexane/dichloromethane = 3/1, $R_f = 0.76$), the solution was diluted with diethylether (10 mL), followed by the addition of sat. aq. NH_4Cl (10 mL). The organic layer was separated and washed with deionized water (10 mL) and brine (10 mL). The organic solution was then dried over $MgSO_4$ and concentrated *in vacuo* to give a brown crude product, which was then purified by column chromatography on silica gel (hexane/dichloromethane = 5/1 to 3/1, v/v) to give **9** as colorless solid: 114 mg (39%).



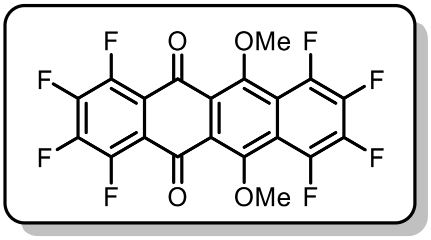
9 **2**

Synthesis of perfluororubrene **2**

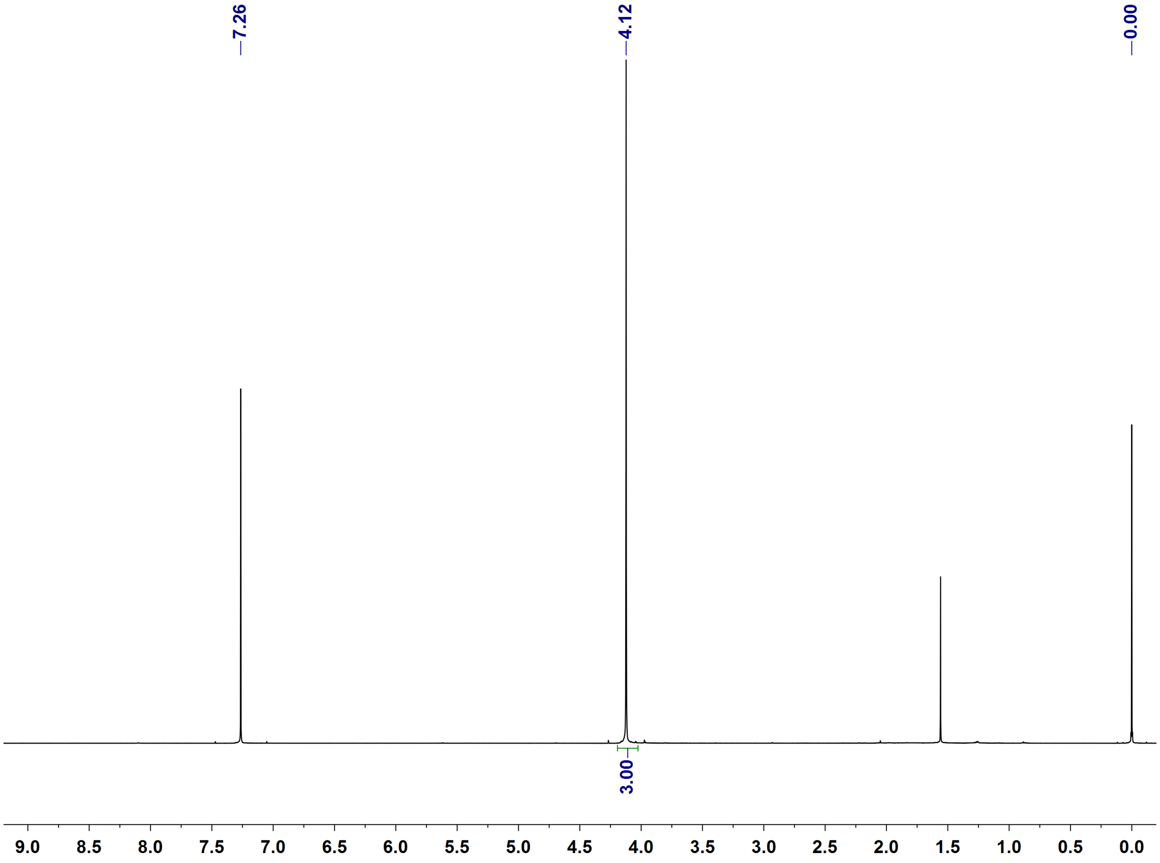
A 20 mL reaction vial was charged with **9** (205 mg, 0.19 mmol), $SnCl_2$ (363 mg, 1.9 mmol) and methanesulfonic acid (5 mL). The vial was then sealed and heated in a 110 °C oil bath for 12 hours. After the reaction was complete as judged by TLC (hexane/dichloromethane = 2/1, $R_f = 0.85$), the mixture was allowed to cool to room temperature and poured into 20 mL 1M aqueous HCl. The resulting red precipitate was collected via vacuum filtration and washed with 5 mL methanol. The crude product was further purified by column chromatography on silica gel (hexane/dichloromethane = 2/1, v/v) to give perfluororubrene (**2**) as a red solid (133 mg, 68%).

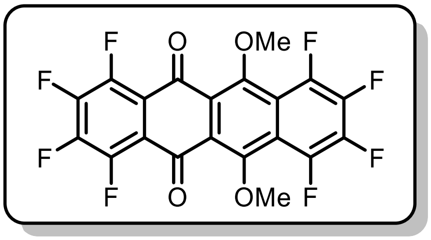
^{13}C-NMR (125 MHz, $CDCl_3$) δ 143.9, 142.2, 141.9, 140.1, 137.2, 130.6, 120.4, 118.9, 113.1.
^{19}F-NMR (282 MHz, $CDCl_3$) δ -138.12 to -138.23 (m, 8F), -143.35 to -143.39 (m, 4F), -150.72 to -150.76 (m, 4F), -151.10 (t, $J_{F\text{-}F}$ = 19.7 Hz, 4F), -162.45 to -162.63 (m, 8F).
LRMS (EI) *m/z* 1036.0 [M^+].
Anal. Calcd for $C_{42}F_{28}$: C, 48.67; F, 51.33. Found: C, 48.21.
IR (neat) 1677, 1575, 1494, 1449, 1417 cm^{-1}.
Melting point: 260–263 °C.

Part III. Copies of NMR and IR spectra of newly synthesized compounds

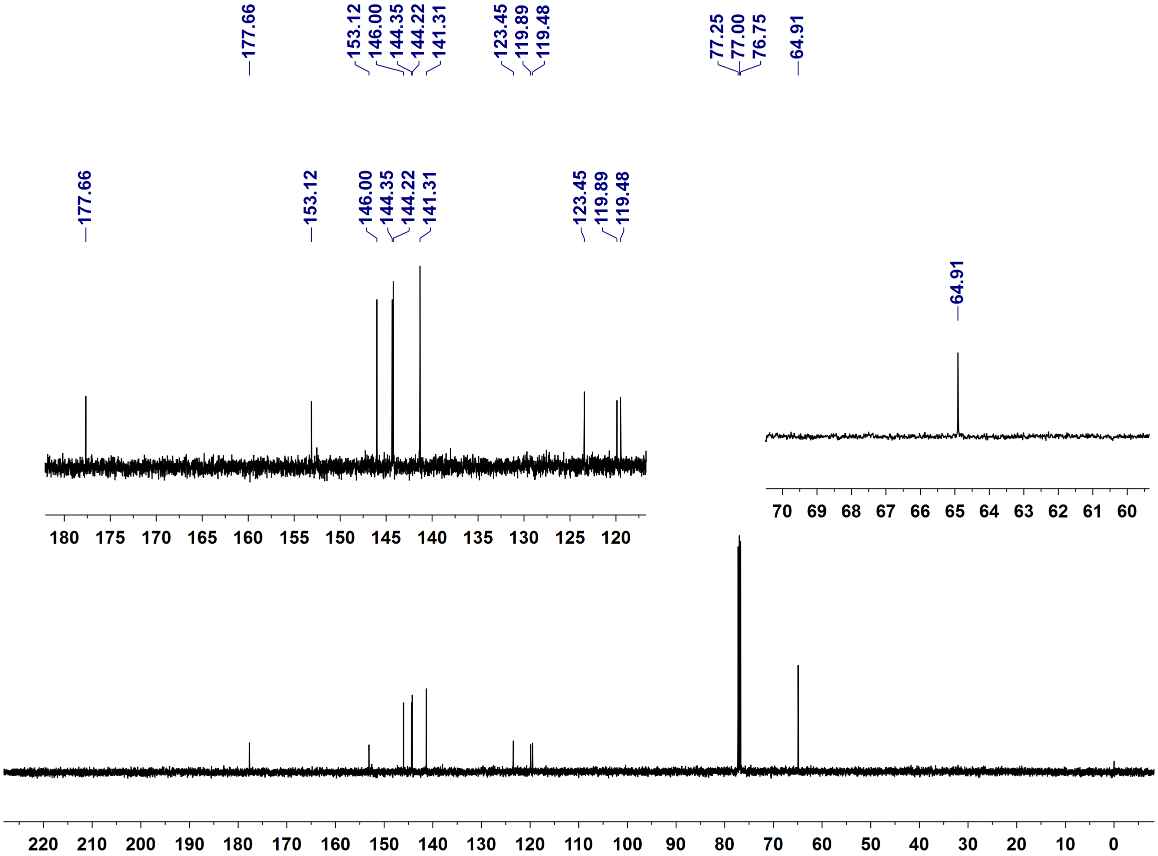


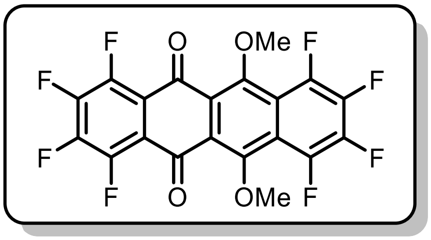
^{1}H-NMR, 500 MHz, $CDCl_3$



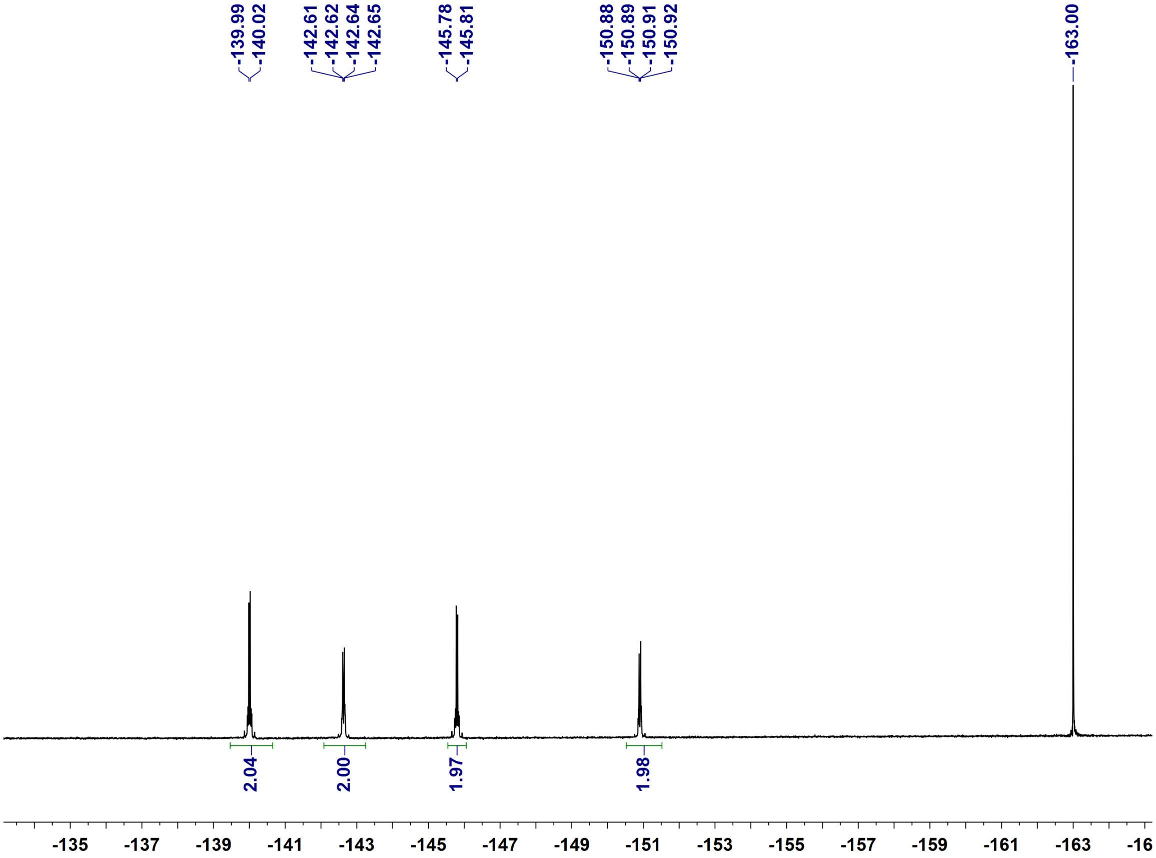


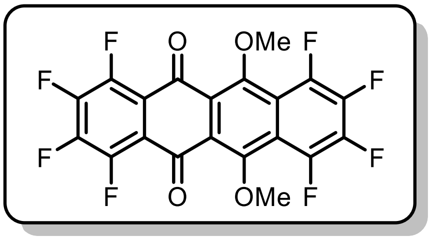
^{13}**C-NMR {^{1}H, ^{19}F}, 125 MHz, CDCl$_3$, decoupler offset = –145 ppm in ^{19}F.**



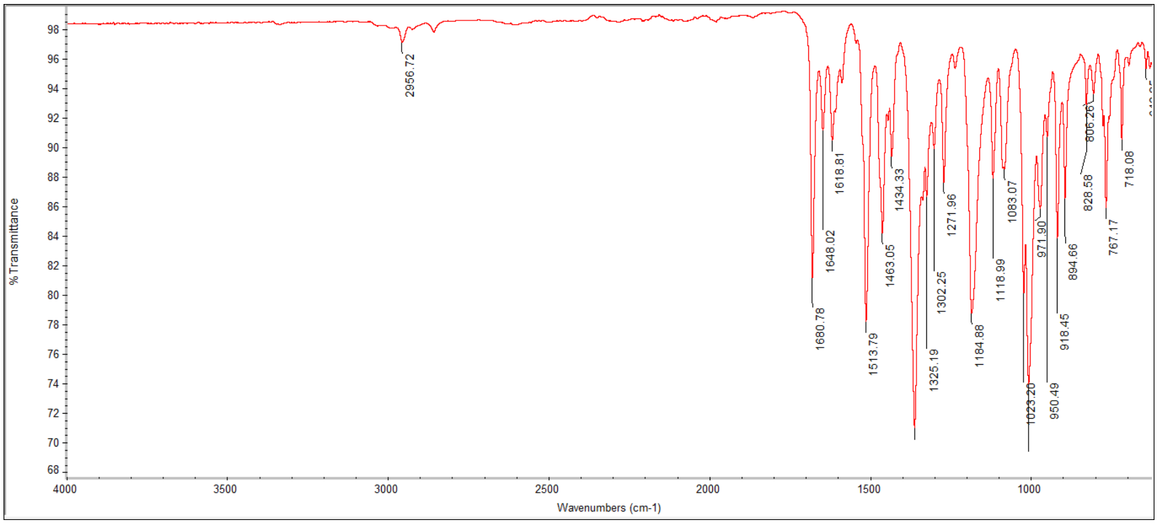


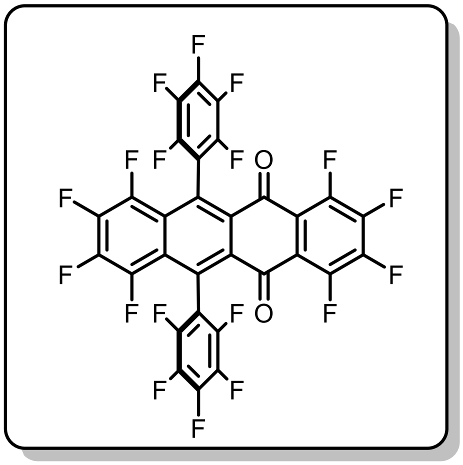
^{19}F-NMR, 282 MHz, CDCl$_3$



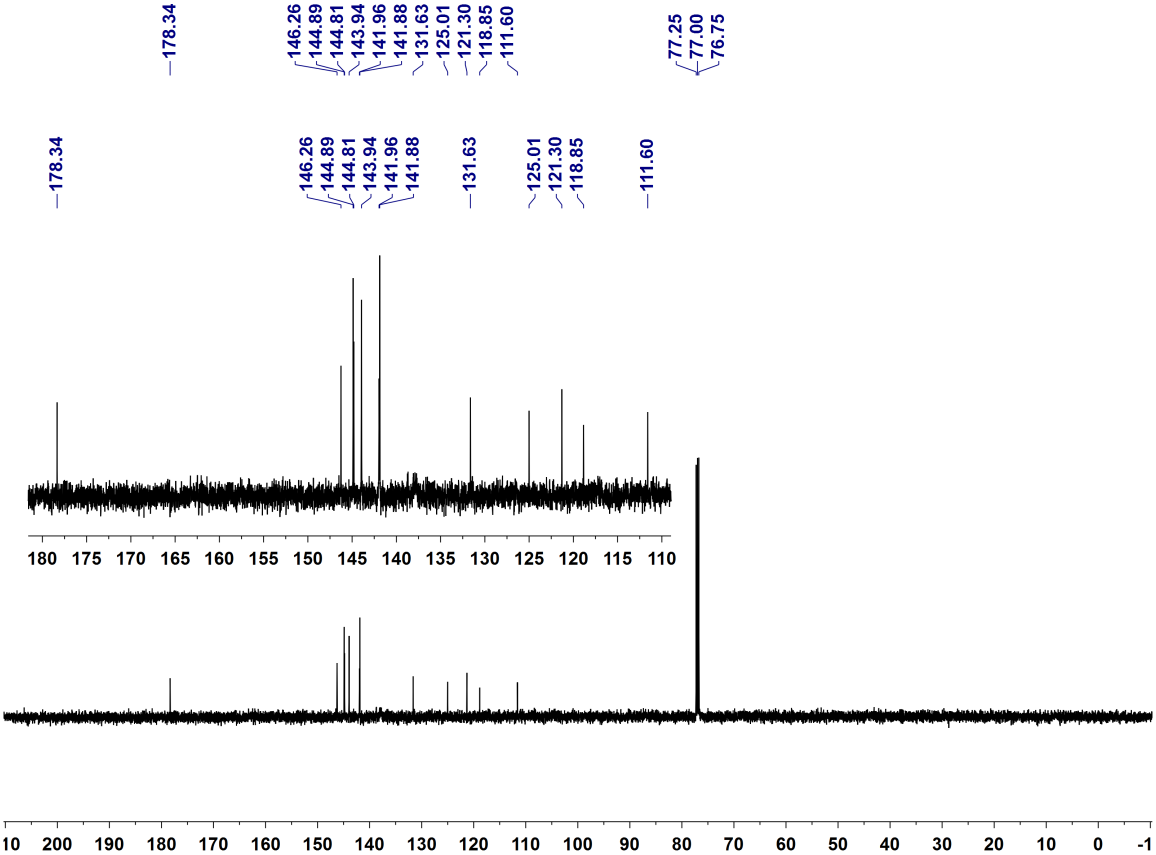

F
O
OMe
F
F
F
F
F
F
O
OMe
F

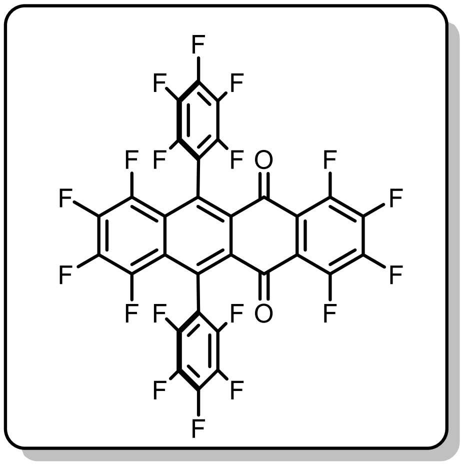
IR


%Transmittance
98
96
94
92
90
88
86
84
82
80
78
76
74
72
70
68
4000
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)
2956.72
1680.78
1648.02
1618.81
1513.79
1463.05
1434.33
1325.19
1302.25
1271.96
1184.88
1118.99
1083.07
1023.20
971.90
950.49
918.45
894.66
828.58
806.26
767.17
718.08

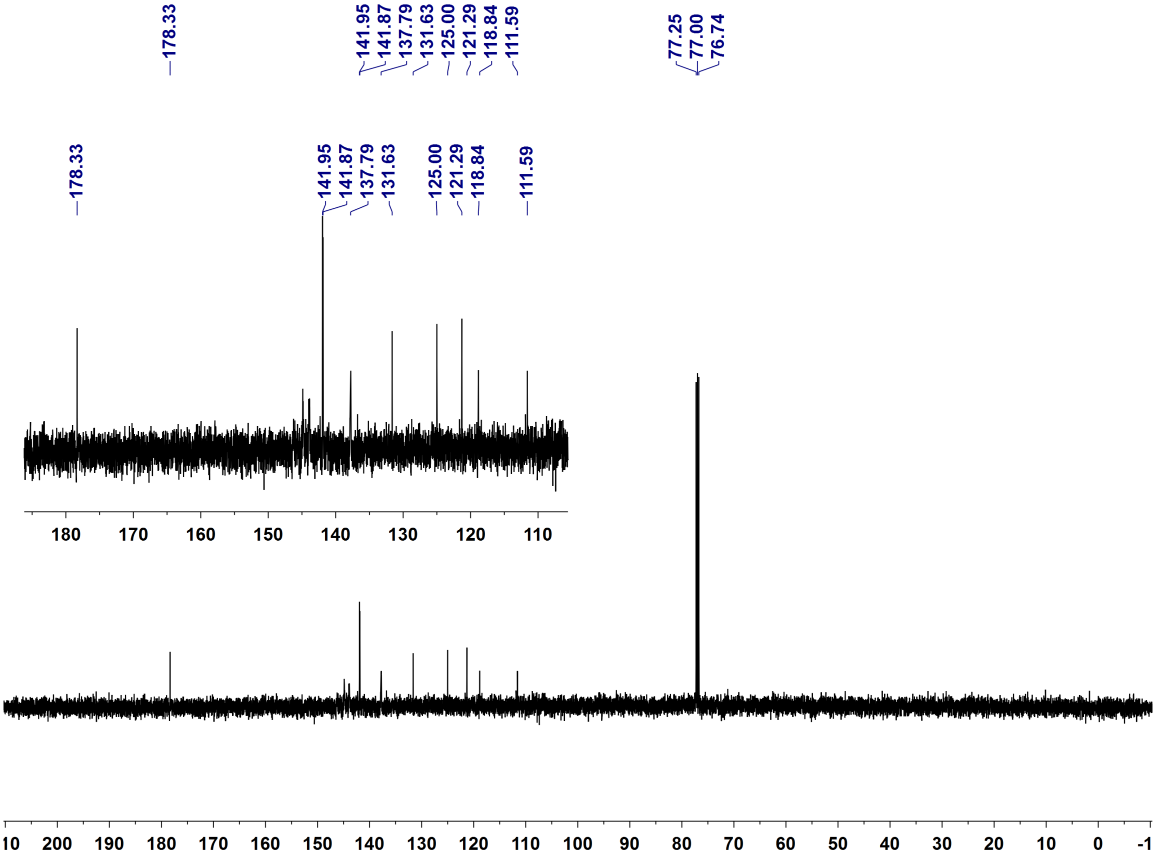


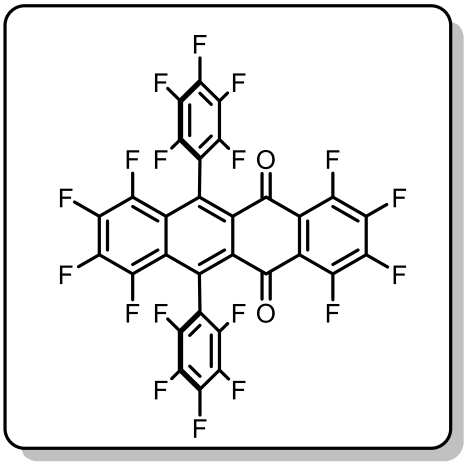
^{13}C-NMR {^{1}H, ^{19}F}, 125 MHz, CDCl$_3$, decoupler offset = –145 ppm in ^{19}F.



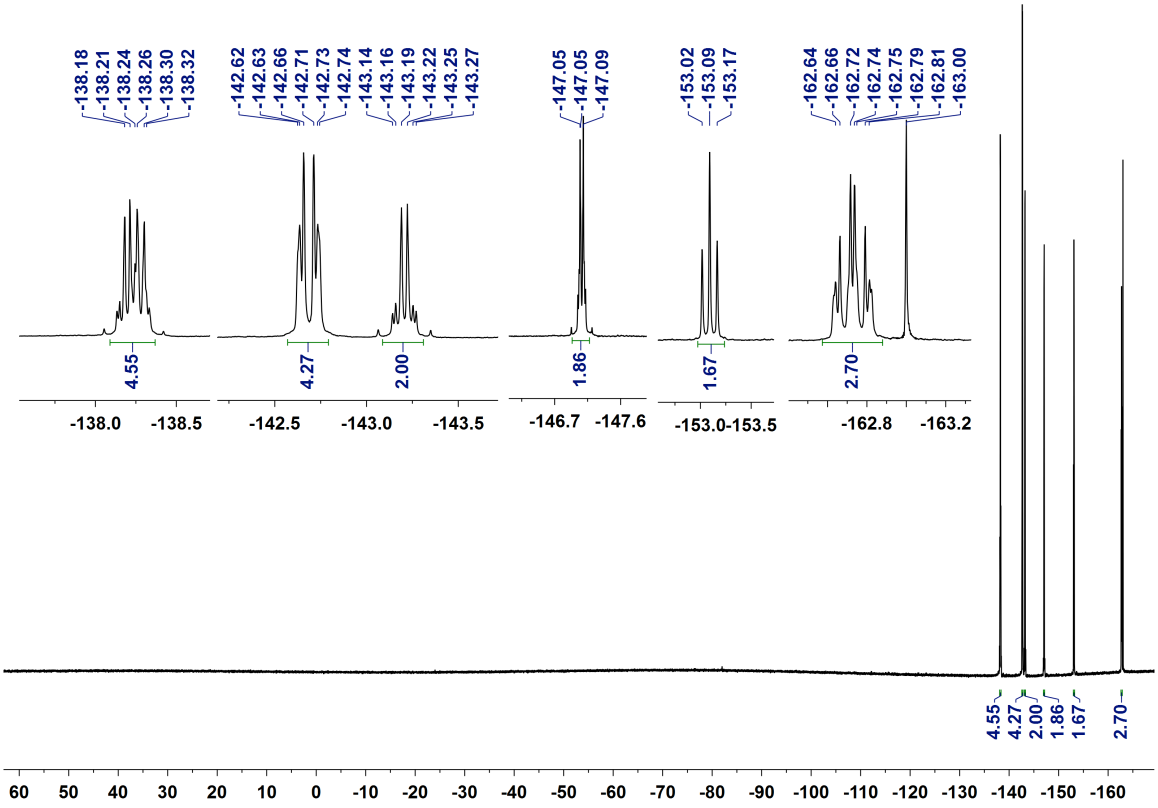


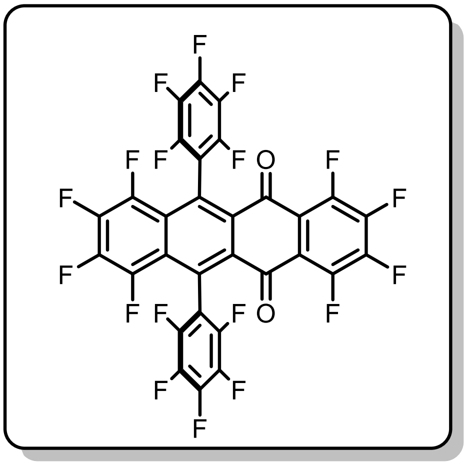
^{13}C-NMR {^{1}H, ^{19}F}, 125 MHz, CDCl$_3$, decoupler offset = –153 ppm in ^{19}F.



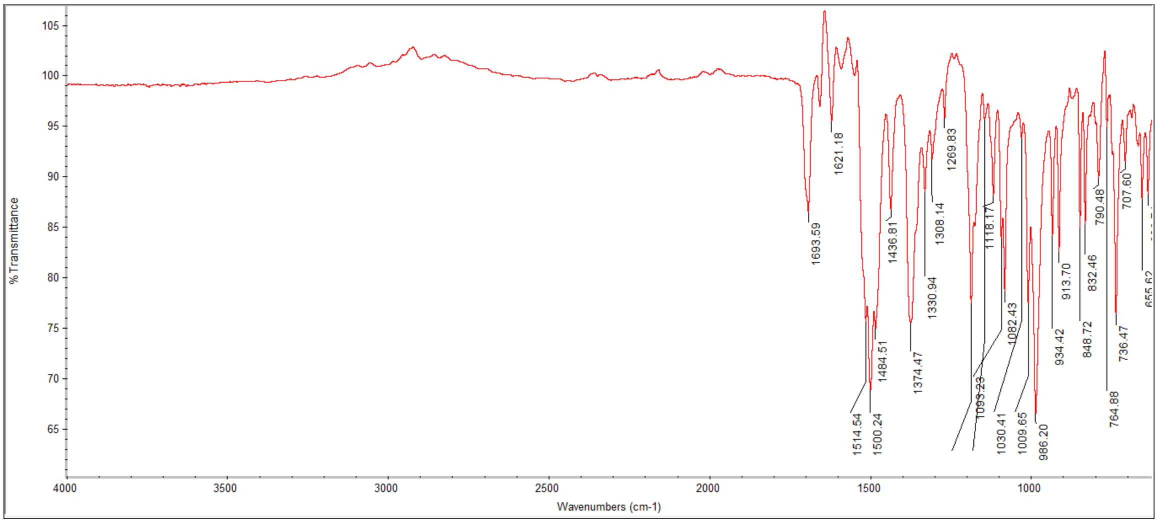


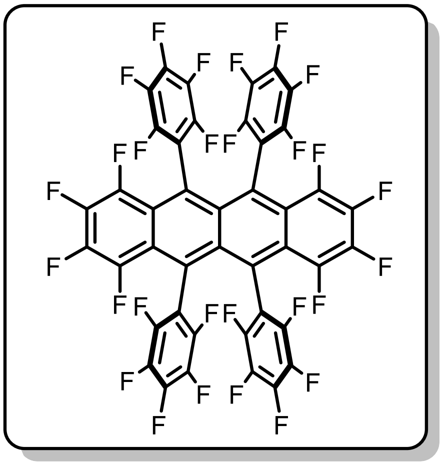
^{19}F-NMR, 282 MHz, CDCl$_3$



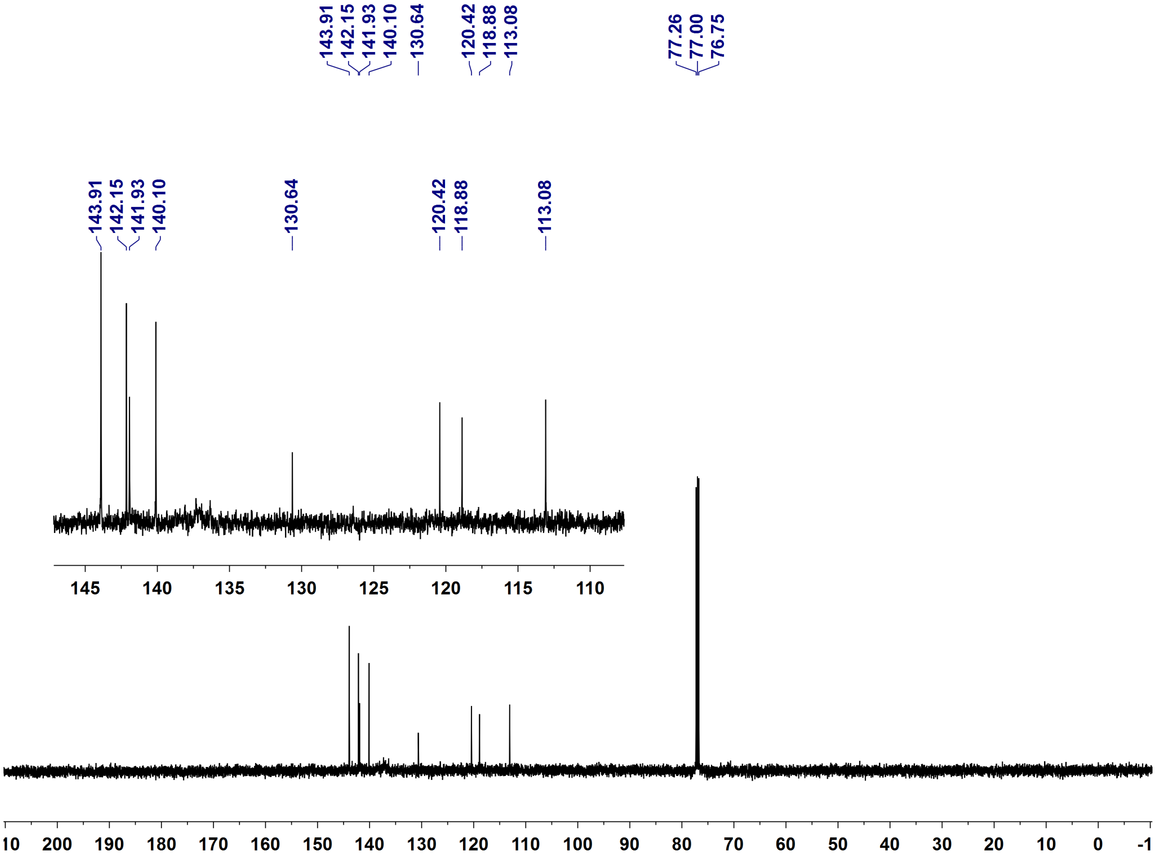

F
F
F
F
F
O
F
F
F
F
F
F
F
F
F
O
F
F
F
F
F

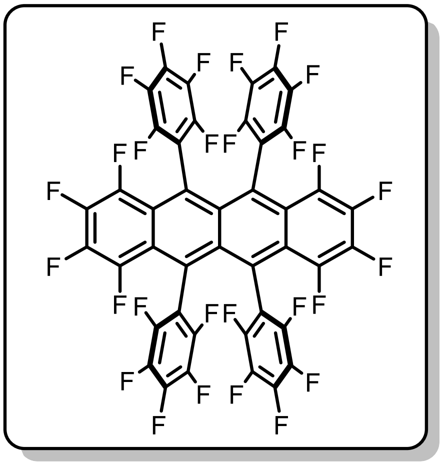
IR


% Transmittance
105
100
95
90
85
80
75
70
65
4000
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)
1693.59
1621.18
1514.54
1500.24
1484.51
1436.81
1374.47
1330.94
1308.14
1269.83
1093.23
1118.17
1082.43
1030.41
1009.65
986.20
934.42
913.70
848.72
832.46
790.48
764.88
736.47
707.60
655.62

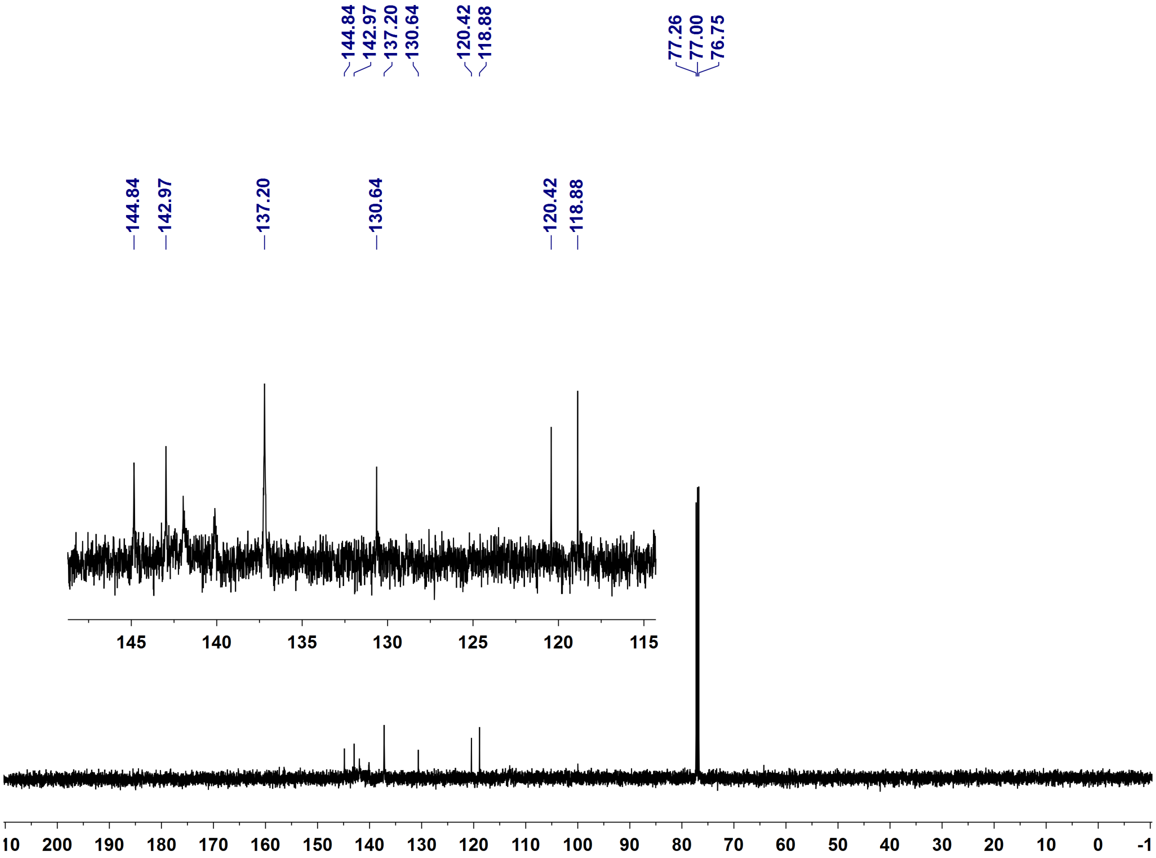


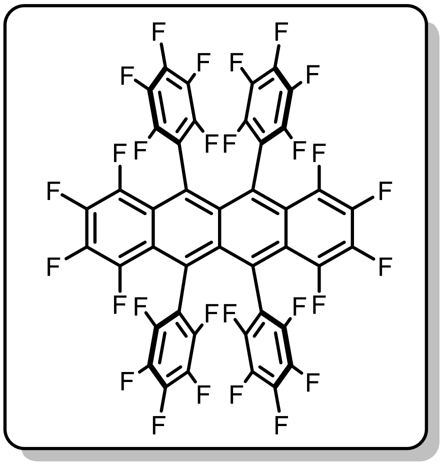
^{13}C-NMR {^{1}H, ^{19}F}, 125 MHz, CDCl$_3$, decoupler offset = –143 ppm in ^{19}F.



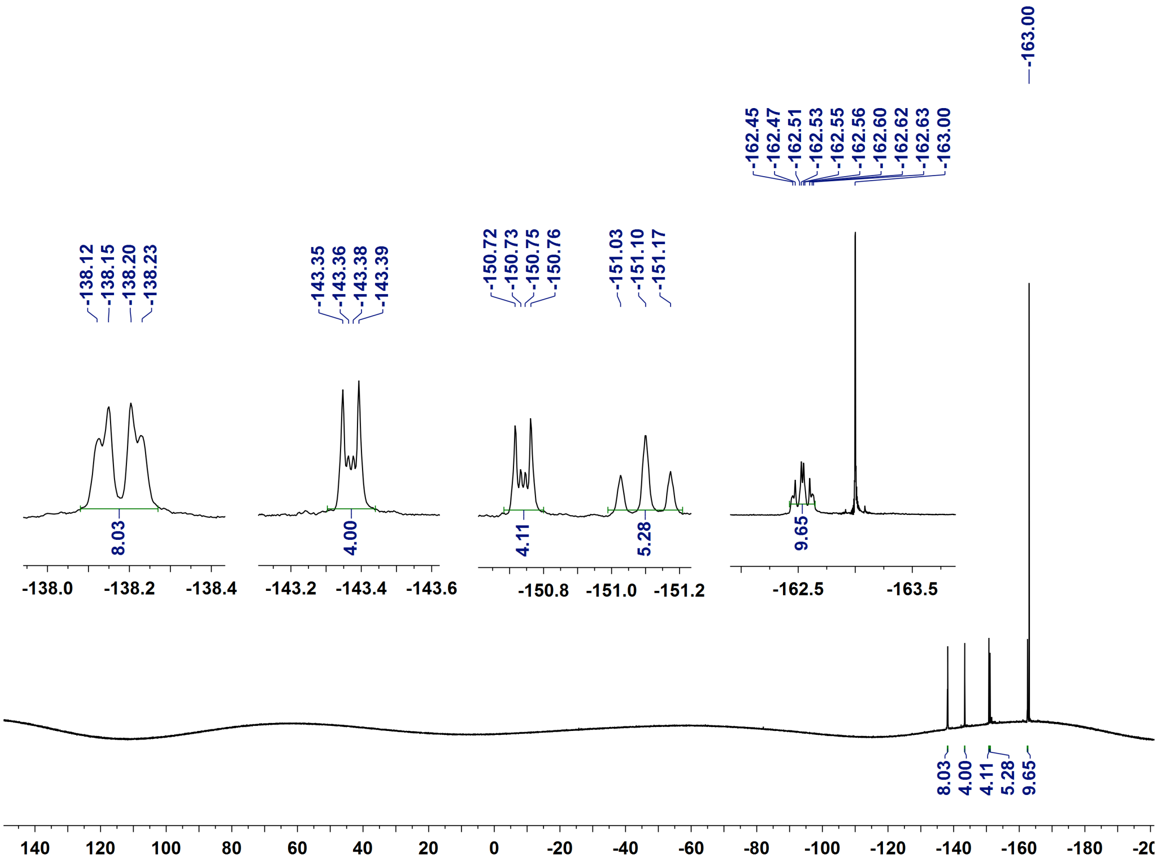


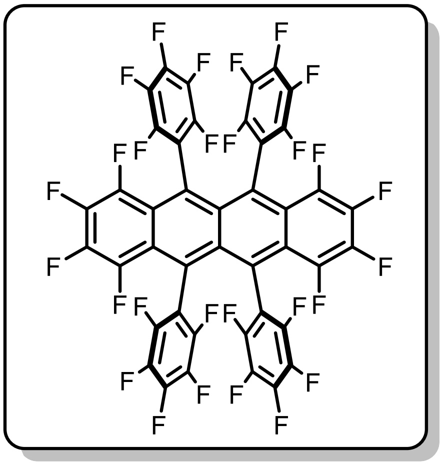
^{13}C-NMR {^{1}H, ^{19}F}, 125 MHz, CDCl$_3$, decoupler offset = –161 ppm in ^{19}F.



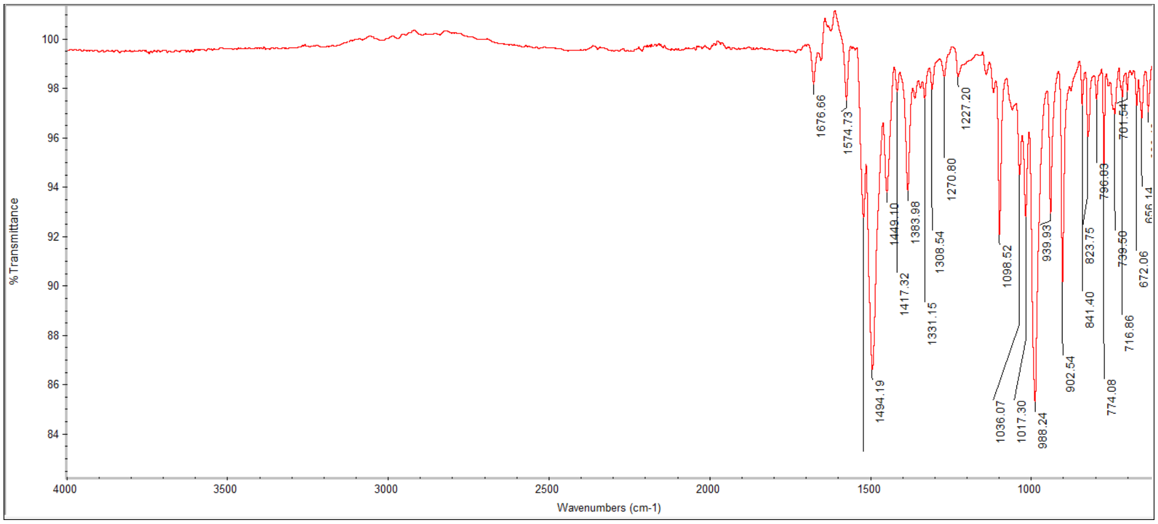


^{19}F-NMR, 282 MHz, CDCl$_3$




F

IR


% Transmittance
100
98
96
94
92
90
88
86
84
4000
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)
1676.66
1574.73
1494.19
1449.10
1417.32
1383.98
1331.15
1308.54
1270.80
1227.20
1098.52
1036.07
1017.30
988.24
939.93
902.54
841.40
823.75
796.03
774.08
739.50
716.86
701.54
672.06
656.14

Part IV: Cyclic voltammograms of rubrene and perfluororubrene

Cyclic voltammograms were recorded on a CHI600C potentiostat. A gold electrode was used as the working electrode, a platinum wire as the counter electrode, and an Ag wire in 10 mM $AgNO_3$/0.1M $TBAClO_4$ in acetonitrile as the reference electrode. The gold electrode was polished with aqueous dispersions of alumina (0.3 and 0.05 μm). Then, the electrode was cleaned in water and ethanol by ultrasonication and dried with nitrogen flow. The scan speed was 50 mV/s. The potential in THF solution was measured with tetrabutylammonium hexafluorophosphate ($TBAPF_6$, 0.1 M) employed as supporting electrolyte. The energy level of Fc/Fc^+ is assumed to be -4.8 eV below the vacuum level. The HOMO/LUMO levels of compound **1** and **2** were estimated from the onset of the first oxidation/reduction peaks.

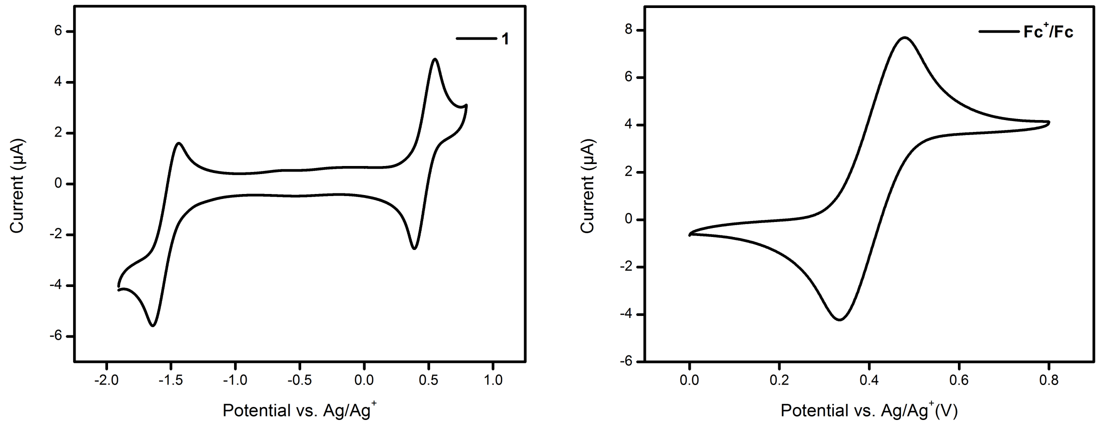


Figure S1. Cyclic voltammogram trace of rubrene (**1**, left) and ferrocene (right).

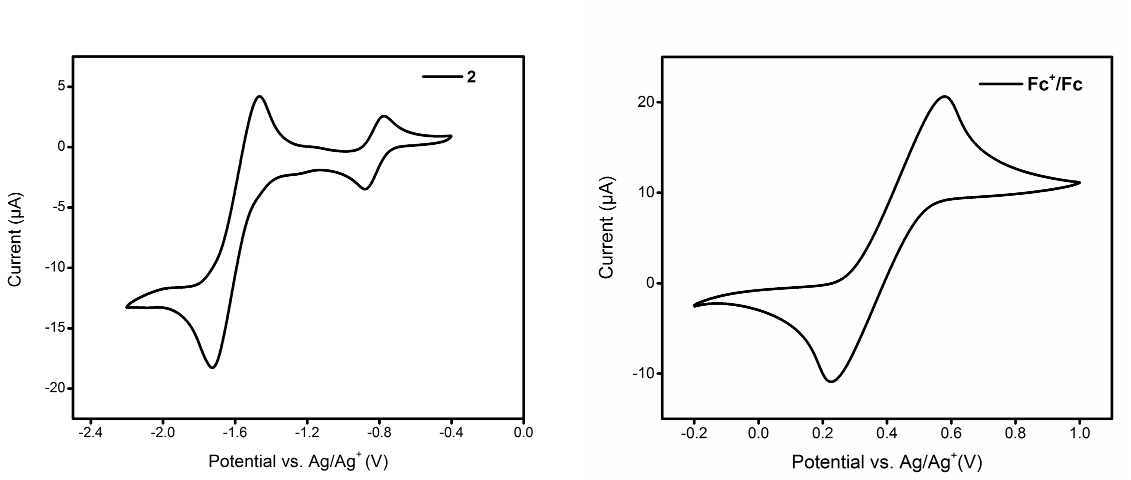


Figure S2. Cyclic voltammogram trace of perfluororubrene (**2**, left) and ferrocene (right).

Part V: X-ray Diffraction tabulated details

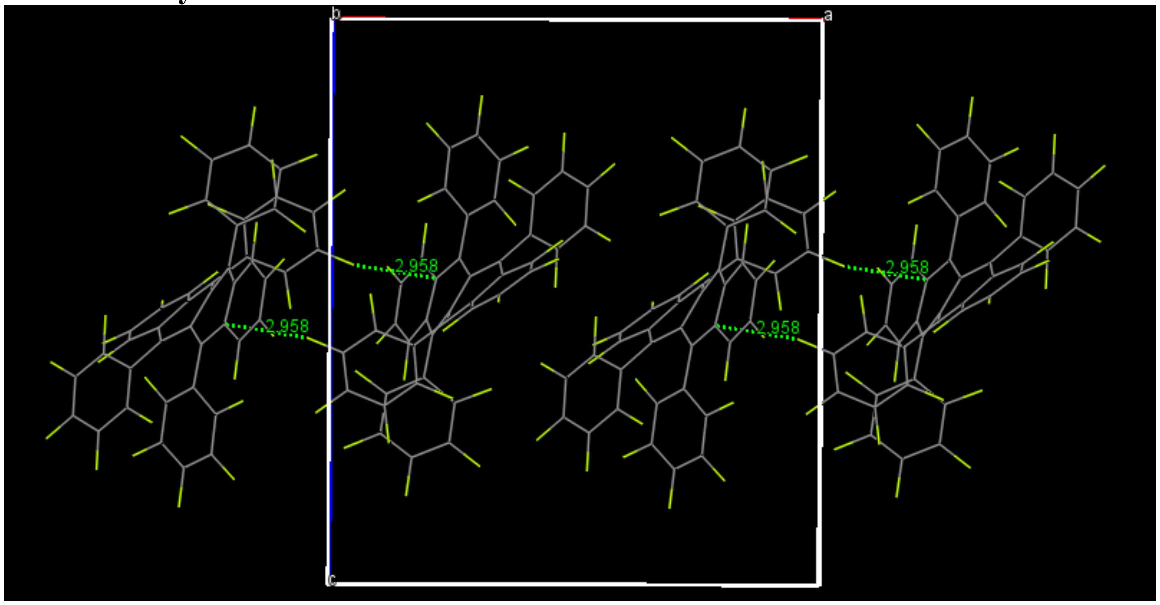


Figure S3. C-F–π interaction in crystal B.

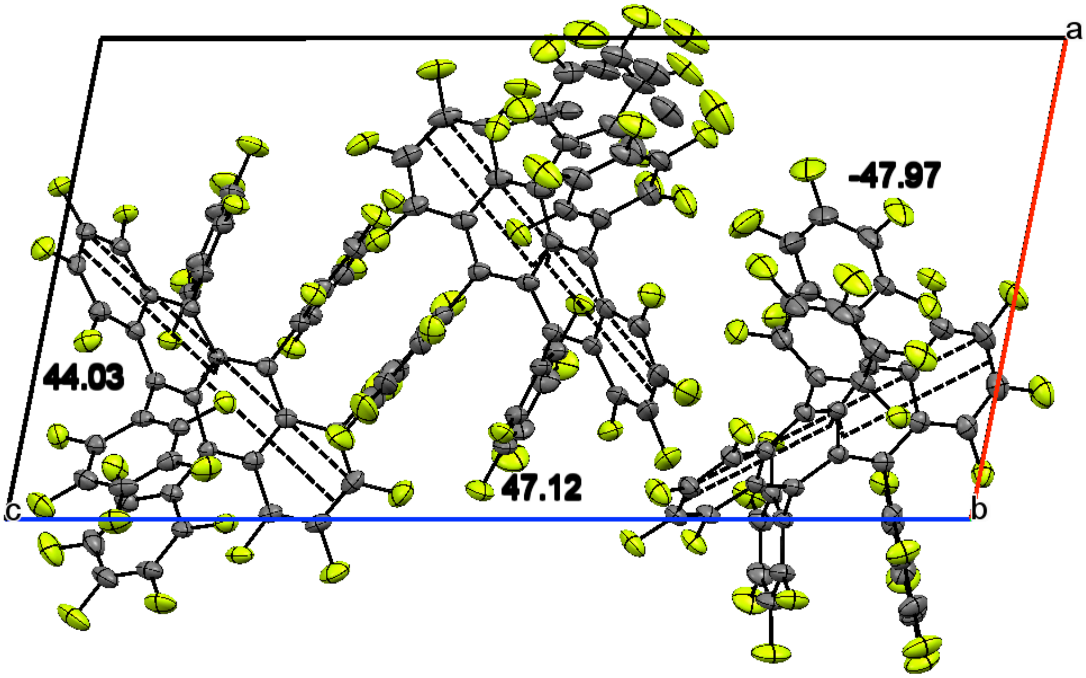


Figure S4. Asymmetric unit of crystal C.

Table S1. X-Ray Diffraction data for crystals A–C.[†]

Crystal	A	B	C
Identification code	14147zz	14152z	15011z
Empirical formula	$C_{42}F_{28}$•$CHCl_3$	$C_{42}F_{28}$	$C_{42}F_{28}$
Formula weight	1036.42	1036.42	1036.42
Temperature	123 K	123 K	123 K
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	$P2_12_12_1$	$P2_1/n$	$P1$
Unit cell dimensions	a = 8.4500(4) Å	a = 16.6651(6) Å	a = 12.5285 Å
	b = 11.004(5) Å	b = 11.1489(5) Å	b = 17.8163 Å
	c = 42.680(2) Å	c = 19.1918(7) Å	c = 24.7339 Å
	α = 90°	α = 90°	α = 90.202(4)°
	β = 90°	β = 90.213(3)°	β = 101.264(3)°
	γ = 90°	γ = 90°	γ = 90.695(3)°
Volume	3967.3(3) Å^3	3565.8(2) Å^3	5414.1(5) Å^3
Z	4	4	6
Crystal color, morphology	Red, Plate	Red, Plate	Bronze, Plate
Goodness-of-fit on *F*2	1.045	1.045	1.053
Final *R* indices [*I*>2sigma(*I*)]	*R*1 = 0.0252 *wR*2 = 0.0648	*R*1 = 0.0562 *wR*2 = 0.1428	*R*1 = 0.0687 *wR*2 = 0.1499
R indices (all data)	*R*1 = 0.0267 *wR*2 = 0.0656	*R*1 = 0.0830 *wR*2 = 0.1636	*R*1 = 0.0946 *wR*2 = 0.1681

[†] We used a SQUEEZE procedure on crystal A to model the solvate.

Part VI: Schematic illustrations of crystal growth methods

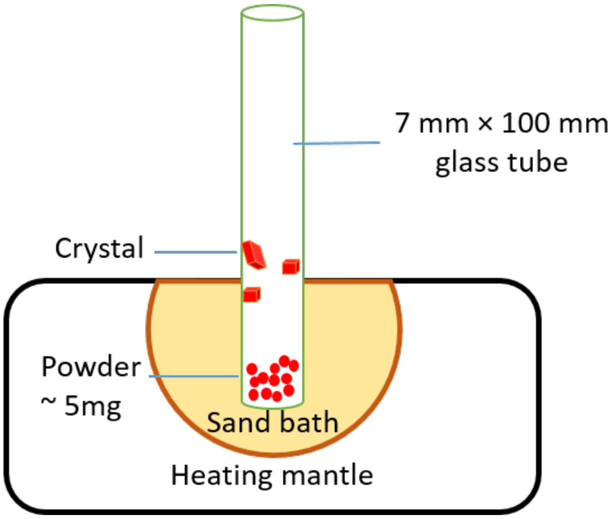


Figure S5. Apparatus setup for small scale sublimation experiment. Sand bath was 290 °C, top of glass tube was ambient temperature.

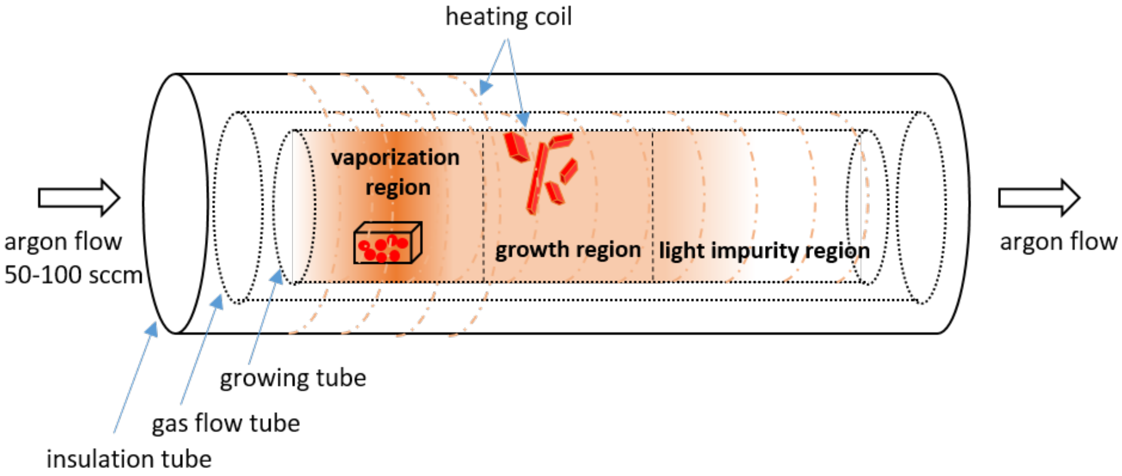


Figure S6. Schematic illustration of physical vapor transport apparatus. Heating coils provided a temperature gradient of 220–230 °C.