Supporting Information for:

A Fluorine-Substituted Hexakisdecyloxyhexa-*peri*-hexabenzocoronene

Qing Zhang[†], Paulette Prins[‡], Simon C. Jones[†], Stephen Barlow[†], Takeshi Kondo[†], Zesheng An[†], Laurens D. A. Siebbeles[‡], Seth R. Marder^{†,*}

Center for Organic Photonics and Electronics and School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta 30332-0400, and Opto-Electronic Materials Section, DelftChemTech, Delft University of Technology, Mekelweg 15, 2629 JB, Delft, The Netherlands

Experimental

All materials were reagent grade and used without further purification. Chromatographic separations were performed using standard column methods with silica gel (230 mesh). Anhydrous diethyl ether and tetrahydrofuran were purchased from Aldrich. All reactions described were carried out under a dinitrogen atmosphere. ¹H and ¹³C NMR were collected on a Varian 300 spectrometer, operating at 300 MHz or 75 MHz respectively, using the residual solvent proton or the solvent carbon resonance as reference. ¹⁹F NMR spectra were collected on a Varian 400 spectrometer, operating at 376.3 MHz, using CF₃COOD as a reference (in a capillary tube $\delta = -76.55$ ppm). The Mass Spectrometry Laboratory at Georgia Tech performed all mass spectrometry analyses. Electrochemical measurements were carried out under dinitrogen on dry solutions ca. 10⁻⁴ M in analyte and 0.1 M in [ⁿBu₄N]⁺[PF₆]⁻ using a BAS Potentiostat, a glassy carbon working electrode, a platinum auxillary electrode, and,

[†] Georgia Institute of Technology

[‡] Delft University of Technology

as a pseudo-reference electrode, a silver wire anodized in 1 M aqueous potassium chloride. Molecular oxidations were investigated in CH₂Cl₂ and molecular reductions in THF. Since the oxidation process was found to be irreversible at glassy carbon the measurements were repeated using a gold working electrode, but the process was still irreversible. Potentials were referenced to ferrocenium / ferrocene by using ferrocene as an internal reference. Cyclic voltammograms were recorded at a scan rates of 50–500 mVs⁻¹.

2-Decyloxy-1,3-difluorobenzene, 2. A mixture of 2,6-difluorophenol, **1** (15.00 g, 115.30 mmol), 1-bromodecane (26.3 mL, 126.83 mmol) and ground potassium carbonate (31.87 g, 230.59 mmol) in acetone (150 mL) was heated to reflux for 60 h under a nitrogen atmosphere. After the reaction cooled down to room temperature, the mixture was filtered and the filtrate was collected. Solvent was evaporated to give 28.34 g (91%) of colorless liquid. The compound was used as starting material for next step of reaction without further purification. ¹H NMR (300 MHz, CDCl₃): δ 6.97-6.81 (m, 3H), 4.12 (t, J = 6.6 Hz, 2H), 1.76 (sext, J = 6.7 Hz, 2H), 1.46 (sext, J = 7.1 Hz, 2H), 1.38-1.20 (br m, 12H), 0.88 (t, J = 7.0 Hz, 3H); ¹³C (75 MHz, CDCl₃) δ 158.11, 154.83, 136.01, 122.67, 112.30, 75.09, 32.25, 30.31, 29.91, 29.69, 26.01, 23.05, 14.51; ¹⁹F NMR (376.3 MHz, CDCl₃): δ -127.29. HRMS EI: Calcd. For C₁₆H₂₄OF₂ 270.1795, Found 270.1818.

2-Decyloxy-1,3-difluoro-5-iodo-benzene, 3. A mixture of iodine (2.44 g, 9.63 mmol), potassium iodate (2.22 g, 9.63 mmol), **2** (5.20 g, 19.23 mmol), glacial acetic acid (15 mL), and sulfuric acid (0.50 mL) was heated to 80 °C for 12 h. After cooling down to room temperature, an aqueous solution of sodium thiosulfate was added until the red color disappeared. The resulting mixture was extracted with diethyl ether three times. The combined organic layer was dried over magnesium sulfate. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with hexane to give a colorless liquid (6.63 g, 87% yield). ¹H NMR (300 MHz, CDCl₃): δ 7.28-7.19 (m, 2H), 4.10 (t, *J* = 6.6 Hz, 2H), 1.73 (p, *J* = 6.8 Hz, 2H), 1.43 (br, 2H), 1.36-1.20 (br, 12H), 0.88 (t, *J* = 6.8 Hz, 3H); ¹³C (75 MHz, CDCl₃): δ 157.80, 154.45, 136.30, 121.90, 82.30, 75.16, 32.24, 30.23, 29.88, 29.66, 29.62, 25.94, 23.05, 14.51. HRMS EI: Calcd. For C₁₆H₂₃F₂IO 396.0762, Found 396.0773.

2-Decyloxy-5-ethynyl-1,3-difluoro-benzene, 4.

3 (8.48 g, 21.40 mmol) was added to a two-neck flask (250 mL). The flask was purged with a small stream of argon for 20 min. Deoxygenated triethylamine (50 mL), dichlorobis(triphenylphosphine) palladium (0.147 g, 0.21 mmol) and copper (I) iodide (0.019 g, 0.10 mmol) were added to the flask under argon. Trimethylsilylacetylene (4.56 mL, 32.10 mmol) was added by syringe to the mixture. The mixture was stirred at room temperature for 12 hrs. The solvent was removed under reduced pressure. The residue was extracted with diethyl ether (20 mL) three times. The combined organic layer was

dried over magnesium sulfate and filtered. Solvent was removed under reduced pressure. To the residue, ground potassium carbonate (5.0 g), tetrahydrofuran (150 mL) and methanol (20 mL) were added and the mixture was stirred at room temperature for 12 h. After removing solvent under reduced pressure, the residue was purified on a silica gel column eluting with hexane to give a light yellow liquid (5.69 g, 90% yield). ^1H NMR (300 MHz, CDCl_3): δ 7.06-6.98 (m, 2H), 4.15 (t, J = 6.6 Hz, 2H), 3.06 (s, 1H), 1.75 (quintet, J = 6.6 Hz, 2H), 1.47-1.20 (br, 14H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C (75 MHz, CDCl_3): δ 157.17, 153.90, 137.00, 116.40, 81.60, 78.29, 75.13, 32.24, 30.28, 29.88, 29.66, 29.62, 25.94, 23.05, 14.49. HRMS EI: Calcd. For $\text{C}_{18}\text{H}_{24}\text{F}_2\text{O}$ 294.1795, Found 294.1778.

Compound 5. Compounds **3** (2.69 g, 6.80 mmol) and **4** (2.00g, 6.80 mmol) were added to a two-neck flask (250 mL). The flask was purged with a small stream of argon for 15 min. Deoxygenated triethylamine (70mL) was added to the flask under argon by a cannula, then dichlorobis(triphenylphosphine) palladium (0.0477 g, 0.068 mmol) and copper(I) iodide (0.0065 g, 0.034 mmol) were added under argon. The mixture was heated to 55 °C for 12 h. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel, eluting with hexane/ ether (100: 10) to give a low melting point colorless solid (3.78 g, 99% yield). ^1H NMR (300 MHz, CDCl_3): δ 7.04-7.00 (m, 4H), 4.16 (t, J = 6.6 Hz, 4H), 1.76 (quintet., J = 6.6 Hz, 4H), 1.43 (br, 4H),

1.39-1.20 (br, 24H), 0.88 (t, $J = 6.8$ Hz, 6H); ^{13}C (75 MHz, CDCl_3) 157.30, 154.00, 136.99, 116.96, 115.80, 88.04, 75.20, 32.24, 30.29, 29.88, 29.64, 25.95, 23.05, 14.48. HRMS EI: Calcd. For $\text{C}_{34}\text{H}_{46}\text{F}_4\text{O}_2$ 562.3434, Found 562.3486. Anal. Calcd. For $\text{C}_{34}\text{H}_{46}\text{F}_4\text{O}_2$: C, 72.57; H, 8.24. Found: C, 72.37; H, 8.23.

Compound 6. Dicobalt octacarbonyl (0.130 g, 0.38 mmol) was added under argon to a deoxygenated solution of compound **5** (1.37 g, 2.43 mmol, in 50 mL of dioxane) in a two-neck flask (250 mL) with refluxing condenser. The mixture was refluxed for 3 h. After cooled down to room temperature, the solvent was removed under reduced pressure. The residue was separated by chromatography on silica gel eluting with hexane/dichloromethane (100: 20), and then (100: 40) to give a colorless liquid (1.01 g, 74% yield). ^1H NMR (300 MHz, CDCl_3): δ 6.40-6.30 (m, 12H), 3.98 (t, $J = 6.6$ Hz, 12H), 1.64 (quintet, $J = 6.6$ Hz, 12H), 1.42-1.20 (br, 84H), 0.88 (t, $J = 6.6$ Hz, 18H); ^{13}C (75 MHz, CDCl_3) 156.90, 153.60, 138.98, 134.39, 133.49, 114.60, 74.95, 32.25, 30.08, 29.90, 29.67, 29.64, 25.92, 23.05, 14.49. HRMS FAB for (M^+) , 1687.042; calcd. For $\text{C}_{102}\text{H}_{138}\text{F}_{12}\text{O}_6$, 1687.0300. Anal. Calcd. For $\text{C}_{102}\text{H}_{138}\text{F}_{12}\text{O}_6$: C, 72.57; H, 8.24. Found: C, 72.63; H, 8.26.

Compound 7. A solution of compound **6** (2.71 g, 1.06 mmol) in dry dichloromethane (150 mL) was placed in a two-neck flask (500 mL). The solution was degassed with argon for 10 min. A solution of anhydrous iron (III) chloride (4.55 g, 30.76 mmol) in nitromethane (100 mL) was added by cannula. The reaction mixture was stirred at room temperature for 30 min, and then methanol (150 mL) was added. The dichloromethane layer was separated. The methanol layer was extracted with dichloromethane (30 mL) for three times. After combining the dichloromethane layers, solvent was removed under reduced pressure. The yellow solid was further purified by column chromatography eluting with hexane/dichloromethane (100: 10), (100: 15) and then (100: 20) to give a bright yellow solid (0.55 g, 20%). A part of starting material (0.27 g, 10%) was also recovered from the same column. ^1H NMR (300 MHz, CDCl_3): δ 4.53 (t, $J = 6.7$ Hz, 12H), 2.01 (quintet, $J = 7.14$ Hz, 12H), 1.68 (br, 12H), 1.60-1.22 (br, 72H), 0.92 (t, $J = 7.14$ Hz, 18H); ^{13}C (75 MHz, CDCl_3): δ 153.80, 150.37, 136.21, 120.44, 118.24, 108.48, 76.13, 32.36, 30.87, 30.14, 30.11, 29.82, 26.32, 23.13, 14.55; ^{19}F NMR (376.3 MHz, CDCl_3): δ -116.37. HRMS MALDI-TOF for (M^+) , 1674.9426; calcd. For $\text{C}_{102}\text{H}_{126}\text{F}_{12}\text{O}_6$, 1674.9363. Anal. Calcd. For $\text{C}_{102}\text{H}_{126}\text{F}_{12}\text{O}_6$: C, 73.09; H, 7.58. Found: C, 73.38; H, 7.62.

X-ray Diffraction Measurements

Data were collected using a θ/θ Scintag powder diffractometer (Cu K α radiation) in reflection mode in the diffraction angle, 2θ , range between 1 ° and 60 ° in 0.02 ° steps. Samples of **7** were prepared either on a copper plate (containing Si as an internal reference), or on a low-background quartz X-ray plate by slow evaporation from a THF solution. The measurements were carried out at 80 °C or at room temperature, respectively.

Table S1. X-ray Data for Bulk LC phase of **7 at 80 °C.**

Index (<i>hkl</i>)	observed		calculated	
	$2\theta / ^\circ$	$d / \text{\AA}$	$2\theta / ^\circ$	$d / \text{\AA}$
(100)	3.80	23.2	3.80	23.2
(110)	6.50	13.6	6.58	13.4
(200)	7.46	11.8	7.60	11.6
(210)	9.92	8.9	10.07	8.8
(300)	11.22	7.9	11.41	7.8

Table S2. X-ray Data for Thin Film of 7 on Quartz at Room Temperature

Index (<i>hkl</i>)	observed		calculated	
	$2\theta / ^\circ$	$d / \text{\AA}$	$2\theta / ^\circ$	$d / \text{\AA}$
(100)	3.84	23.0	3.84	23.0
(110)	6.74	13.1	6.65	13.3
(200)	7.64	11.6	7.68	11.5
(210)	10.22	8.6	10.18	8.7
(300)	11.48	7.7	11.53	7.7
(310)	13.86	6.4	13.87	6.4
(410)	17.64	5.0	17.65	5.0
(500)	19.26	4.6	19.28	4.6
(510)	21.46	4.1	21.49	4.1
(600)	23.14	3.8	23.19	3.8
(530)	27.06	3.3	27.06	3.3

Polarized microscopy. A small amount of **7** was melted to form an apparently isotropic phase on an a glass slide on a digital hot plate at a temperature of 330 °C in air; while still in the isotropic phase on the first glass slide, another glass slide was placed on top of the compound to form a sandwich-geometry sample. The sample, with the compound still in the isotropic phase, was removed from the hot plate and allowed to cool down in air to room temperature. No attempt was made to control the film thickness. The picture of the thin film was taken between two crossed polarizers under a microscope at room temperature with an Olympus digital camera. The texture does not change qualitatively from room temperature to 220 °C (the highest temperature our instrument can go).

NMR of Compounds

Pulse Sequence: s2pul

USER: qzhang
DATE: Jan 23 2005
File: ex3
Solvent: CDCl3
Ambient temperature
Mercury-300 "r2d2"
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 52.4 degrees
Acq. time 1.998 sec
Width 4590.5 Hz
16 repetitions
OBSERVE H1, 300.0462672 MHz
DATA PROCESSING
FI size 32768
Total time 8 min, 0 sec

02-116-75

13C OBSERVE

Pulse Sequence: s2pul

USER: qzhang
DATE: Jan 23 2005
File: ex3
Solvent: CDCl3
Ambient temperature
Mercury-300 "r2d2"
PULSE SEQUENCE
Relax. delay 3.000 sec
Pulse 45.0 degrees
Acq. time 0.853 sec
Width 13761.7 Hz
1344 repetitions
OBSERVE C15, 75.4466758 MHz
DECOUPLE H1, 300.0477348 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FI size 32768
Total time 12 hr, 10 min, 55 sec

QZ-118-15

F13 OBSERVE
STANDARD PARAMETERS
Pulse Sequence: s2pu1
USER: qzhang
DATE: Jan 23 2005
File: exp
Solvent: CDCl3
Ambient temperature
Mercury-4000B "amfala"
PULSE SEQUENCE
Relax. delay 4.000 sec
Pulse 27.7 degrees
Acq. time 0.800 sec
Width 100.0 kHz
16 repetitions
OBSERVE F13, 376.365864 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 131375
Total time 1 min, 21 sec

QZ-118-09 1
Pulse Sequence: s2pu1
USER: qzhang
DATE: Jan 17 2005
File: exp
Solvent: CDCl3
Ambient temperature
Mercury-300 "r200"
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 32.4 degrees
Acq. time 1.988 sec
Width 4500.5 Hz
16 repetitions
OBSERVE H1, 300.6462672 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 49 sec

13C OBSERVE

Pulse Sequence: s2pu1
 USER: qzhang
 DATE: Jan 17 2005
 File: exp
 Solvent: CDCl3
 Ambient temperature
 Mercury-300 "r2d2"
 PULSE SEQUENCE
 Relax. delay 3.000 sec
 Pulse 45.0 degrees
 Acq. time 0.853 sec
 Width 18761.7 Hz
 555 repetitions
 OBSERVE C13, 75.4465758 MHz
 DECOUPLE H1, 300.0477348 MHz
 Power 38 dB
 Continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 32768
 Total time 53 hr, 28 min, 23 sec

12-18-97

Pulse Sequence: s2pu1
 USER: qzhang
 DATE: Mar 28 2004
 File: exp
 Solvent: CDCl3
 Ambient temperature
 Mercury-300 "r2d2"
 PULSE SEQUENCE
 Relax. delay 1.000 sec
 Pulse 32.4 degrees
 Acq. time 1.938 sec
 Width 4590.5 Hz
 16 repetitions
 OBSERVE H1, 300.0461672 MHz
 DATA PROCESSING
 FT size 32768
 Total time 6 min, 0 sec

qz-10-07
Pulse Sequence: s2pul
USER: qzhang
DATE: Mar 28 2004
File: exp
Solvent: CDCl3
Ambient temperature
Mercury-300 "r2d2"
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.853 sec
Width 18781.7 Hz
333 repetitions
OBSERVE C13, PS 4466759 MHz
DECOUPLE H1, 300.0477348 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 32768
Total time 50 min, 25 sec

qz-10-07
Pulse Sequence: s2pul
USER: qzhang
DATE: Mar 28 2004
File: exp
Solvent: CDCl3
Ambient temperature
Mercury-300 "r2d2"
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 32.4 degrees
Acq. time 1.980 sec
Width 4500.5 Hz
16 repetitions
OBSERVE H1, 300.0462872 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 49 sec

QZ-10-91
Pulse Sequence: zgpg30
USER: qzhang
DATE: Mar 28 2004
File: exp
Solvent: CDCl3
Ambient Temperature
Mercury-300 "r2d2"
PULSE SEQUENCE
Relax. delay 3.000 sec
Pulse 45.0 degrees
Acq. time 0.853 sec
Width 18761.7 Hz
837 repetitions
OBSERVE C13, 75.4466759 MHz
DECOUPLE H1, 300.0477348 MHz
Power 38 dB
continuously on
WALTZ-16 accumulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 32768
Total time 1 hr, 6 min, 57 sec

QZ-10-91
Pulse Sequence: zgpg30

USER: qzhang
DATE: Mar 30 2004
File: exp
Solvent: CDCl3
Ambient Temperature
Mercury-300 "r2d2"
PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse 32.4 degrees
Acq. time 1.930 sec
Width 4500.5 Hz
18 repetitions
OBSERVE H1, 300.0462671 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 49 sec

```

Pulse Sequence: s2pul

USER: qzhang
DATE: Apr 3 2004
File: exp

Solvent: CDCl3
Ambient temperature
Mercury-300
PULSE SEQUENCE
1. Relax 3.000 sec
Pulse 45.0 degrees
Acc. time 6.853 sec
Width 18781.7 Hz
1723 observations
OBSERVE C13, 75.466575 MHz
DECOUPLE H1, 300.047348 MHz
PUSH 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
T1 rho 1.22768
Total time 2 hr, 13 min, 53 sec

```

```
QZ-1110-30
Pulse Sequence: s2pu1

USER: qzhang
DATE: Oct 15 2004
File: exp

Solvent: CDC13
Ambient temperature
Mercury-300 "r2d2"

PULSE SEQUENCE
Relax. delay 1.000 sec
Pulse width 4 degrees
Acq. time 1.938 sec
Width 4500.5 Hz
16 repetitions
OBSERVE W1, 300.0461672 MHZ
GATA PROCESSING
FT size 32768
Total time 0 min, 49 sec
```

02-1118-38
Pulse Sequence: s2pu1
USER: qzhang
DATE: Oct 17 2004
File: exp
Solvent: CDCl3
Ambient temperature
Mercury-300 "r4d5"
PULSE SEQUENCE
Relax. delay 6.000 sec
Pulse 45.0 degrees
Acq. time 9.853 sec
Width 10701.7 Hz
2288 repetitions
OBSERVE C13, 75.4469759 MHz
DECOUPLE H1, 300.0477348 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 32768
Total time 18 hr, 28 min, 27 sec

02-1118-38
CDCl₃ / TFA

F13 OBSERVE
STANDARD PARAMETERS
Pulse Sequence: s2pu1
USER: qzhang
DATE: Jan 23 2005
File: exp
Solvent: CDCl3
Ambient temperature
Mercury-400MS "amdala"
PULSE SEQUENCE
Relax. delay 4.000 sec
Pulse 27.7 degrees
Acq. time 6.809 sec
Width 102.6 kHz
18 repetitions
OBSERVE F19, 376.365986 MHz
DATA PROCESSING
Line broadening 6.3 Hz
FT size 131072
Total time 1 min, 21 sec

4700 Reflector Spec #1 MC[BP = 1675.9, 10376]