Synthesis, Mesomorphism, Photophysics and Device Properties of Liquid-crystalline Pincer Complexes of Gold(III) Containing Semi-perfluorinated Chains

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Instrumentation

$^1$H NMR spectra were measured on a Jeol ECS400 spectrometer operating at 400 MHz with chemical shifts referred to residual non-deuterated CHCl$_3$ signals. Concentration-dependent $^1$H spectra were measured on a Bruker 500 AVANCE II spectrometer operating at 500 MHz. Mass spectra (ESI and APCI) were collected on Bruker compact time of flight mass spectrometer; spectra were internally calibrated using sodium formate as the calibrant. Samples were transferred to the spectrometer an Agilent 1260 Infinity LC system.

Cyclic Voltammetry was performed using an EmStat3+. A glassy carbon working electrode and platinum wire counter electrode were used to study solutions containing 1 mM of [Au], where [Au] is the gold complex in question, and 0.1 M [NBu$_4$][PF$_6$] in a CH$_2$Cl$_2$ solution. Ferrocene was used as an internal reference. Cyclic voltammetry was performed between +0.7 and -2.5 V for 3 scans at a scan rate of (100 mV s$^{-1}$).

Elemental analysis was carried out using an Exeter Analytical Inc. CE-440 Analyser and Sartorius S2 analytical balance; calibration was performed against acetonilide standards and checked by the use of S-benzyl thiouronium chloride as internal standard. Obtaining good CHN data for materials containing perfluorocarbon units is often rather challenging and for complex 19a we found an error in carbon of 0.9%, while in a couple of other complexes the error was ca 0.7%. Such complexes were prepared more than once with similar results. However, their thermal transitions were as sharp as those for which the CHN data were within normally acceptable limits and so we believed that it was appropriate to report their properties, none of which appear out of line when compared with close homologues.

Polarising optical microscopy was carried out using an Olympus BX50 polarising microscope equipped with a Linkam scientific LTS350 heating stage, Linkam LNP2 cooling pump, and Linkam TMS92 controller, differential scanning calorimetry was performed on a Mettler DSC822 using Mettler STAR-E software, which was calibrated before use against indium and zinc standards under an atmosphere of dry nitrogen. Small-angle X-ray scattering was recorded using a Bruker
D8 Discover equipped with a temperature controlled, bored graphite rod furnace, custom built at the University of York. Cu-Kα (\(\lambda = 0.154056\) nm) radiation was used, generated from a 1 μS microfocus source. Diffraction patterns were recorded on a 2048 × 2048 pixel Bruker VANTEC 500 area detector set at a distance of 121 mm from the sample, allowing simultaneous collection of small angle and wide angle scattering data. Samples were measured in 1 mm capillary tubes in a magnetic field of ca 1 T.

The absorption spectra of the complexes were measured in solution in CH₂Cl₂ in 1 cm pathlength quartz cuvettes using a Biotek Instruments XS spectrometer. Emission spectra were recorded using a Jobin Yvon Fluoromax-2 spectrometer equipped with a Hamamatsu R928 photomultiplier tube (PMT). For the measurements at 298 K, the solutions were contained within 1 cm pathlength quartz cuvettes modified for connection to a vacuum line. Degassing was achieved via a minimum of three freeze-pump-thaw cycles whilst connected to the vacuum manifold; final vapour pressure at 77 K was < 5 x 10⁻² mbar, as monitored using a Pirani gauge. Luminescence quantum yields were determined using aqueous [Ru(bipy)₃]Cl₂ as the standard (\(\phi = 0.040\) in air-equilibrated aqueous solution). Emission spectra at 77 K were recorded in a glass of EPA (= diethyl ether / isopentane / ethanol, 2:2:1 v/v) in 4 mm diameter tubes held within a liquid-nitrogen-cooled quartz dewar. The luminescence lifetimes of the complexes in deoxygenated solution and at 77 K were measured by multi-channel scaling following excitation into the lowest-energy absorption band using a microsecond pulsed xenon lamp; an appropriate excitation wavelength corresponding to the low-energy absorption band of the complexes was selected by means of a monochromator. The emitted light was detected at 90° using a Peltier-cooled R928 PMT after passage through a monochromator. The lifetimes in air-equilibrated solution (<10 μs) were measured by time-correlated single photon counting (TCSPC), following excitation at 374 nm with a pulsed laser diode.

**General Procedure for 1H,1H,2H,2H-perfluoro(alkyl)trifluoromethanesulfonate:** Triflic anhydride was taken into dry CH₂Cl₂ and the solution degassed with N₂ and cooled to 0 °C. 1H,1H,2H,2H-perfluoroalkan-1-ol and pyridine were added (in varying solvents) and the reaction mixture was stirred under a flow of N₂ for 1 hour. The resulting precipitate was removed by
filtration and volatiles removed from the filtrate in vacuo. The residue was then purified by flash column chromatography on silica gel.

**1H,1H,2H,2H-Perfluoro(octyl)trifluoromethanesulfonate**: As above, with triflic anhydride (5.1 cm³, 30.2 mmol), 1H,1H,2H,2H- perfluorooctan-1-ol (11.0 g, 30.2 mmol) and pyridine (2.9 cm³, 28.6 mmol), which were added in CH₂Cl₂:dioxane (1:1). The product was purified using petroleum ether(40-60):CH₂Cl₂ (8:2) as eluent. 10.7 g. (71%).

¹H NMR (400 MHz, CDCl₃): δ = 4.77 (2H, t, ³J₉₉ = 6.3 Hz), 2.67 (2H, m) ppm. ¹⁹F NMR (376 MHz, MeOD-d₄): δ = -74.63 (3F, s), -82.26 (3F, t, ³J₉₉ = 9.7 Hz), -113.6 (2F, m), -121.8 (2F, m), -122.9 (2F,m), -123.4 (2F,m), -126.2 (2F,m) ppm.

**1H,1H,2H,2H-Perfluoro(decyl)trifluoromethanesulfonate**: As above, with triflic anhydride (3.62 cm³, 21.6 mmol), 1H,1H,2H,2H- perfluorodecan-1-ol (10.1 g, 21.8 mmol) and pyridine (1.73 cm³, 21.3 mmol), which were added in CH₂Cl₂:dioxane (1:1). The product was purified using 8:2 petroleum ether(40-60):ethyl acetate as eluent. 8.80 g. (68%).

¹H NMR (400 MHz, CDCl₃): δ = 4.77 (2H, t, ³J₉₉ = 6.3 Hz), 2.67 (2H, m) ppm. ¹⁹F NMR (376 MHz, MeOD-d₄): δ = -74.63 (3F, s), -82.26 (3F, t, ³J₉₉ = 10.0 Hz), -114.3 (2F, m), -122.6 (2F, m), -122.8 (4F, m), -123.7 (2F, m), -124.5 (2F, m), -127.2 (2F, m) ppm.
**1H,1H,2H,2H-Perfluoro(dodecyl)trifluoromethanesulfonate**: As above, with triflic anhydride (1.55 cm$^3$, 9.22 mmol), 1H,1H,2H,2H- perfluorododecan-1-ol (4.98 g, 8.91 mmol) and pyridine (0.75 cm$^3$, 9.32 mmol), which were added in dioxane:trifluoromethylbenzene (2:1). The product was purified using 8:2 CH$_2$Cl$_2$:petroleum ether(40-60) as eluent. 5.21 g. (85%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 4.77$ (2H, t, $^3J_{HH} = 6.3$ Hz), 2.67 (2H, m). $^{19}$F NMR (376 MHz, MeOD-d$_4$): $\delta = -80.59$ (3F, t, $^3J_{FF} = 9.4$ Hz), -113.18 (2F, m), -121.62 (10F, m), -121.56 (2F, m), -122.37 (2F, m), -125.97 (2F, m). -80.59 (3F, t, $^3J_{FF} = 9.4$ Hz), -113.18 (2F, m), -121.62 (10F, m), -121.56 (2F, m), -122.37 (2F, m), -125.97 (2F, m) ppm.

**General Procedure for Synthesis of 4-(1H,1H,2H,2H-Perfluoro(alkoxy))benzaldehyde:**

4-Hydroxybenzaldehyde and K$_2$CO$_3$ (1.1 eq. per hydroxy group) were dissolved in acetonitrile (20 cm$^3$) and stirred at room temperature. The appropriate perfluorinated triflate (1.1 eq. per hydroxy group) was dissolved in acetonitrile (40 cm$^3$) and added to the benzaldehyde solution. The resulting reaction mixture was stirred at room temperature for 16 hours. The K$_2$CO$_3$ was removed via filtration and the filtrate concentrated in vacuo. The residue was dissolved ethyl acetate and washed with aqueous 1 M NaOH, dried over MgSO$_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel using petroleum ether(40-60):ethyl acetate (8:2) as the eluent.
4-\((1H,1H,2H,2H\text{-}\text{Perfluoro(octyloxy)})\)benzaldehyde: As above, using \(1H,1H,2H,2H\text{-}\text{perfluoro(octyl)}\)trifluoromethanesulfonate (2.50 g, 5.01 mmol), 4-hydroxybenzaldehyde (563 mg, 4.58 mmol) and \(K_2CO_3\) (402 mg, 2.87 mmol). 1.62 g. (75%).

\(1H\) NMR (400 MHz, CDCl\(_3\)): \(\delta = 9.88 (1H, s), 7.90 (2H, \text{AA'XX'}), 7.14 (2H, \text{AA'XX'}), 4.43 (2H, t, \text{J}_{HH} = 6.1 \text{ Hz}), 2.77 (2H, m) \text{ ppm.} \) \(19F\) NMR (376 MHz, MeOD-\(d_4\)): \(\delta = -80.6 (3F, t, \text{J}_{FF} = 9.7 \text{ Hz}), -113.6 (2F, m), -121.8 (2F, m), -122.9 (2F,m), -123.4 (2F,m), -126.2 (2F,m) \text{ ppm.} \)

4-\((1H,1H,2H,2H\text{-}\text{Perfluoro(decyloxy)})\)benzaldehyde: As above, using \(1H,1H,2H,2H\text{-}\text{perfluoro(decyl)}\)trifluoromethanesulfonate (3.01 g, 5.03 mmol), 4-hydroxybenzaldehyde (564 mg, 4.58 mmol) and \(K_2CO_3\) (633 mg, 4.57 mmol). 1.23 g. (47%).

\(1H\) NMR (400 MHz, MeOH-\(d_4\)): \(\delta = 9.86 (1H, s), 7.90 (2H, \text{AA'XX'}), 7.14 (2H, \text{AA'XX'}), 4.43 (2H, t, \text{J}_{HH} = 6.1 \text{ Hz}), 2.77 (2H, m) \text{ ppm.} \) \(19F\) NMR (376 MHz, MeOD-\(d_4\)): \(\delta = -82.3 (3F, t, \text{J}_{FF} = 10.0 \text{ Hz}), -114.3 (2F, m), -122.6 (2F, m), -122.8 (4F, m), -123.7 (2F, m), -124.5 (2F, m), -127.2 (2F, m) \text{ ppm.} \)

4-\((1H,1H,2H,2H\text{-}\text{Perfluoro(dodecyloxy)})\)benzaldehyde: As above, using \(1H,1H,2H,2H\text{-}\text{perfluoro(dodecyl)}\)trifluoromethanesulfonate (0.8484 g, 1.2186 mmol), 4-hydroxybenzaldehyde (0.1353 g, 1.1079 mmol) and \(K_2CO_3\) (0.1735 g, 1.2553 mmol). 0.5153 g. (70%).

\(1H\) NMR (400 MHz, CDCl\(_3\)): \(\delta = 9.91 (1H, s), 7.86 (2H, \text{AA'XX'}), 7.02 (2H, \text{AA'XX'}), 4.36 (2H, t, \text{J}_{HH} = 6.7 \text{ Hz}), 2.68 (2H, m) \text{ ppm.} \) \(19F\) NMR (376 MHz, CDCl\(_3\)): \(\delta = -80.60 (3F, t, \text{J}_{FF} = 10.8 \text{ Hz}), -110.15 (2F, m), -121.62 (10F, m), -122.57 (2F, m), -123.35 (2F, m), -125.97 (2F, m) \text{ ppm.} \)
General Procedure for Synthesis of 3,4-bis(1H,1H,2H,2H-perfluoro(alkoxy))benzaldehyde:

4-Hydroxybenzaldehyde and K$_2$CO$_3$ (1.1 eq. per hydroxy group) were dissolved in acetonitrile (20 cm$^3$) and stirred at room temperature. The appropriate perfluorinated triflate (1.1 eq. per hydroxy group) was dissolved in acetonitrile (50 cm$^3$) and added to the benzaldehyde solution. The resulting reaction mixture was stirred at room temperature for 16 hours, after which the precipitate which formed was isolated by filtration and washed with water and acetonitrile and air dried. The product was used without further purification.

3,4-Bis(1H,1H,2H,2H-perfluoro(octyloxy))benzaldehyde: As above, using 1H,1H,2H,2H-perfluoro(octyl)trifluoromethanesulfonate (7.08 g, 14.3 mmol), 3,4-di(hydroxy)benzaldehyde (891 mg, 6.44 mmol) and K$_2$CO$_3$ (2.21 g, 15.9 mmol). 2.66 g. (50%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 9.87 (1H, s), 7.52 (1H, dd, $^3$J$_{HH}$ = 8.2, $^4$J$_{HH}$ = 1.8), 7.45 (1H, d, $^4$J$_{HH}$ = 1.8), 7.02 (1H, d, $^3$J$_{HH}$ = 8.2), 4.39 (2H, t, $^3$J$_{HH}$ = 6.5 Hz), 4.35 (2H, t, $^3$J$_{HH}$ = 6.5 Hz), 2.68 (4H, m) ppm; $^{19}$F NMR $\delta_F$ (376 MHz, CDCl$_3$): -80.7 (6F, t, $^3$J$_{FF}$ = 9.8 Hz), -113.2 (4F, m), -121.8 (4F, m), -122.8 (4F, m), -123.5 (4F, m), -126.1 (4F, m) ppm

3,4-Bis(1H,1H,2H,2H-perfluoro(decyloxy))benzaldehyde: As above, using 1H,1H,2H,2H-perfluoro(decyl)trifluoromethanesulfonate (7.39 g, 12.4 mmol), 3,4-di(hydroxy)benzaldehyde (781 mg, 5.70 mmol) and K$_2$CO$_3$ (1.72 g, 12.4 mmol). 5.14g. (87%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 9.87 (1H, s), 7.52 (1H, dd, $^3$J$_{HH}$ = 8.2, $^4$J$_{HH}$ = 1.8), 7.45 (1H, d, $^4$J$_{HH}$ = 1.8), 7.02 (1H, d, $^3$J$_{HH}$ = 8.2), 4.38 (2H, t, $^3$J$_{HH}$ = 6.5 Hz), 4.36 (2H, t, $^3$J$_{HH}$ = 6.5 Hz), 2.69 (4H, m) ppm; $^{19}$F NMR $\delta_F$ (376 MHz, CDCl$_3$): -80.7 (6F, t, $^3$J$_{FF}$ = 9.8 Hz), -113.2 (4F, m), -121.8 (4F, m), -121.9 (8F, m), -122.7 (4F, m), -123.5 (4F, m), -126.1 (4F, m) ppm
3,4-Bis(1H,1H,2H,2H-perfluoro(dodecyloxy))benzaldehyde: As above, using 1H,1H,2H,2H-perfluoro(dodecyl)trifluoromethanesulfonate (4.48 g, 6.46 mmol), 3,4-di(hydroxy)benzaldehyde (410 mg, 2.97 mmol) and K₂CO₃ (903 mg, 6.52 mmol). 2.89 g. (79%).

¹H NMR (400 MHz, CDCl₃): δ = 9.87 (1H, s), 7.52 (1H, dd, ³J₆₇ = 8.2, ⁴J₆₅ = 1.8), 7.45 (1H, d, ⁴J₆₅ = 1.8), 7.02 (1H, d, ³J₆₇ = 8.2), 4.38 (2H, t, ³J₆₇ = 6.5 Hz), 4.35 (2H, t, ³J₆₇ = 6.5 Hz), 2.69 (4H, m) ppm; ¹⁹F NMR δF (376 MHz, CDCl₃): -80.7 (6F, t, ³J₈ = 9.8 Hz), -113.2 (4F, m), -121.8 (20F, m), -122.7 (4F, m), -123.5 (4F, m), -126.1 (4F, m) ppm.

General Procedure for the Synthesis of Methyl 3,4,5-tri(1H,1H,2H,2H-perfluoro(alkoxy))benzoate:

Methyl 3,4,5-tri(hydroxy)benzoate and K₂CO₃ (3.3 eq) were dissolved in either acetone or acetonitrile (specified for individual reactions below) and stirred at room temperature. A solution of 1H,1H,2H,2H-perfluoro(alkyl)trifluoromethanesulfonate in the same solvent was added and the reaction mixture stirred at room temperature for 48 hours. The resultant precipitate was isolated via filtration and washed with water and acetonitrile and air dried. The product was used without further purification.

Methyl 3,4,5-tris(1H,1H,2H,2H -perfluoro(octyloxy))benzoate: As above, using 1H,1H,2H,2H-perfluoro(octyl)trifluoromethanesulfonate (10.0 g, 20.2 mmol), methyl 3,4,5-tri(hydroxy)benzoate (804 mg, 4.41 mmol) and K₂CO₃ (1.94 g, 14.0 mmol), using acetonitrile (200 cm³) as the reaction solvent. 4.31 g. (81%).
Methyl 3,4,5-tris(1H,1H,2H,2H-perfluoro(decyloxy))benzoate: As above, using 1H,1H,2H,2H-perfluoro(decyl)trifluoromethanesulfonate (11.6 g, 16.7 mmol), methyl 3,4,5-tri(hydroxy)benzoate (1.13 mg, 8.02 mmol) and K₂CO₃ (2.70 g, 19.5 mmol), using acetone (400 cm³) as the reaction solvent. 3.91 g. (32%).

Methyl 3,4,5-tris(1H,1H,2H,2H-perfluoro(dodecyloxy))benzoate: As above, using 1H,1H,2H,2H-perfluoro(dodecyl)trifluoromethanesulfonate (18.7 g, 26.9 mmol), methyl 3,4,5-tri(hydroxy)benzoate (1.50 g, 8.11 mmol) and K₂CO₃ (3.71 g, 26.8 mmol), using a 2:1 mixture of acetonitrile (300 cm³) and hexafluorobenzene (150 cm³) as the reaction solvent. 1H,1H,2H,2H-perfluoro(dodecyl)trifluoromethanesulfonate was added in acetone only. 3.90 g. (26%).
**General Procedure for the Synthesis of 3,4,5-tris(1H,1H,2H,2H-perfluoro(alkoxy))benzyl alcohol:**

Under an atmosphere of nitrogen at room temperature, methyl 3,4,5-tris(1H,1H,2H,2H-perfluoro(alkoxy))benzoate was dissolved in THF (130 cm³). LiAlH₄ (1 M solution in THF) was added dropwise and the resultant solution was stirred at room temperature for 16 hours, after which time ethyl acetate was added to quench the reaction. The reaction mixture was concentrated *in vacuo* and dissolved in boiling hexane; insoluble impurities were isolated via filtration. The filtrate was concentrated *in vacuo* and recrystallised from CHCl₃.

![Chemical Structure](image)

**3,4,5-Tris(1H,1H,2H,2H-perfluoro(octyloxy))benzyl alcohol:** As above, using methyl 3,4,5-tris(1H,1H,2H,2H-perfluoro(octyloxy))benzoate (4.10 g, 3.35 mmol) and LiAlH₄ (1 M in THF) (4.0 cm³, 12.0 mmol). 3.71 g. (90%).

\[ ^1H\text{ NMR (400 MHz, CDCl}_3\text{)}: \delta = 6.65 (2H, s), 4.65 (2H, \text{ }^4J_{HH} = 4.0 \text{ Hz}) 4.31 (4H, t, \text{ }^3J_{HH} = 6.4 \text{ Hz}), 4.20 (2H, t, \text{ }^3J_{HH} = 6.9 \text{ Hz}), 2.63 (6H, m) \text{ ppm}; ^19F\text{ NMR } \delta_F (376 \text{ MHz, CDCl}_3): -80.7 (6F, t, \text{ }^3J_{FF} = 9.9 \text{ Hz}), -80.9 (3F, t, \text{ }^3J_{FF} = 9.8 \text{ Hz}), -113.3 (4F, m), -113.5 (2F, m), -121.9 (4F, m), -122.0 (2F, m), -122.9 (6F, m), -123.6 (4F, m), -123.7 (2F, m), -126.1 (4F, m) -126.3 (2F, m) \text{ ppm.} \]

**3,4,5-Tris(1H,1H,2H,2H-perfluoro(decyloxy))benzyl alcohol:** As above, using methyl 3,4,5-tris(1H,1H,2H,2H-perfluoro(decyloxy))benzoate (3.71 g, 2.40 mmol) and LiAlH₄ (1 M in THF) (2.9 cm³, 8.72 mmol). 2.50 g. (69%).

\[ ^1H\text{ NMR (400 MHz, CDCl}_3\text{)}: \delta = 6.66 (2H, s), 4.65 (2H, \text{ }^4J_{HH} = 4.7 \text{ Hz}) 4.32 (4H, t, \text{ }^3J_{HH} = 6.4 \text{ Hz}), 4.22 (2H, t, \text{ }^3J_{HH} = 6.9 \text{ Hz}), 2.62 (6H, m) \text{ ppm}; ^19F\text{ NMR } \delta_F (376 \text{ MHz, CDCl}_3): -80.8 (6F, t, \text{ }^3J_{FF} = 9.8 \text{ Hz}), - \]
80.9 (3F, t, $^3J_{FF} = 9.9$ Hz), -112.9 (4F, m), -113.1 (2F, m), -121.3 (4F, m), -121.6 (14F, m), -122.5 (6F, m), -123.3 (4F, m), -123.5 (2F, m), -125.9 (6F, m) ppm.

General Procedure for the Synthesis of 3,4,5-tris(1H,1H,2H,2H-perfluoro(alkoxy))-benzaldehyde:

3,4,5-Tris(1H,1H,2H,2H-perfluoro(alkoxy))benzyl alcohol and MnO$_2$ (excess) were taken into CH$_2$Cl$_2$ and stirred it either room temperature or 45 °C (specified below) for 36 hours. The reaction mixture was filtered through Celite to remove the MnO$_2$ and the filtrate was concentrated in vacuo. The residue was purified by column chromatography on silica gel.

3,4,5-Tris(1H,1H,2H,2H-perfluoro(octyloxy))benzaldehyde: As above, with 3,4,5-tris(1H,1H,2H,2H-perfluoro(octyloxy))benzyl alcohol (3.69 g, 3.09 mmol) and MnO$_2$ (2.69 g, 31.0 mmol) in CH$_2$Cl$_2$ (200 cm$^3$), at room temperature, residue purified using petroleum ether(40-60):ethyl acetate (7:3) as the eluent. 3.10 g. (84%).

$^1$H NMR (400 MHz, CDCl$_3$): δ = 9.88 (1H, s), 7.16 (2H, s), 4.38 (4H, t, $^3J_{HH} = 6.3$ Hz), 4.30 (2H, t, $^3J_{HH} = 6.8$ Hz), 2.65 (6H, m) ppm; $^{19}$F NMR δ$_F$ (376 MHz, CDCl$_3$): -80.8 (6F, t, $^3J_{FF} = 9.9$ Hz), -80.9 (3F, t, $^3J_{FF} = 9.8$ Hz), -113.4 (4F, m), -113.6 (2F, m), -121.9 (4F, m), -122.0 (2F, m), -122.9 (4F, m), -123.0 (2F, m), -123.6 (4F, m), -123.7 (2F, m), -126.2 (4F, m) -126.3 (2F, m) ppm.

3,4,5-Tris(1H,1H,2H,2H-perfluoro(decyloxy))benzaldehyde: As above, with 3,4,5-tris(1H,1H,2H,2H-perfluoro(octyloxy))benzyl alcohol (2.31 g, 1.51 mmol) and MnO$_2$ (1.31 g, 15.1 mmol), at 45 °C, using a reaction solvent of 1:1 trifluoromethylbenzene:CH$_2$Cl$_2$ (200 cm$^3$), residue purified using petroleum ether(40-60):ethyl acetate (1:1) as the eluent. 1.04 g (51%).
Synthesis for 3,4,5-tris(1H,1H,2H,2H-perfluoro(dodecyl)oxy)benzaldehyde

3,4,5-Trihydroxybenzaldehyde (0.0594 g, 0.3854 mmol) and K₂CO₃ (0.1768 g, 1.2793 mmol) were dissolved in 2:1 acetonitrile:hexafluorobenzene (30 mL) and stirred at room temperature. AJM254e (0.8827 g, 1.2679 mmol) dissolved in acetone (10 mL) was added and the resulting solution stirred at room temperature under a nitrogen atmosphere for 4 days. The solution was filtered and the solid precipitate washed with distilled water (50 mL) and acetonitrile (25 mL) and air dried to give a white solid. Yield: 0.1607 g (23.3%)

Formed a 1:0.44 ratio of di-substituted to trisubstituted from ¹H NMR.

General Procedure for the Synthesis of 4-(2,2-dibromovinyl)-1-(1H,1H,2H,2H-perfluoro(alkoxy))benzene, 4-(2,2-dibromovinyl)-1,2-bis(1H,1H,2H,2H-perfluoro(alkoxy))benzene and 5-(2,2-dibromovinyl)-1,2,3-tris(1H,1H,2H,2H-perfluoro(alkoxy))benzene:

Under a nitrogen atmosphere and cooled in an ice bath to 0 °C, a solution of tetrabromomethane (1.3 equiv.) in CH₂Cl₂ (50 cm³) was added to a solution of triphenylphosphine (2.6 equiv.) in CH₂Cl₂ (20 cm³), with the temperature maintained below 15 °C. After full addition the mixture was cooled again to 0 °C. A solution of the appropriate 1H,1H,2H,2H-perfluoro(alkoxy)benzaldehyde and triethylamine (1.0 equiv.) in CH₂Cl₂ was added dropwise and the mixture stirred for 30 minutes. The mixture was warmed to room temperature and stirred for 1 hour and then poured into hexane. The resulting precipitate was removed via filtration and
the filtrate was concentrated in vacuo to give a residue which was purified by column chromatography on silica gel using CH$_2$Cl$_2$:petroleum ether(40-60) (1:1) as eluent.

4-(2,2-Dibromovinyl)-1-(1H,1H,2H,2H-perfluoro(alkoxy))benzene:

4-(2,2-Dibromovinyl)-1-(1H,1H,2H,2H-perfluoro(octyloxy))benzene: As above, using 4-(1H,1H,2H,2H-perfluoro(octyloxy))benzaldehyde (1.14 g, 2.43 mmol) in CH$_2$Cl$_2$ (30 cm$^3$), triphenylphosphine (1.66 g, 6.32 mmol) and tetrabromomethane (1.05 g, 3.16 mmol). 1.21 g. (79%).

$^1$H NMR (400 MHz, CDCl$_3$): δ = 7.52 (2H, AA'XX'), 7.41 (1H, s), 6.90 (2H, AA'XX'), 4.29 (2H, t, $^3$J$_{HH}$ = 6.8 Hz), 2.64 (2H, m) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$): δ = -80.6 (3F, t, $^3$J$_{FF}$ = 9.7 Hz), -113.6 (2F, m), -121.8 (2F, m), -122.9 (2F, m), -123.4 (2F, m), -126.2 (2F, m) ppm.

4-(2,2-Dibromovinyl)-1-(1H,1H,2H,2H-perfluoro(decyloxy))benzene: As above, using 4-(1H,1H,2H,2H-perfluoro(decyloxy))benzaldehyde (1.37 g, 2.48 mmol) in CH$_2$Cl$_2$ (30 cm$^3$), triphenylphosphine (1.79 g, 6.84 mmol) and tetrabromomethane (1.05 g, 3.16 mmol). 562 mg. (31%).

$^1$H NMR (400 MHz, CDCl$_3$): δ = 7.52 (2H, AA'XX'), 7.41 (1H, s), 6.89 (2H, AA'XX'), 4.29 (2H, t, $^3$J$_{HH}$ = 6.8 Hz), 2.64 (2H, m) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$): δ = -82.3 (3F, t, $^3$J$_{FF}$ = 10.0 Hz), -114.3 (2F, m), -122.6 (2F, m), -122.8 (4F, m), -123.7 (2F, m), -124.5 (2F, m), -127.2 (2F, m) ppm.
4-(2,2-Dibromovinyl)-1-(1H,1H,2H,2H-perfluoro(dodecyloxy))benzene: As above, using 4-(1H,1H,2H,2H-perfluoro(dodecyloxy))benzaldehyde (0.7582 g, 1.1346 mmol) in CH₂Cl₂ (20 cm³), triphenylphosphine (0.7768 g, 2.9616 mmol) and tetrabromomethane (0.4929 g, 1.4863 mmol). 0.4702 g (50%).

¹H NMR (400 MHz, CDCl₃): δ = 7.52 (2H, AA'XX'), 7.41 (1H, s), 6.90 (2H, AA'XX'), 4.29 (2H, t, 3J_HH = 6.8 Hz), 2.64 (2H, m) ppm. ¹⁹F NMR (376 MHz, CDCl₃): δ = -80.59 (3F, t, 3J_FF = 10.2 Hz), -113.15 (2F, m), -121.60 (10F, m), -122.56 (2F, m), -123.36 (2F, m), -125.97 (2F, m).

4-(2,2-Dibromovinyl)-1,2-bis(1H,1H,2H,2H-perfluoro(alkoxy))benzene:

4-(2,2-Dibromovinyl)-1,2-bis(1H,1H,2H,2H-perfluoro(octyloxy))benzene: As above, using 3,4-bis(1H,1H,2H,2H-perfluoro(octyloxy))benzaldehyde (2.18 g, 2.65 mmol) in CH₂Cl₂ (30 cm³), triphenylphosphine (1.81 g, 6.86 mmol) and tetrabromomethane (1.14 g, 3.44 mmol), purified using CH₂Cl₂ as eluent. 2.59 g (99%).

¹H NMR (400 MHz, CDCl₃): δ = 7.40 (1H, s), 7.23 (1H, d, 4J_HH = 2.0), 7.15 (1H, dd, 3J_HH = 8.3, 4J_HH = 2.0), 6.91 (1H, d, 3J_HH = 8.3), 4.31 (2H, t, 3J_HH = 6.6 Hz), 4.30 (2H, t, 3J_HH = 6.6 Hz), 2.65 (4H, m) ppm; ¹⁹F NMR (376 MHz, CDCl₃): δ = -80.7 (6F, t, 3J_FF = 9.8 Hz), -113.2 (4F, m), -121.8 (4F, m), -122.8 (4F, m), -123.5 (4F, m), -126.1 (4F, m) ppm.

4-(2,2-Dibromovinyl)-1,2-bis(1H,1H,2H,2H-perfluoro(decyloxy))benzene: As above, using 3,4-bis(1H,1H,2H,2H-perfluoro(decyloxy))benzaldehyde (4.52 g, 4.37 mmol) in CH₂Cl₂ (40 cm³), triphenylphosphine (2.98 g, 11.4 mmol) and tetrabromomethane (1.88 g, 5.67 mmol);
benzaldehyde was added in CHCl₃ due to increased solubility. Purified using CH₂Cl₂ as eluent. 4.22 g. (81%).

¹H NMR (400 MHz, CDCl₃): δ = 7.40 (1H, s), 7.23 (1H, d, ³JHH = 2.0), 7.15 (1H, dd, ³JHH = 8.3, ⁴JHH = 2.0), 6.91 (1H, d, ³JHH = 8.3), 4.31 (2H, t, ³JHH = 6.6 Hz), 4.30 (2H, t, ³JHH = 6.6 Hz), 2.65 (4H, m) ppm; ¹⁹F NMR (376 MHz, CDCl₃): δ = - 80.7 (6F, t, ³JFF = 9.8 Hz), -113.2 (4F, m), -121.8 (4F, m), -121.9 (8F, m), -122.7 (4F, m), -123.5 (4F, m), -126.1 (4F, m) ppm.

4-(2,2-Dibromovinyl)-1,2-bis(1H,1H,2H,2H-perfluoro(dodecyl)oxy)benzene: As above, using 3,4-bis(1H,1H,2H,2H-perfluoro(dodecyl)oxy)benzaldehyde (2.62 g, 2.13 mmol) in CH₂Cl₂ (30 cm³), triphenylphosphine (1.44 g, 5.49 mmol) and tetrabromomethane (909 mg, 2.74 mmol); benzaldehyde was added in 1:1 trifluoromethylbenzene:CHCl₃ due to increased solubility. Purified using petroleum ether(40-60):ethyl acetate (7:3) as eluent. 2.23 g. (76%).

¹H NMR (400 MHz, CDCl₃): δ = 7.40 (1H, s), 7.23 (1H, d, ³JHH = 2.0), 7.15 (1H, dd, ³JHH = 8.3, ⁴JHH = 2.0), 6.91 (1H, d, ³JHH = 8.3), 4.31 (2H, t, ³JHH = 6.6 Hz), 4.30 (2H, t, ³JHH = 6.6 Hz), 2.65 (4H, m) ppm; ¹⁹F NMR (376 MHz, CDCl₃): δ = - 80.7 (6F, t, ³JFF = 9.8 Hz), -113.2 (4F, m), -121.8 (20F, m), -122.7 (4F, m), -123.5 (4F, m), -126.1 (4F, m) ppm.

5-(2,2-Dibromovinyl)-1,2,3-tris(1H,1H,2H,2H-perfluoro(alkoxy))benzene:

Note: for these two complexes, the reaction mixture was not poured into hexane, but rather the whole reaction mixture was concentrated in vacuo and this residue purified by column chromatography.
5-(2,2-Dibromovinyl)-1,2,3-tris(1H,1H,2H,2H-perfluoro(octyloxy))benzene: As above, using 3,4,5-tris(1H,1H,2H,2H-perfluoro(octyloxy))benzaldehyde (2.46 g, 2.06 mmol) in CH$_2$Cl$_2$ (40 cm$^3$), triphenylphosphine (1.41 g, 5.40 mmol) and tetrabromomethane (892 mg, 2.69 mmol), purified using petroleum ether(40-60):CH$_2$Cl$_2$ (1:1) as eluent. 2.11 g. (76%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.40$ (1H, s), 6.82 (2H, s), 4.30 (4H, t, $^3J_{HH} = 6.3$ Hz), 4.23 (2H, t, $^3J_{HH} = 6.9$ Hz), 2.62 (6H, m) ppm; $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta = -80.9$ (6F, t, $^3J_{FF} = 9.9$ Hz), -81.0 (3F, t, $^3J_{FF} = 9.7$ Hz), -113.4 (4F, m), -113.6 (2F, m), -121.9 (4F, m), -122.1 (2F, m), -122.9 (4F, m), -123.0 (2F, m), -123.6 (4F, m), -123.8 (2F, m), -126.2 (4F, m) -126.3 (2F, m) ppm

5-(2,2-Dibromovinyl)-1,2,3-tris(1H,1H,2H,2H-perfluoro(decyloxy))benzene: As above, using 3,4,5-tris(1H,1H,2H,2H-perfluoro(octyloxy))benzaldehyde (802 mg, 5.41 mmol), triphenylphosphine (374 mg, 1.43 mmol) and tetrabromomethane (232 mg, 6.92 mmol); benzaldehyde was dissolved and added in trifluoromethylbenzene (40 cm$^3$) instead of CH$_2$Cl$_2$ as outlined above. Purified using petroleum ether(40-60):CH$_2$Cl$_2$ (7:3) as eluent. 754 mg. (85%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.40$ (1H, s), 6.82 (2H, s), 4.30 (4H, t, $^3J_{HH} = 6.2$ Hz), 4.23 (2H, t, $^3J_{HH} = 6.9$ Hz), 2.62 (6H, m) ppm; $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta = -80.7$ (6F, t, $^3J_{FF} = 9.7$ Hz), -80.8 (3F, t, $^3J_{FF} = 9.8$ Hz), -113.3 (4F, m), -113.5 (2F, m), -121.4 (4F, m), -122.0 (14F, m), -122.8 (6F, m), -123.5 (4F, m), -123.7 (2F, m), -126.1 (4F, m), -126.2 (2F, m) ppm

General Procedure for 1-(1H,1H,2H,2H-perfluoro(alkoxy))-4-ethynylbenzene, 1,2-bis(1H,1H,2H,2H-perfluoro(alkoxy))-4-ethynylbenzene and 1,2,3-tris(1H,1H,2H,2H-perfluoro(alkoxy))-5-ethynylbenzene:

The appropriate (2,2-dibromovinyl)-(1H,1H,2H,2H-perfluoro(alkoxy))benzene was dissolved in THF (50 cm$^3$) under an atmosphere of dinitrogen. A solution of EtMgBr (3M in diethyl ether) was added dropwise, with stirring at room temperature, and the resulting reaction mixture was stirred for 2 hours. Solid NH$_4$Cl (excess) was then added to quench the reaction. Excess and
resultant salts were removed via filtration, and the filtrate concentrated in vacuo. The residue was purified by column chromatography on silica gel.

1-(1H,1H,2H,2H-Perfluoro(alkoxy))-4-ethynylbenzene:

\[
\begin{align*}
\text{O(CH}_2\text{)}_2\text{(CF}_2\text{)}_m\text{CF}_3
\end{align*}
\]

1-(1H,1H,2H,2H-Perfluoro(alkoxy))-4-ethynylbenzene: As above, using 4-(2,2-dibromovinyl)-1-(1H,1H,2H,2H-perfluoro(alkoxy))benzene (440 mg, 0.712 mmol) and EtMgBr (3M in ether) (0.3 cm\(^3\), 0.902 mmol), purified using petroleum ether(40-60):ethyl acetate (6:4) as the eluent. 162 mg. (49%).

\(^1\)H NMR \(\delta_H\) (400 MHz, CDCl\(_3\)): 7.43 (2H, AA’XX’), 6.84 (2H, AA’XX’), 4.26 (2H, t, \(^3J_{HH} = 6.8\) Hz), 3.00 (1H, s), 2.62 (2H, m) ppm. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta = -80.6\) (3F, t, \(^3J_{FF} = 9.8\) Hz), -113.2 (2F, m), -121.8 (2F, m), -122.8 (2F, m), -123.4 (2F, m), -126.0 (2F, m) ppm.

1-(1H,1H,2H,2H-Perfluoro(octyloxy))-4-ethynylbenzene: As above, using 4-(2,2-dibromovinyl)-1-(1H,1H,2H,2H-perfluoro(octyloxy))benzene (875 mg, 1.23 mmol) and EtMgBr (3M in ether) (0.5 cm\(^3\), 1.51 mmol), purified using petroleum ether(40-60):ethyl acetate (6:4) as the eluent. 571 mg. (84%).

\(^1\)H NMR \(\delta_H\) (400 MHz, CDCl\(_3\)): 7.44 (2H, AA’XX’), 6.84 (2H, AA’XX’), 4.28 (2H, t, \(^3J_{HH} = 6.8\) Hz), 3.01 (1H, s), 2.63 (2H, m) ppm. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \(\delta = -82.3\) (3F, t, \(^3J_{FF} = 10.0\) Hz), -114.3 (2F, m), -122.6 (2F, m), -122.8 (4F, m), -123.7 (2F, m), -124.5 (2F, m), -127.2 (2F, m) ppm; CHN elemental analysis: observed (calculated): %C 38.4 (38.3), %H 1.3 (1.6)
1-(1H,1H,2H,2H-Perfluoro(dodecyl))-4-ethynylbenzene: As above, using 4-(2,2-dibromovinyl)-1-(1H,1H,2H,2H-perfluoro(dodecyl))benzene (0.4702 g, 0.5706 mmol) and EtMgBr (3M in ether) (0.3 cm$^3$, 0.84 mmol), purified using petroleum ether(40-60):ethyl acetate (6:4) as the eluent. 0.2477 g. (65%).

$^1$H NMR $\delta$ (400 MHz, CDCl$_3$): 7.44 (2H, AA′XX′), 6.84 (2H, AA′XX′), 4.28 (2H, t, $^3J_{HH} = 6.8$ Hz), 3.01 (1H, s), 2.63 (2H, m) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ = -80.59 (3F, t, $^3J_{FF} = 9.5$ Hz), -113.15 (2F, m), -121.54 (10F, m), -122.56 (2F, m), -123.37 (2F, m), -125.97 (2F, m).

1,2-Bis(1H,1H,2H,2H-Perfluoro(alkoxy))-4-ethynylbenzene:

1,2-Bis(1H,1H,2H,2H-perfluoro(octyloxy))-4-ethynylbenzene: As above, using 3,4-bis(2,2-dibromovinyl)-1-(1H,1H,2H,2H-perfluoro(octyloxy))benzene (1.72 g, 1.74 mmol) and EtMgBr (3M in ether) (0.97 cm$^3$, 2.90 mmol), purified using CH$_2$Cl$_2$:petroleum ether(40-60) (3:2) as the eluent. 1.22 g. (83%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.15 (1H, dd, $^3J_{HH} = 8.4$, $^4J_{HH} = 2.0$), 7.05 (1H, d, $^4J_{HH} = 2.0$), 6.86 (1H, d, $^3J_{HH} = 8.5$), 4.30 (2H, t, $^3J_{HH} = 6.6$ Hz), 4.28 (2H, t, $^3J_{HH} = 6.6$ Hz), 3.03 (1H, s), 2.65 (4H, m) ppm; $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ = -80.7 (6F, t, $^3J_{FF} = 9.8$ Hz), -113.2 (4F, m), -121.8 (4F, m), -122.8 (4F, m), -123.5 (4F, m), -126.1 (4F, m) ppm; CHN elemental analysis: observed (calculated): %C 34.7 (34.9), %H 1.5 (1.5)

1,2-Bis(1H,1H,2H,2H-perfluoro(decyloxy))-4-ethynylbenzene: As above, using 3,4-bis(2,2-dibromovinyl)-1-(1H,1H,2H,2H-perfluoro(decyloxy))benzene (4.02 g, 3.37 mmol) and EtMgBr (3M in ether) (2.2 cm$^3$, 6.62 mmol), purified using CH$_2$Cl$_2$:petroleum ether(40-60) (3:2) as the eluent. 1.97 g. (57%).
\[^1\]H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta = 7.15 \ (1H, \text{dd, } ^3J_{HH} = 8.4, \ ^4J_{HH} = 2.0), 7.05 \ (1H, \text{dd, } ^4J_{HH} = 2.0), 6.86 \ (1H, \text{d, } ^3J_{HH} = 8.5), 4.30 \ (2H, \text{t, } ^3J_{HH} = 6.6 \text{ Hz}), 4.28 \ (2H, \text{t, } ^3J_{HH} = 6.6 \text{ Hz}), 3.03 \ (1H, \text{s}), 2.65 \ (4H, \text{m}) \text{ ppm; } \[^1\]H NMR (376 MHz, CDCl\textsubscript{3}): \delta = -80.7 \ (6F, \text{t, } ^3J_{FF} = 9.8 \text{ Hz}), -113.2 \ (4F, \text{m}), -121.8 \ (4F, \text{m}), -121.9 \ (8F, \text{m}), -122.7 \ (4F, \text{m}), -123.5 \ (4F, \text{m}), -126.1 \ (4F, \text{m}) \text{ ppm}; \text{CHN elemental analysis: observed (calculated): %C 32.6 (32.8), %H 1.2 (1.2)}.

1,2,-Bis\((1H,1H,2H,2H\text{-perfluoro(dodecyloxy)})\)-4-ethynylbenzene: As above, using 3,4-bis(2,2-dibromovinyl)-1-(1H,1H,2H,2H-perfluoro(dodecyloxy))benzene (1.43 g, 1.00 mmol) and EtMgBr (3M in ether) (0.38 cm\textsuperscript{3}, 1.14 mmol), purified using petroleum ether(40-60):CH\textsubscript{2}Cl\textsubscript{2} (7:3) as the eluent. 813 mg. (64%).

\[^1\]H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta = 7.15 \ (1H, \text{dd, } ^3J_{HH} = 8.4, \ ^4J_{HH} = 2.0), 7.05 \ (1H, \text{d, } ^4J_{HH} = 2.0), 6.86 \ (1H, \text{d, } ^3J_{HH} = 8.5), 4.30 \ (2H, \text{t, } ^3J_{HH} = 6.6 \text{ Hz}), 4.28 \ (2H, \text{t, } ^3J_{HH} = 6.6 \text{ Hz}), 3.03 \ (1H, \text{s}), 2.65 \ (4H, \text{m}) \text{ ppm; } \[^1\]F NMR (376 MHz, CDCl\textsubscript{3}): \delta = -80.7 \ (6F, \text{t, } ^3J_{FF} = 9.8 \text{ Hz}), -113.2 \ (4F, \text{m}), -121.8 \ (4F, \text{m}), -121.9 \ (8F, \text{m}), -122.7 \ (4F, \text{m}), -123.5 \ (4F, \text{m}), -126.1 \ (4F, \text{m}) \text{ ppm.}

1,2,3-Tris\((1H,1H,2H,2H\text{-perfluoro(alkoxy)})\)-5-ethynylbenzene

1,2,3-Tris\((1H,1H,2H,2H\text{-perfluoro(octyloxy)})\)-5-ethynylbenzene: As above, using 3,4,5-tris(2,2-dibromovinyl)-1-(1H,1H,2H,2H-perfluoro(octyloxy))benzene (1.86 g, 1.38 mmol) and EtMgBr (3M in ether) (1.8 cm\textsuperscript{3}, 5.42 mmol), purified using petroleum ether(40-60):CH\textsubscript{2}Cl\textsubscript{2} (7:3) as the eluent. 1.45 g. (88%).

\[^1\]H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta = 6.76 \ (2H, \text{s}), 4.29 \ (4H, \text{t, } ^3J_{HH} = 6.3 \text{ Hz}), 4.22 \ (2H, \text{t, } ^3J_{HH} = 6.9 \text{ Hz}), 3.07 \ (1H, \text{s}), 2.62 \ (6H, \text{m}) \text{ ppm; } \[^1\]F NMR (376 MHz, CDCl\textsubscript{3}): \delta = -80.8 \ (6F, \text{t, } ^3J_{FF} = 9.8 \text{ Hz}).-80.8
(3F, t, $^3J_{HF} = 10.0$ Hz), -113.3 (4F, m), -113.5 (2F, m), -121.8 (4F, m), -122.0 (2F, m), -122.9 (4F, m), -123.0 (2F, m), -123.6 (4F, m), -123.7 (2F, m), -126.1 (4F, m) -126.2 (2F, m) ppm; CHN elemental analysis: observed (calculated): %C 32.4 (32.3), %H 1.1 (1.3).

1,2,3-Tris(1H,1H,2H,2H-perfluoro(decyloxy))-5-ethynylbenzene: As above, using 3,4,5-bis(2,2-dibromovinyl)-1-(1H,1H,2H,2H-perfluoro(dodecyloxy))benzene (752 mg, 4.55 mmol) and EtMgBr (3M in ether) (0.64 cm$^3$, 1.92 mmol), purified using petroleum ether(40-60):CH$_2$Cl$_2$ (7:3) as the eluent. 641 mg. (95%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 6.76$ (2H, s), 4.29 (4H, t, $^3J_{HH} = 6.3$ Hz), 4.21 (2H, t, $^3J_{HH} = 6.9$ Hz), 3.07 (1H, s), 2.62 (6H, m) ppm; $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta = -80.7$ (6F, t, $^3J_{FF} = 9.8$ Hz), -80.8 (3F, t, $^3J_{FF} = 9.9$ Hz), -113.3 (4F, m), -113.5 (2F, m), -121.6 (4F, m), -122.0 (14F, m), -122.8 (6F, m), -123.5 (4F, m), -123.7 (2F, m), -126.1 (4F, m), -126.2 (2F, m) ppm; CHN elemental analysis: observed (calculated): %C 30.9 (30.7), %H 0.6 (1.0).

General Procedure for Synthesis of Gold(III) Semi-Perfluorinated-Alkynyl Complexes

The [Au(C$^N$C)Cl] precursor (14 or 15) and CuI (10 mol%) were added to a 3-necked flask which was placed under N$_2$. Dry, degassed dichloromethane (40 cm$^3$) was added, followed by the appropriate acetylene (2.5 eq.) and triethylamine (45 mol%). The reaction mixture was stirred at reflux for 5 h under a N$_2$ atmosphere, after which the reaction mixture was filtered through a pad of Celite and the solvent was removed in vacuo. The residue was purified by flash chromatography on silica gel using petroleum ether/CH$_2$Cl$_2$ (initially 7:3, followed by 1:1) as eluent and subsequently recrystallized from hexane, CH$_2$Cl$_2$/acetonitrile or CHCl$_3$/acetonitrile.
16a: Synthesised as above using 14 (102 mg, 121 µmol) and 4-((1H,1H,2H,2H-)perfluorooctyloxy)ethynylbenzene (82.1 mg, 182 µmol) and was recrystallised from CH$_2$Cl$_2$/acetonitrile. 130 mg (86%).

$^1$H NMR $\delta$ (400 MHz, CDCl$_3$): 7.71 (1H, t, $^3J_{HH} = 8.1$ Hz), 7.67 (2H, d, $^4J_{HH} = 2.6$ Hz), 7.55 (2H, AA’XX’), 7.49 (2H, d, $^3J_{HH} = 8.6$ Hz), 7.22 (2H, d, $^3J_{HH} = 8.2$ Hz), 6.87 (2H, AA‘XX’), 6.72 (2H, dd, $^3J_{HH} = 8.6$ Hz, $^4J_{HH} = 2.7$ Hz), 4.30 (2H, t, $^3J_{HH} = 6.8$ Hz), 4.06 (4H, t, $^3J_{HH} = 6.6$ Hz), 2.67 (4H, m), 1.81 (4H, m), 1.47 (4H, m), 1.21 (32H, broad m), 0.87 (6H, t, $^3J_{HH} = 7.0$ Hz) ppm; $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ = -80.64 (3F, t, $^3J_{FF} = 9.8$ Hz), -113.20 (2F, m), -121.75 (2F, m), -122.44 (2F, m), -126.02 (2F, m) ppm; MS m/z (APCI+): 1258.47 (calc. 1258.11); CHN elemental analysis: observed (calculated): %C 54.8 (54.4), %H 5.4 (5.4), %N 1.0 (1.1)

16b: Synthesised as above using 14 (101 mg, 120 µmol) and 4-((1H,1H,2H,2H-)perfluorodecyloxy)ethynylbenzene (100 mg, 181 µmol) and was recrystallised from CH$_2$Cl$_2$/acetonitrile. 160 mg (98%).

$^1$H NMR $\delta$ (400 MHz, CDCl$_3$): 7.71 (1H, t, $^3J_{HH} = 8.1$ Hz), 7.67 (2H, d, $^4J_{HH} = 2.6$ Hz), 7.55 (2H, AA’XX’), 7.49 (2H, d, $^3J_{HH} = 8.6$ Hz), 7.22 (2H, d, $^3J_{HH} = 8.2$ Hz), 6.87 (2H, AA‘XX’), 6.72 (2H, dd, $^3J_{HH} = 8.6$ Hz, $^4J_{HH} = 2.7$ Hz), 4.30 (2H, t, $^3J_{HH} = 6.8$ Hz), 4.06 (4H, t, $^3J_{HH} = 6.6$ Hz), 2.67 (4H, m), 1.81 (4H, m), 1.47 (4H, m), 1.21 (32H, broad m), 0.87 (6H, t, $^3J_{HH} = 7.0$ Hz) ppm; $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ = -82.26 (3F, t, $^3J_{FF} = 10.0$ Hz), -114.28 (2F, m), -122.55 (2F, m), -122.81 (4F, m), -123.65 (2F, m),
-124.47 (2F, m), -127.20 (2F, m) ppm; MS m/z (APCI+): 1358.13 (calc. 1358.46); CHN elemental analysis: observed (calculated): %C 52.3 (52.2), %H 4.8 (5.0), %N 0.9 (1.0)

16c: Synthesised as above using 14 (0.0492 g, 0.0593 mmol) and 4-(1H,1H,2H,2H-perfluorododecyl)ethynylbenzene (0.0497 g, 0.0748 mmol), and was recrystallised from CH$_2$Cl$_2$/acetonitrile. 0.0481 g (70%).

$^1$H NMR $\delta_H$ (400 MHz, CDCl$_3$): 7.71 (1H, t, $^{3}J_{HH} = 8.1$ Hz), 7.67 (2H, d, $^{4}J_{HH} = 2.6$ Hz), 7.55 (2H, AA'XX'), 7.49 (2H, d, $^{3}J_{HH} = 8.6$ Hz), 7.22 (2H, d, $^{3}J_{HH} = 8.2$ Hz), 6.87 (2H, AA'XX'), 6.72 (2H, dd, $^{3}J_{HH} = 8.6$ Hz, $^{4}J_{HH} = 2.7$ Hz), 4.30 (2H, t, $^{3}J_{HH} = 6.8$ Hz), 4.06 (4H, t, $^{3}J_{HH} = 6.6$ Hz), 2.67 (4H, m), 1.81 (4H, m), 1.47 (4H, m), 1.21 (32H, broad m), 0.87 (6H, t, $^{3}J_{HH} = 7.0$ Hz) ppm; $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta = -80.59$ (3F, t, $^{3}J_{FF} = 9.4$ Hz), -113.18 (2F, m), -121.62 (10F, m), -121.56 (2F, m), -122.37 (2F, m), -125.97 (2F, m) ppm; MS m/z (APCI+): 1458.14 (M$^+$, calc. 1458.45); CHN elemental analysis: observed (calculated): %C 49.7 (50.3), %H 4.8 (4.6), %N 0.4 (1.0).

17a: Synthesised as above using 14 (61.2 mg, 70.1 µmol) and 3,4-bis(1H,1H,2H,2H-perfluorooctyl)ethynylbenzene (82.1 mg, 104 µmol) and was crystallised from hexane. 70.2 mg (60%).

$^1$H NMR $\delta_H$ (400 MHz, CDCl$_3$): 7.72 (1H, t, $^{3}J_{HH} = 7.9$ Hz), 7.64 (2H, d, $^{4}J_{HH} = 2.6$ Hz), 7.49 (2H, d, $^{3}J_{HH} = 8.7$ Hz), 7.23 (1H, dd, $^{3}J_{HH} = 8.4$ Hz), 7.23 (2H, d, $^{3}J_{HH} = 7.9$ Hz, $^{4}J_{HH} = 1.8$ Hz), 7.18 (1H, d, $^{4}J_{HH} = 1.8$ Hz), 6.89 (1H, d, $^{3}J_{HH} = 8.1$ Hz), 6.73 (2H, dd, $^{3}J_{HH} = 8.5$ Hz, $^{4}J_{HH} = 2.6$ Hz), 4.31 (2H, t, $^{3}J_{HH} = 6.6$ Hz), 4.30 (2H, t, $^{3}J_{HH} = 6.6$ Hz), 4.05 (4H, t, $^{3}J_{HH} = 6.5$ Hz), 2.67 (4H, m), 1.79 (4H, m), 1.44 (4H, m),
1.25 (32H, m), 0.87 (6H, t, \text{J}_{HH} = 7.0 \text{ Hz}) \text{ ppm.}^{19} \text{F NMR (376 MHz, CDCl}_3): \delta = -80.7 (6F, m), -113.3 (4F, m), -121.8 (4F, m), -122.8 (4F, m), -123.5 (4F, m), -126.1 (4F, m) \text{ ppm; MS m/z (APCI+):} \\
1620.26 (\text{calc.} 1620.20); \text{CHN elemental analysis: observed (calculated): } %C 48.3 (48.2), %H 4.1 (4.4), %N 0.7 (0.9)

**17b**: Synthesised as above using 14 (62.0 mg, 70.5 \mu\text{mol}) and 3,4-bis(1H,1H,2H,2H-perfluorodecyloxy)ethynylbenzene (126 mg, 123 \mu\text{mol}) and was recrystallised from hexane. 116 mg (89%).

$^1$H NMR $\delta_H$ (400 MHz, CDCl$_3$): 7.71 (1H, t, $^3J_{HH} = 7.9$ Hz), 7.64 (2H, d, $^4J_{HH} = 2.6$ Hz), 7.48 (2H, d, $^3J_{HH} = 8.7$ Hz), 7.23 (1H, dd, $^3J_{HH} = 8.4$ Hz), 7.21 (2H, d, $^4J_{HH} = 7.9$ Hz, $^4J_{HH} = 1.8$ Hz), 7.18 (1H, d, $^4J_{HH} = 1.8$ Hz), 6.89 (1H, d, $^3J_{HH} = 8.1$ Hz), 6.75 (2H, dd, $^3J_{HH} = 8.5$ Hz, $^4J_{HH} = 2.6$ Hz), 4.31 (2H, t, $^3J_{HH} = 6.6$ Hz), 4.30 (2H, t, $^3J_{HH} = 6.6$ Hz), 4.05 (4H, t, $^3J_{HH} = 6.5$ Hz), 2.67 (4H, m), 1.79 (4H, m), 1.44 (4H, m), 1.25 (32H, m), 0.87 (6H, t, $^3J_{HH} = 7.0$ Hz) ppm; $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta = -80.7 (6F, m), -113.3 (4F, m), -121.8 (4F, m), -121.9 (8F, m), -122.8 (4F, m), -123.5 (4F, m), -126.1 (4F, m) \text{ ppm; MS m/z (APCI+):} 1820.45 (\text{calc.} 1820.23); \text{CHN elemental analysis: observed (calculated): } %C 44.8 (45.5), %H 3.7 (3.9), %N 0.6 (0.8).

**17c**: Synthesised as above using 14 (80.1 mg, 101 \mu\text{mol}) and 3,4-bis(1H,1H,2H,2H-perfluorododecyloxy)ethynylbenzene (177 mg, 140 \mu\text{mol}) and was recrystallised from hexane. 148 mg (76%).

$^1$H NMR $\delta_H$ (400 MHz, CDCl$_3$): 7.70 (1H, t, $^3J_{HH} = 7.9$ Hz), 7.64 (2H, d, $^4J_{HH} = 2.6$ Hz), 7.48 (2H, d, $^3J_{HH} = 8.7$ Hz), 7.23 (1H, dd, $^3J_{HH} = 8.4$ Hz), 7.21 (2H, d, $^4J_{HH} = 7.9$ Hz, $^4J_{HH} = 1.8$ Hz), 7.18 (1H, d, $^4J_{HH} = 1.8$ Hz), 6.89 (1H, d, $^3J_{HH} = 8.1$ Hz), 6.71 (2H, dd, $^3J_{HH} = 8.5$ Hz, $^4J_{HH} = 2.6$ Hz), 4.31 (2H, t, $^3J_{HH} = 6.6$ Hz), 4.30 (2H, t, $^3J_{HH} = 6.6$ Hz), 4.05 (4H, t, $^3J_{HH} = 6.5$ Hz), 2.67 (4H, m), 1.79 (4H, m), 1.44 (4H, m), 1.25 (32H, m), 0.87 (6H, t, $^3J_{HH} = 7.0$ Hz) ppm; $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta = -80.7 (6F, m), -113.3 (4F, m), -121.8 (4F, m), -121.9 (8F, m), -122.8 (4F, m), -123.5 (4F, m), -126.1 (4F, m) \text{ ppm; MS m/z (APCI+):} 2020.44 (M$^+$ calc. 2020.27), 1920.45 (M$^+$ with 1x C10 chain), 1820.45 (M$^+$ with 2x...
C10 chain); CHN elemental analysis: observed (calculated): %C 44.1 (43.4), %H 3.6 (3.5), %N 0.6 (0.7).

\[
\text{C}_{12}H_{25}O \quad \text{Au} \quad \text{OC}_{12}H_{25} \\
\text{CF}_3(\text{F}_2\text{C})_m(\text{H}_2\text{C})_2\text{O} \quad \text{O}(\text{CH}_2)_2(\text{CF}_2)_m\text{CF}_3
\]

**18a:** Synthesised as above using **14** (81.1 mg, 104 µmol) and 3,4,5-tris(1H,1H,2H,2H-perfluorooctyloxy)ethynylbenzene (172 mg, 141 µmol) and was recrystallised from hexane. 144 mg (75%).

\[
^1\text{H NMR } \delta_H (400 \text{ MHz, CDCl}_3): 7.72 (1H, t, ^3J_{HH} = 7.9 \text{ Hz}), 7.61 (2H, d, ^4J_{HH} = 2.6 \text{ Hz}), 7.50 (2H, d, ^3J_{HH} = 8.7 \text{ Hz}), 7.23 (2H, d, ^3J_{HH} = 8.1 \text{ Hz}), 6.87 (2H, s), 6.72 (2H, dd, ^3J_{HH} = 8.5 \text{ Hz}, ^4J_{HH} = 2.6 \text{ Hz}), 4.33 (4H, t, ^3J_{HH} = 6.5 \text{ Hz}), 4.24 (2H, t, ^3J_{HH} = 6.8 \text{ Hz}), 4.05 (4H, t, ^3J_{HH} = 6.5 \text{ Hz}), 2.65 (6H, m), 1.79 (4H, m), 1.44 (4H, m), 1.25 (32H, m), 0.87 (6H, t, ^3J_{HH} = 7.0 \text{ Hz}) \text{ ppm.} ^{19}\text{F NMR (376 MHz, CDCl}_3): \delta = -80.7 (6F, t, ^3J_{HH} = 9.9 \text{ Hz}), -80.9 (3F, t), -113.3 (6F, m), -121.8 (4F, m), -122.0 (2F, m), -122.8 (6F, m), -123.5 (4F, m), -123.7 (2F, m), -126.2 (6F, m) \text{ ppm}; MS m/z (APCI+): 1982.46 (calc. 1982.29); CHN elemental analysis: observed (calculated): %C 43.9 (44.2), %H 3.6 (3.7), %N 0.7 (0.7)

**18b:** Synthesised as above using **14** (80.0 mg, 101 µmol) and 3,4,5-tris(1H,1H,2H,2H-perfluorodecyloxy)ethynylbenzene (216 mg, 143 µmol) and was recrystallised from hexane. 135 mg (61%).

\[
^1\text{H NMR } \delta_H (400 \text{ MHz, CDCl}_3): 7.74 (1H, t, ^3J_{HH} = 7.9 \text{ Hz}), 7.61 (2H, d, ^4J_{HH} = 2.6 \text{ Hz}), 7.50 (2H, d, ^3J_{HH} = 8.7 \text{ Hz}), 7.25 (2H, d, ^3J_{HH} = 8.1 \text{ Hz}), 6.87 (2H, s), 6.72 (2H, dd, ^3J_{HH} = 8.5 \text{ Hz}, ^4J_{HH} = 2.6 \text{ Hz}), 4.33 (4H, t, ^3J_{HH} = 6.5 \text{ Hz}), 4.24 (2H, t, ^3J_{HH} = 6.8 \text{ Hz}), 4.05 (4H, t, ^3J_{HH} = 6.5 \text{ Hz}), 2.65 (6H, m), 1.79 (4H,
m), 1.44 (4H, m), 1.25 (32H, m), 0.87 (6H, t, $^3J_{HH} = 7.0$ Hz) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta = -80.7$ (6F, t, $^3J_{FF} = 9.9$ Hz), -80.9 (3F, t, $^3J_{FF} = 9.9$ Hz), -113.3 (6F, m), -121.8 (18F, m), -122.8 (6F, m), -123.5 (6F, m), -126.2 (6F, m) ppm; MS m/z (APCI+): 2282.44 (calc. 2282.34); CHN elemental analysis: observed (calculated): %C 41.8 (41.6), %H 3.3 (3.2), %N 1.3 (0.6)

19a: Synthesised as above using 15, (101 mg, 83.2 µmol) and 4-((1H,1H,2H,2H-perfluorooctyloxy)ethynylbenzene (56.3 mg, 131 µmol) and was recrystallised from hexane. 113 mg (84%).

$^1$H NMR $\delta_H$ (400 MHz, CDCl$_3$): 7.66 (1H, t, $^3J_{HH} = 8.0$ Hz), 7.59 (2H, s), 7.51 (2H, AA’XX’), 7.11 (2H, d, $^3J_{HH} = 8.1$ Hz), 7.05 (2H, s), 6.86 (2H, AA’XX’), 4.29 (2H, t, $^3J_{HH} = 6.9$ Hz), 4.14 (4H, t, $^3J_{HH} = 6.7$ Hz), 3.99 (4H, t, $^3J_{HH} = 6.7$ Hz), 2.65 (2H, m), 1.84 (8H, m), 1.47 (8H, m), 1.25 (64H, broad s), 0.88 (12H, m) ppm; $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta = -80.64$ (3F, t, $^3J_{FF} = 9.8$ Hz), -113.20 (2F, m), -121.75 (2F, m), -122.75 (2F, m), -123.44 (2F, m), -126.02 (2F, m) ppm; MS m/z (APCI+): 1626.76 (calc. 1626.83); CHN elemental analysis: observed (calculated): %C 60.7(59.8), %H 7.0 (7.1), %N 1.1 (0.9)

19b: Synthesised as above using 15 (84.2 mg, 70.0 µmol) and 4-((1H,1H,2H,2H-perfluorodecyloxy)ethynylbenzene (59.2 mg, 131 µmol) and was recrystallised from hexane. 98.1 mg (82%).

$^1$H NMR $\delta_H$ (400 MHz, CDCl$_3$): 7.66 (1H, t, $^3J_{HH} = 7.9$ Hz), 7.59 (2H, s), 7.51 (2H, AA’XX’), 7.11 (2H, d, $^3J_{HH} = 8.1$ Hz), 7.05 (2H, s), 6.86 (2H, AA’XX’), 4.29 (2H, t, $^3J_{HH} = 6.9$ Hz), 4.14 (4H, t, $^3J_{HH} = 6.6$
Hz), 3.99 (4H, t, $^3J_{HH} = 6.7$ Hz), 2.65 (2H, m), 1.84 (8H, m), 1.47 (8H, m), 1.25 (64H, broad s), 0.88 (12H, m) ppm; $^{19}$F NMR (376 MHz, CDCl$_3$): δ = -82.26 (3F, t, $^3J_{FF} = 10.0$ Hz), -114.28 (2F, m), -122.55 (2F, m), -122.81 (4F, m), -123.65 (2F, m), -124.47 (2F, m), -127.20 (2F, m); MS m/z (APCl+): 1726.82 (calc. 1726.77); CHN elemental analysis: observed (calculated): %C 58.2 (57.7), %H 6.8 (6.7), %N 1.3 (0.8)  

19c: Synthesised as above using 15 (0.0650 g, 0.542 mmol) and 4-(1H,1H,2H,2H-perfluorododecyloxy)ethynylbenzene (0.0397 g, 0.0239 mmol) and was recrystallised from hexane. 0.0800 g (80%).

$^1$H NMR δ$_H$ (400 MHz, CDCl$_3$): 7.67 (1H, t, $^3J_{HH} = 8.0$ Hz), 7.60 (2H, s), 7.51 (2H, AA’XX’), 7.13 (2H, d, $^3J_{HH} = 8.1$ Hz), 7.06 (2H, s), 6.86 (2H, AA’XX’), 4.29 (2H, t, $^3J_{HH} = 6.9$ Hz), 4.15 (4H, t, $^3J_{HH} = 6.6$ Hz), 3.99 (4H, t, $^3J_{HH} = 6.7$ Hz), 2.64 (2H, m), 1.84 (8H, m), 1.47 (8H, m), 1.25 (64H, broad s), 0.87 (12H, m) ppm; $^{19}$F NMR (376 MHz, CDCl$_3$): δ = -80.59 (3F, t, $^3J_{FF} = 10.1$ Hz), -113.20 (2F, m), -121.54 (10F, m), -121.57 (2F, m), -122.37 (2F, m), -125.98 (2F, m); MS m/z (APCl+): 1826.82 (M$^+$, calc. 1826.79); CHN elemental analysis: observed (calculated): %C 55.5 (55.9), %H 6.0 (6.4), %N 0.3 (0.8).

20a: Synthesised as above using 15, (129 mg, 111 µmol) and 3,4-bis(1H,1H,2H,2H-perfluorooctyloxy)ethynylbenzene (224 mg, 272 µmol) and was recrystallised from hexane. 167 mg (78%).
$^1$H NMR δ_H (400 MHz, CDCl$_3$): 7.68 (1H, t, $^3$J$_{HH}$ = 8.0 Hz), 7.58 (2H, s), 7.21 (1H, dd, $^3$J$_{HH}$ = 8.1 Hz, $^4$J$_{HH}$ = 1.8 Hz), 7.15 (1H, d, $^4$J$_{HH}$ = 2.0 Hz), 7.13 (2H, d, $^3$J$_{HH}$ = 8.5 Hz), 7.06 (2H, s), 6.87 (2H, d, $^3$J$_{HH}$ = 8.2 Hz), 4.31 (2H, t, $^3$J$_{HH}$ = 6.6 Hz), 4.30 (2H, t, $^3$J$_{HH}$ = 6.6 Hz), 4.13 (4H, t, $^3$J$_{HH}$ = 6.6 Hz), 4.00 (4H, t, $^3$J$_{HH}$ = 6.6 Hz), 2.66 (4H, m), 1.84 (8H, m), 1.47 (8H, m), 1.25 (64H, broad s), 0.87 (12H, m) ppm;

$^{19}$F NMR (376 MHz, CDCl$_3$): δ = 80.7 (6F, t, $^3$J$_{FF}$ = 9.9 Hz), -113.18 (4F, m), -121.8 (4F, m), -122.8 (4F, m), -126.1 (4F, m) ppm; MS m/z (APCI+): 1988.82 (M+H, calc. 1987.81);

CHN elemental analysis: observed (calculated): %C 53.6 (53.8), %H 6.1 (6.0), %N 0.6 (0.7).

20b: Synthesised as above using 15, (129 mg, 112 µmol) and 3,4-bis(1H,1H,2H,2H-perfluorodecyloxy)ethynylbenzene (278 mg, 270 µmol) and was recrystallised from hexane. 146 mg (62%).

$^1$H NMR δ_H (400 MHz, CDCl$_3$): 7.68 (1H, t, $^3$J$_{HH}$ = 8.0 Hz), 7.58 (2H, s), 7.21 (1H, dd, $^3$J$_{HH}$ = 8.1 Hz, $^4$J$_{HH}$ = 1.8 Hz), 7.15 (1H, d, $^4$J$_{HH}$ = 2.0 Hz), 7.13 (2H, d, $^3$J$_{HH}$ = 8.5 Hz), 7.06 (2H, s), 6.87 (2H, d, $^3$J$_{HH}$ = 8.2 Hz), 4.31 (2H, t, $^3$J$_{HH}$ = 6.6 Hz), 4.30 (2H, t, $^3$J$_{HH}$ = 6.6 Hz), 4.13 (4H, t, $^3$J$_{HH}$ = 6.6 Hz), 4.00 (4H, t, $^3$J$_{HH}$ = 6.6 Hz), 2.66 (4H, m), 1.84 (8H, m), 1.47 (8H, m), 1.25 (64H, broad s), 0.87 (12H, m) ppm;

$^{19}$F NMR (376 MHz, CDCl$_3$): δ = 80.7 (6F, t, $^3$J$_{FF}$ = 9.9 Hz), -113.18 (4F, m), -121.8 (4F, m), -122.8 (4F, m), -123.5 (4F, m), -126.1 (4F, m) ppm; MS m/z (APCI+): 2188.82 (M+H, calc. 2187.81);

CHN elemental analysis: observed (calculated): %C 50.9 (51.0), %H 5.3 (5.4), %N 0.5 (0.6).

20c: Synthesised as above using 15, (91 mg, 80.2 µmol) and 3,4-bis(1H,1H,2H,2H-perfluorododecyloxy)ethynylbenzene (138 mg, 114 µmol) and was recrystallised from hexane. 110 mg (61%).

$^1$H NMR δ_H (400 MHz, CDCl$_3$): 7.68 (1H, t, $^3$J$_{HH}$ = 8.0 Hz), 7.58 (2H, s), 7.21 (1H, dd, $^3$J$_{HH}$ = 8.1 Hz, $^4$J$_{HH}$ = 1.8 Hz), 7.15 (1H, d, $^4$J$_{HH}$ = 2.0 Hz), 7.13 (2H, d, $^3$J$_{HH}$ = 8.5 Hz), 7.06 (2H, s), 6.87 (2H, d, $^3$J$_{HH}$ = 8.2 Hz), 4.31 (2H, t, $^3$J$_{HH}$ = 6.6 Hz), 4.30 (2H, t, $^3$J$_{HH}$ = 6.6 Hz), 4.13 (4H, t, $^3$J$_{HH}$ = 6.6 Hz), 4.00 (4H, t, $^3$J$_{HH}$ = 6.6 Hz), 2.66 (4H, m), 1.84 (8H, m), 1.47 (8H, m), 1.25 (64H, broad s), 0.87 (12H, m) ppm;

$^{19}$F NMR (376 MHz, CDCl$_3$): δ = 80.7 (6F, m), -113.18 (4F, m), -121.8 (4F, m), -121.9 (8F, m), -122.8 (4F, m), -123.5 (4F, m), -126.1 (4F, m); MS m/z (APCI+): 2188.82 (M+H, calc. 2187.81);

CHN elemental analysis: observed (calculated): %C 50.9 (51.0), %H 5.3 (5.4), %N 0.5 (0.6).
122.8 (4F, m), -123.5 (4F, m), -126.1 (4F, m); MS m/z (APCI+): 2389.80 (M+H, calc. 2388.91), 2289.81 (M+H with 1x C10 chain), 2189.81 (M+H with 2x C10 chain, 15-10); CHN elemental analysis: observed (calculated): %C 49.7 (49.8), %H 5.1 (5.0), %N 0.5 (0.6).

21a: Synthesised as above using 15, (92.2 mg, 80.1 µmol) and 3,4,5-tris(1H,1H,2H,2H-perfluorooctyloxy)ethynylbenzene (134 mg, 114 µmol) and was recrystallised from hexane. 144 mg (82%).

1H NMR δH (400 MHz, CDCl3): 7.70 (1H, t, 3JHH = 8.0 Hz), 7.54 (2H, s), 7.15 (2H, d, 3JHH = 8.3 Hz), 7.07 (2H, s), 6.85 (2H, s), 4.30 (4H, t, 3JHH = 6.6 Hz), 4.23 (2H, t, 3JHH = 6.6 Hz), 4.11 (4H, t, 3JHH = 6.6 Hz), 4.00 (4H, t, 3JHH = 6.6 Hz), 2.66 (4H, m), 1.84 (8H, m), 1.47 (8H, m), 1.25 (64H, broad s), 0.87 (12H, m) ppm; 19F NMR (376 MHz, CDCl3): δ = -80.7 (6F, m), -80.9 (3F, m), -113.4 (6F, m), -121.8 (4F, m), -122.0 (2F, m), -122.9 (6F, m), -123.5 (6F, m), -126.1 (6F, m); MS m/z (APCI+): 2350.82 (calc. 2350.94); CHN elemental analysis: observed (calculated): %C 50.0 (49.6), %H 5.3 (5.2), %N 1.3 (0.6)

21b: Synthesised as above using 15, (91.1 mg, 80.3 µmol) and 3,4,5-tris(1H,1H,2H,2H-perfluorodecyloxy)ethynylbenzene (168 mg, 112 µmol) and was recrystallised from hexane. 161 mg (81%).

1H NMR δH (400 MHz, CDCl3): 7.70 (1H, t, 3JHH = 8.0 Hz), 7.54 (2H, s), 7.15 (2H, d, 3JHH = 8.3 Hz), 7.07 (2H, s), 6.85 (2H, s), 4.30 (4H, t, 3JHH = 6.6 Hz), 4.23 (2H, t, 3JHH = 6.6 Hz), 4.11 (4H, t, 3JHH = 6.6 Hz), 4.00 (4H, t, 3JHH = 6.6 Hz), 2.66 (4H, m), 1.84 (8H, m), 1.47 (8H, m), 1.25 (64H, broad s),
0.87 (12H, m) ppm; $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ = -80.7 (6F, m), -80.9 (3F, m), -113.4 (6F, m), -121.8 (18F, m), -122.8 (6F, m), -123.5 (6F, m), -126.1 (6F, m); MS m/z (APCI+): 2650.81 (calc. 2650.99); CHN elemental analysis: observed (calculated): %C 46.8 (46.7), %H 4.4 (4.6), %N 0.5 (0.5).

**Alternative Synthesis of Benzaldehydes (see main text)**

![Chemical Structure](image)

Figure S2: Alternative synthesis of benzaldehydes. Reagents are given but details can be found in *J. Mater. Chem. C.*, 2021, 9, 1287-1302. Reagents: (i) K$_2$CO$_3$/RBr; (ii) Li[AlH$_4$]; (iii) MnO$_2$.

In Figures S3-S8, the structure of **21a** and **21b** are:

![Chemical Structure](image)

**21a** $m = 6$

**21b** $m = 8$
Figure S3 $^1$H NMR spectra showing the downfield shift of the aromatic protons on the pincer ligand and of the phenylethynyl ligand of 21b (see p S29 for structure).
Figure S4 $^1$H NMR spectra showing the downfield shift of the O-CH$_2$ protons of the alkyl chains of 21b (see p S29 for structure).
Figure S5 $^{19}$F NMR spectra showing the consistency of chemical shift of the –CF$_2$– atoms of the perfluoroalkyl chains of 21a (see p S29 for structure).
Figure S6 $^{19}$F NMR spectra showing the consistency of chemical shift of the $\text{–CF}_2\text{–}$ atoms of the perfluoroalkyl chains of 21a (see p S29 for structure).
Figure S7 $^{19}$F NMR spectra showing the small downfield shift of the $-\text{CF}_2-$ atoms of the perfluoroalkyl chains of 21b (see p S29 for structure).
Figure S8 $^{19}$F NMR spectra showing the downfield shift of the –CF₃ atoms of the perfluoroalkyl chains of a) 21a and b) 21b (see p S29 for structure).
Figure S9 Back-to-back arrangement of the complexes proposed for complexes 2.
Table S1 X-Ray diffraction data for the mesomorphic complexes.

| Complex | Phase | Phase Temperature | 2θ / ° | d_{obs} / Å | d_{calc} / Å | hk | a, b / Å |
|---------|-------|-------------------|--------|-------------|-------------|----|---------|
| 16a     | Colₗ | T = 122.9 °C cooling | 3.07   | 28.7        | 28.7        | 10 |         |
|         |       |                   | 5.33   | 16.6        | 16.6        | 11 | a = 33.1|
|         |       |                   | 6.11   | 14.4        | 14.4        | 20 |         |
|         | Colᵣ | T = 105.0 °C cooling | 2.28   | 38.6        |             |    |         |
|         |       |                   | 2.80   | 30.9        |             |    |         |
|         |       |                   | 5.68   | 15.5        |             |    |         |
|         |       |                   | 10.88  | 8.1         |             |    |         |
| 16c     | Colₗ | T = 115.0 °C cooling | 2.83   | 31.1        | 31.1        | 10 |         |
|         |       |                   | 5.71   | 15.5        | 15.6        | 20 | a = 35.9|
|         |       |                   | 10.81  | 8.2         | 8.0         |    |         |
| 17a     | Colₗ | T = 130.0 °C cooling | 2.92   | 30.2        | 30.2        | 10 |         |
|         |       |                   | 5.03   | 17.5        | 17.4        | 11 |         |
|         |       |                   | 5.84   | 15.1        | 15.1        | 20 | a = 34.9|
|         |       |                   | 8.76   | 10.1        |             |    |         |
|         |       |                   | 10.52  | 8.4         |             |    |         |
|         |       |                   | 11.66  | 7.6         |             |    |         |
| 17b     | Colᵣ | T = 140.0 °C cooling | 2.74   | 32.2        | 32.2        | 11 |         |
|         |       |                   | 3.62   | 24.4        | 24.4        | 20 |         |
|         |       |                   | 4.61   | 19.3        | 19.5        | 12 |         |
|         |       |                   | 5.39   | 16.4        | 16.2        | 30 | a = 48.8|
|         |       |                   | 6.15   | 14.4        | 14.2        | 03 | b = 42.6|
|         |       |                   | 9.61   | 9.2         | 9.5         |    |         |
|         |       |                   | 11.99  | 7.4         | 7.2         |    |         |
| 17c     | Colᵣ | T = 100 °C heating  | 2.79   | 31.6        | 31.6        | 11 | a = 48.0|
|         |       |                   | 3.67   | 24.0        | 24.0        | 20 | b = 42.0|
|         |       |                   | 4.52   | 19.5        | 19.3        | 12 |         |
| 19a     | Colₗ | T = 177.5 cooling  | 3.44   | 25.7        | 25.7        | 10 |         |
|         |       |                   | 5.95   | 14.8        | 14.8        | 11 | 29.7     |
|         |       |                   | 6.87   | 12.9        | 12.9        | 20 |         |
| 19b     | Colₗ | T = 81.6 cooling   | 2.95   | 29.9        | 29.9        | 10 |         |
|         |       |                   | 5.34   | 16.5        | 17.2        | 11 | 34.5     |
|         |       |                   | 6.02   | 14.7        | 15          | 20 |         |
| 19c     | Colₗ | T = 89.7 cooling   | 2.97   | 29.7        | 29.7        | 10 |         |
|         |       |                   | 5.37   | 16.4        | 17.1        | 11 | 34.3     |
|         |       |                   | 5.97   | 14.8        | 14.9        | 20 |         |
| Complex | Phase | 2θ/° | d_{obs}/Å | d_{calc}/Å | hk | a, b/Å |
|---------|-------|-------|-----------|-----------|----|-------|
| 20a     | Col_r | 2.75  | 32.1      | 32.1      | 11 |       |
|         |       | 3.17  | 27.8      | 27.8      | 20 |       |
|         |       | 4.43  | 19.9      |           |    |       |
|         |       | 5.27  | 16.7      | 16.8      | 31 |       |
|         |       | 6.34  | 13.9      | 13.9      | 40 |       |
|         |       | 8.19  | 10.8      | 10.7      | 33 |       |
|         | Col_h | 3.30  | 26.7      | 26.7      | 10 |       |
|         |       | 5.69  | 15.5      | 15.4      | 11 |       |
|         |       | 6.61  | 13.4      | 13.4      | 20 |       |
|         |       | 8.70  | 10.2      | 10.1      | 21 |       |
| 20b     | Col_r | 2.07  | 42.6      | 42.6      | 11 |       |
|         |       | 2.95  | 29.9      | 29.9      | 20 |       |
|         |       | 4.44  | 19.9      | 19.9      | 30 |       |
|         |       | 5.52  | 16.0      |           |    |       |
|         |       | 5.90  | 14.9      | 14.9      | 40 |       |
|         | Col_h | 3.13  | 28.2      | 28.2      | 10 |       |
|         |       | 5.39  | 16.4      | 16.3      | 11 |       |
|         |       | 5.90  | 14.9      |           |    |       |
| 21a     | Col_h | 3.18  | 27.8      | 27.8      | 10 |       |
|         |       | 5.50  | 16.0      | 16.0      | 11 |       |
|         |       | 6.41  | 13.8      | 13.9      | 20 |       |
|         |       | 8.42  | 10.5      | 10.5      | 21 |       |
| 21b     | Col_h | 3.05  | 28.9      | 28.9      | 10 |       |
|         |       | 5.26  | 16.8      | 16.7      | 11 |       |
|         |       | 6.12  | 14.4      | 14.4      | 20 |       |
|         |       | 8.05  | 11.0      | 10.9      | 21 |       |

Figure S10 Hexasubstituted truxenes showing a frustrated/re-entrant nematic phase. LHS compounds n = 6 to 15; RHS compounds n = 6 to 12.
Figure S11: Photophysical spectra, including absorption (black), excitation (dashed green), and emission at 298 (red) and 77 K (blue) spectra for a) 17a and b) 18a.

Figure S12 Photophysical spectra, including absorption (black), excitation (dashed green), and emission at 298 (red) and 77 K (blue) spectra for a) 20a and b) 21a.

**Cyclic Voltammetry**

Data were recorded as described previously,\(^1\) although the lower solubility for 21b limited the amount that could be dissolved. The combined voltammograms are shown as Figure S13.
Device Preparation

Preparation:

The patterned ITO substrates were washed with acetone and isopropyl alcohol under sonication for 15 min, followed by 15 min of UV-ozone-treatment. After surface treatment, the PEDOT:PSS layer was spin-coated onto the ITO substrate as the hole-injecting layer, followed by annealing at 150 °C for 15 min. The emissive layers were prepared by spin-coating onto the PEDOT:PSS followed by annealing at 60 °C for 30 min. The electron-transporting layer and the cathode materials were thermally evaporated and deposited onto the emitter layer in a vacuum chamber. The thermally evaporated deposition rates were 0.6–1 Å s⁻¹ for the organic layers, 0.1 Å s⁻¹ for LiF and 1.5-1.8 Å s⁻¹ for the Al electrode, respectively.

In the devices, the emitter layer is a blend of the host matrix poly(9-vinylcarbazole) (PVK), 1,3-Bis[2-(4-tert-butyphenyl)-1,3,4-oxadiazol-5-yl] benzene (OXD-7) and the dyes. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS) serves as the hole injection layer,
while 1,3,5-tri(\textit{m}-pyrid-3-yl-phenyl)benzene (TmPyPB) acts as electron-transport layers. LiF and Al serve as the cathode.

![Figure S14. The CBP-based device performance for 20b: (a) EQE-current density curve. Inset: EL spectrum; (b) J-V-L curve](image)

**Computational Chemistry**

All calculations were performed using the TURBOMOLE V6.4 package using the resolution of identity (RI) approximation.\textsuperscript{2-9} Initial optimisations were performed at the (RI-)BP86/SV(P) level with an m5 grid, followed by frequency calculations at the same level. All minima were confirmed as such by the absence of imaginary frequencies. Single-point and TD-DFT calculations on the (RI-)BP86/SV(P) optimised geometries were performed using the hybrid PBE0 functional and the flexible def2-TZVPP basis set with a 60-electron effective core potential. Energies, xyz coordinates and the first 50 lines of the vibrational spectra are presented. Calculations with a solvent model were performed in Gaussian16\textsuperscript{10} using the PBE0 functional and def2-TZVPP basis set with an SCRF solvent model for CH\textsubscript{2}Cl\textsubscript{2}. 
Table S2 Three lowest-energy transition calculated for the complexes indicated. The predicted oscillator strengths are given (in brackets) with the dominant orbital contributions. Calculations performed in the gas phase.

|       | X = F          | X = H          |
|-------|----------------|----------------|
| **16-Me** |                |                |
|        | 432 nm (0.052) | HOMO – LUMO    |
|        | 398 nm (0.145) | HOMO-1 – LUMO  |
|        | 371 nm (0.0042)| HOMO – LUMO+1  |
|        | 443 nm (0.042) | HOMO – LUMO    |
|        | 398 nm (0.142) | HOMO-1 – LUMO  |
|        | 381 nm (0.0073)| HOMO – LUMO+1  |
| **17-Me** |                |                |
|        | 422 nm (0.047) | HOMO – LUMO    |
|        | 398 nm (0.145) | HOMO-1 – LUMO  |
|        | 363 nm (0.0029)| HOMO – LUMO+1  |
|        | 439 (0.058)    | HOMO – LUMO    |
|        | 398 nm (0.142) | HOMO-1 – LUMO  |
|        | 378 nm (0.0053)| HOMO – LUMO+1  |
| **18-Me** |                |                |
|        | 419 nm (0.048) | HOMO – LUMO    |
|        | 398 nm (0.143) | HOMO-2 – LUMO  |
|        | 361 nm (0.0027)| HOMO-1 – LUMO  |
|        | 448 nm (0.060) | HOMO – LUMO    |
|        | 398 nm (0.137) | HOMO-2 – LUMO  |
|        | 385 nm (0.0077)| HOMO – LUMO+1  |
### SCF Energy (au) BP86/SV(P)
-1871.603582557

### SCF Energy (au) PBE0/def2-TZVPP
-1871.370497339

### Zero Point Energy (au)
0.448378

### Chemical potential (kJ mol$^{-1}$)
986.14

### xyz coordinates

| Atom | X   | Y   | Z   |
|------|-----|-----|-----|
| Au   | -0.9907587 | -1.6273974 | -1.2798634 |
| C    | -0.0899459  | -0.1904229  | -0.2752420  |
| N    | -1.9300094  | -3.1284607  | -2.3268131  |
| C    | -2.7889547  | -0.6390260  | -1.7715716  |
| C    | -3.1713109  | -2.8592355  | -2.8262058  |
| C    | 2.1749126   | -5.4098834  | -1.2108608  |
| H    | 2.8187942   | -6.3005710  | -1.2438831  |
| C    | 0.4875846   | -3.1261947  | -1.1441748  |
| C    | -3.6561195  | -1.5016811  | -2.5318224  |
| C    | -3.2061551  | 0.6555276   | -1.4724203  |
| H    | -2.5641344  | 1.3395904   | -0.8947622  |
| C    | -4.4715147  | 1.1310162   | -1.9050459  |
| C    | 1.7323500   | -3.0970999  | -0.5207220  |
| H    | 2.0823506   | -2.1955127  | 0.0069250   |
| C    | -3.8241930  | -3.8836204  | -3.545856   |
| C    | -4.8254219  | -3.7158785  | -3.9678077  |
| C    | 0.9221993   | -5.4455035  | -1.839534   |
| H    | 0.6189523   | -6.3742045  | -2.3519012  |
| C    | 2.5861419   | -4.2307326  | -0.5464608  |
| C    | -3.1743843  | -5.1174452  | -3.712536   |
| H    | -3.6779101  | -5.9222554  | -4.2733048  |
| C    | -1.8956259  | -3.547659   | -3.1789107  |
| H    | -1.3963576  | -6.3157715  | -3.315927   |
| C    | 0.0650290   | -4.3250939  | -1.8211798  |
| C    | -1.2588879  | -4.3092356  | -2.4622121  |
| C    | -4.9112533  | -1.0176207  | -2.9566914  |
| H    | -5.5913062  | -1.6610202  | -3.5402046  |
| C    | -5.3261623  | 0.2864390   | -2.6513020  |
| H    | -6.3106983  | 0.6324706   | -2.9976413  |
| O    | 3.7768285   | -4.0891288  | 0.0934163   |
| O    | -4.7748770  | 2.4093475   | -1.5551561  |
| C    | 0.4762532   | 0.7097528   | 0.3571527   |
| C    | 1.1341142   | 1.7498516   | 1.0858766   |
| C    | 2.4450901   | 3.8230916   | 2.5352283   |
| C    | 3.1421806   | 3.0864196   | 1.5511438   |
| C    | 2.5001414   | 2.0696166   | 0.843481    |
| C    | 0.4524976   | 2.5001720   | 2.0763792   |
| C    | 1.0919285   | 3.5212024   | 2.7968881   |
| H    | 3.0535671   | 1.5005886   | 0.0797919   |
| H    | -0.6045481  | 2.2711793   | 2.2853164   |
| C    | 4.6839610   | -5.1788649  | 0.1151831   |
| C    | -6.0202662  | 2.9574452   | -1.9537993  |
| H    | -6.1218100  | 2.9867287   | -3.0645351  |
| H    | -6.0396508  | 3.9939392   | -1.5609044  |
| H    | -6.8784460  | 2.3884186   | -1.5239797  |
| C    | 5.0053038   | -5.4689658  | -0.9131664  |
| H    | 4.2468712   | -6.0693814  | 0.6258586   |
| H    | 5.5679512   | -4.8310485  | 0.686080    |
| O    | 3.1620444   | 4.8013728   | 3.1708908   |
| C    | 2.5227615   | 5.5768111   | 4.1712637   |
| H    | 2.1441856   | 4.9257409   | 4.9948763   |
| H    | 1.6500191   | 6.1261830   | 3.7418004   |
| C    | 3.5241072   | 6.5907877   | 4.7195374   |
| C    | 4.6625493   | 6.0001946   | 5.5415982   |
| # | mode | symmetry | wave number (cm^{-1}) | IR intensity (km/mol) | selection rules |
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| 2 | 2 | a | 0.00 | 0.00000 | - - |
| 3 | 3 | a | 0.00 | 0.00000 | - - |
| 4 | 4 | a | 0.00 | 0.00000 | - - |
| 5 | 5 | a | 0.00 | 0.00000 | - - |
| 6 | 6 | a | 0.00 | 0.00000 | - - |
| 7 | 7 | a | 7.55 | 0.50066 | YES YES |
| 8 | 8 | a | 10.14 | 0.24629 | YES YES |
| 9 | 9 | a | 14.04 | 0.82949 | YES YES |
| 10 | 10 | a | 21.72 | 0.36588 | YES YES |
| 11 | 11 | a | 27.52 | 2.20817 | YES YES |
| 12 | 12 | a | 31.78 | 0.46506 | YES YES |
| 13 | 13 | a | 44.51 | 1.00035 | YES YES |
| 14 | 14 | a | 56.13 | 0.00437 | YES YES |
| 15 | 15 | a | 62.01 | 0.28371 | YES YES |
| 16 | 16 | a | 69.16 | 0.15384 | YES YES |
| 17 | 17 | a | 80.64 | 0.52006 | YES YES |
| 18 | 18 | a | 84.09 | 1.12308 | YES YES |
| 19 | 19 | a | 86.27 | 0.00441 | YES YES |
| 20 | 20 | a | 100.61 | 3.55877 | YES YES |
| 21 | 21 | a | 106.39 | 0.63641 | YES YES |
| 22 | 22 | a | 134.11 | 0.41079 | YES YES |
| 23 | 23 | a | 141.20 | 0.05668 | YES YES |
| 24 | 24 | a | 148.24 | 0.56376 | YES YES |
| 25 | 25 | a | 169.26 | 0.13450 | YES YES |
| 26 | 26 | a | 179.16 | 0.20303 | YES YES |
| 27 | 27 | a | 186.95 | 0.01462 | YES YES |
| 28 | 28 | a | 216.17 | 2.42252 | YES YES |
| 29 | 29 | a | 221.56 | 0.08071 | YES YES |
| 30 | 30 | a | 223.99 | 0.72472 | YES YES |
| 31 | 31 | a | 226.04 | 1.55995 | YES YES |
| 32 | 32 | a | 232.45 | 2.53342 | YES YES |
| 33 | 33 | a | 242.92 | 0.01417 | YES YES |
| 34 | 34 | a | 243.21 | 1.22036 | YES YES |
| 35 | 35 | a | 253.13 | 1.11219 | YES YES |
| 36 | 36 | a | 273.10 | 2.47571 | YES YES |
| 37 | 37 | a | 286.81 | 0.34579 | YES YES |
| 38 | 38 | a | 299.76 | 7.73731 | YES YES |
| 39 | 39 | a | 304.57 | 6.14245 | YES YES |
| 40 | 40 | a | 320.82 | 0.06173 | YES YES |
| 41 | 41 | a | 335.56 | 0.14151 | YES YES |
| 42 | 42 | a | 336.38 | 0.10424 | YES YES |
| 43 | 43 | a | 362.53 | 0.91716 | YES YES |
| 44 | 44 | a | 370.47 | 0.05182 | YES YES |
| 45 | 45 | a | 408.26 | 2.04277 | YES YES |
| 46 | 46 | a | 409.82 | 0.38800 | YES YES |
| 47 | 47 | a | 413.67 | 0.24240 | YES YES |
| 48 | 48 | a | 426.22 | 0.15671 | YES YES |
| 49 | 49 | a | 435.61 | 2.92318 | YES YES |
| 50 | 50 | a | 447.98 | 2.17073 | YES YES |
**16Me-H**

SCF Energy (au) BP86/SV(P)  
-1574.072944684

SCF Energy (au) PBE0/def2-TZVPP  
-1573.770144462

Zero Point Energy (au)  
0.4703613

Chemical potential (kJ mol\(^{-1}\))  
1054.27

xyz coordinates

61

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-1.2784936

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H  
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O  
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H  
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5.0171666

C  
1.5870293  
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C  
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4.7813994

C  
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| # | mode | symmetry | wave number | IR intensity | selection rules |
|---|------|----------|-------------|--------------|-----------------|
| 1 |      |          | 0.00        | 0.00000      | -               |
| 2 |      |          | 0.00        | 0.00000      | -               |
| 3 |      |          | 0.00        | 0.00000      | -               |
| 4 |      |          | 0.00        | 0.00000      | -               |
| 5 |      |          | 0.00        | 0.00000      | -               |
| 6 |      |          | 0.00        | 0.00000      | -               |
| 7 | a    |          | 8.69        | 0.48737      | YES             |
| 8 | a    |          | 11.84       | 0.12536      | YES             |
| 9 | a    |          | 15.09       | 0.53971      | YES             |
| 10| a    |          | 25.43       | 2.25156      | YES             |
| 11| a    |          | 34.34       | 0.64497      | YES             |
| 12| a    |          | 55.73       | 0.32967      | YES             |
| 13| a    |          | 56.18       | 0.00675      | YES             |
| 14| a    |          | 69.36       | 0.01772      | YES             |
| 15| a    |          | 77.90       | 0.50151      | YES             |
| 16| a    |          | 81.33       | 0.95001      | YES             |
| 17| a    |          | 85.98       | 0.32305      | YES             |
| 18| a    |          | 86.13       | 0.07806      | YES             |
| 19| a    |          | 100.42      | 3.67103      | YES             |
| 20| a    |          | 128.14      | 0.45979      | YES             |
| 21| a    |          | 140.02      | 0.10873      | YES             |
| 22| a    |          | 141.27      | 0.06944      | YES             |
| 23| a    |          | 149.15      | 0.46924      | YES             |
| 24| a    |          | 168.08      | 0.48025      | YES             |
| 25| a    |          | 178.69      | 0.31075      | YES             |
| 26| a    |          | 186.93      | 0.01581      | YES             |
| 27| a    |          | 214.48      | 1.64889      | YES             |
| 28| a    |          | 220.58      | 0.77911      | YES             |
| 29| a    |          | 222.62      | 0.28312      | YES             |
| 30| a    |          | 225.47      | 0.22404      | YES             |
| 31| a    |          | 232.43      | 2.30228      | YES             |
| 32| a    |          | 238.89      | 5.10693      | YES             |
| 33| a    |          | 243.16      | 0.00264      | YES             |
| 34| a    |          | 253.80      | 1.80398      | YES             |
| 35| a    |          | 286.80      | 0.36769      | YES             |
| 36| a    |          | 299.53      | 5.14203      | YES             |
| 37| a    |          | 303.15      | 7.43589      | YES             |
| 38| a    |          | 310.39      | 1.61713      | YES             |
| 39| a    |          | 320.94      | 0.06877      | YES             |
| 40| a    |          | 335.45      | 0.28480      | YES             |
| 41| a    |          | 336.18      | 0.07802      | YES             |
| 42| a    |          | 370.49      | 0.11081      | YES             |
| 43| a    |          | 408.07      | 2.27668      | YES             |
| 44| a    |          | 409.73      | 0.14359      | YES             |
| 45| a    |          | 416.88      | 0.23938      | YES             |
| 46| a    |          | 426.25      | 0.18611      | YES             |
| 47| a    |          | 434.24      | 1.06033      | YES             |
| 48| a    |          | 435.77      | 3.15057      | YES             |
| 49| a    |          | 451.10      | 1.16705      | YES             |
| 50| a    |          | 476.06      | 1.96406      | YES             |
### 17Me-F

| SCF Energy (au) BP86/SV(P) | -2362.138766173 |
|---------------------------|------------------|
| SCF Energy (au) PBE0/def2-TZVPP | -2361.970034996 |
| Zero Point Energy (au) | 0.5128255 |
| Chemical potential (kJ mol⁻¹) | 1123.50 |

**xyz coordinates**

| 71 |
|-----|
| Au  | -1.8313971 | -2.1932591 | -1.2637795 |
| C   | -0.9276421 | -0.8430804 | -0.1474485 |
| N   | -2.7785495 | -3.5992288 | -2.4284502 |
| C   | -3.6621903 | -1.1984060 | -1.5926219 |
| C   | -4.0408821 | -3.3062026 | -2.8573028 |
| C   | 1.3999858  | -5.8995396 | -1.6807915 |
| H   | 2.0554175  | -6.7698845 | -1.8241999 |
| C   | -0.3224526 | -3.6675911 | -1.3299855 |
| C   | -4.5393213 | -1.9969770 | -2.4093159 |
| C   | -4.0911277 | 0.0490612  | -1.1472208 |
| H   | -3.4425606 | 0.6836016  | -0.5223750 |
| C   | -5.3791476 | 0.5397289  | -1.4870317 |
| C   | 0.9415169  | -3.6781212 | -0.7452950 |
| H   | 1.2929043  | -2.8289345 | -0.1376161 |
| C   | -4.6995941 | -4.2654592 | -3.6570138 |
| H   | -5.7175204 | -4.0765555 | -4.0271437 |
| C   | 0.1271919  | -5.8953865 | -2.2712255 |
| H   | -0.1775105 | -6.7731872 | -2.8657477 |
| C   | 1.8122761  | -4.7863499 | -0.9125271 |
| C   | -4.0344237 | -5.4616476 | -3.9707726 |
| H   | -4.5425644 | -6.2152661 | -4.5948843 |
| C   | -2.7342848 | -5.7165881 | -3.5046332 |
| H   | -2.223138  | -6.659153  | -3.7562119 |
| C   | -0.7469362 | -4.796808  | -2.1122076 |
| C   | -2.0921546 | -4.7457249 | -2.7060265 |
| C   | -5.8168853 | -1.4983727 | -2.7405411 |
| H   | -6.502640  | -0.297066  | -3.3648425 |
| C   | -6.2439241 | 0.2418171  | -2.2885051 |
| H   | -7.2458426 | 0.1171393  | -2.5646781 |
| O   | 3.0213110  | -4.6877060 | -0.2978763 |
| O   | -5.6919764 | 1.7678476  | -0.9973009 |
| C   | -0.3683604 | 0.0081109  | 0.5548836 |
| C   | 0.2795018  | 0.9924285  | 1.3658647 |
| C   | 1.5885472  | 2.9538516  | 2.9575312 |
| C   | 2.2700479  | 2.3556989  | 1.8581566 |
| C   | 1.6134312  | 1.3927375  | 1.0746883 |
| C   | -0.3797092 | 1.5846488  | 2.4710146 |
| C   | 0.2746239  | 2.5522695  | 3.2455124 |
| O   | 3.5652224  | 2.7639204  | 1.6547431 |
| H   | 2.1167628  | 0.9218801  | 0.2192655 |
| H   | -1.4098514 | 1.2812216  | 2.7119200 |
| C   | 3.9408306  | -5.7617306 | -0.4074803 |
| C   | -6.9606402 | 2.3284440  | -1.2935907 |
| H   | -7.1024938 | 2.4704771  | -2.3910639 |
| H   | -6.9831311 | 3.3177917  | -0.7940879 |
| H   | -7.7922587 | 1.6999018  | -0.8959751 |
| H   | 4.2371943  | -5.9453454 | -1.4674124 |
| O   | 3.5279111  | -6.7039518 | 0.0242525 |
| C   | 4.8363939  | -5.4600435 | 0.1722015 |
| C   | 4.3224981  | 2.1170641  | 0.6422223 |
| O   | 2.2004528  | 3.8587685  | 3.7895895 |
| C   | 2.5770013  | 5.1174057  | 3.2204077 |
| H   | 3.8619054  | 2.2773545  | -0.3611367 |
| H   | 4.3539215  | 1.0180759  | 0.8312491 |
$vibrational spectrum (first 50 lines)$

| # | mode | symmetry | wave number | IR intensity | selection rules |
|---|------|----------|-------------|--------------|-----------------|
| 1 | 0.00 | 0.00000  | -           | -            |                 |
| 2 | 0.00 | 0.00000  | -           | -            |                 |
| 3 | 0.00 | 0.00000  | -           | -            |                 |
| 4 | 0.00 | 0.00000  | -           | -            |                 |
| 5 | 0.00 | 0.00000  | -           | -            |                 |
| 6 | 0.00 | 0.00000  | -           | -            |                 |
| 7 | a    | 3.22     | 0.11898     | YES          | YES             |
| 8 | a    | 7.77     | 0.12834     | YES          | YES             |
| 9 | a    | 12.81    | 0.30527     | YES          | YES             |
| 10 | a | 13.99    | 0.21957     | YES          | YES             |
| 11 | a | 21.16    | 0.23792     | YES          | YES             |
| 12 | a | 22.77    | 0.34792     | YES          | YES             |
| 13 | a | 25.06    | 1.75260     | YES          | YES             |
| 14 | a | 33.07    | 1.16444     | YES          | YES             |
| 15 | a | 36.31    | 0.15835     | YES          | YES             |
| 16 | a | 46.44    | 1.45174     | YES          | YES             |
| 17 | a | 52.76    | 1.11637     | YES          | YES             |
| 18 | a | 56.24    | 0.00336     | YES          | YES             |
| 19 | a | 62.30    | 0.32621     | YES          | YES             |
| 20 | a | 80.29    | 1.20000     | YES          | YES             |
| 21 | a | 82.80    | 1.87569     | YES          | YES             |
| 22 | a | 86.30    | 0.02811     | YES          | YES             |
| 23 | a | 87.22    | 0.98040     | YES          | YES             |
| 24 | a | 99.17    | 1.00700     | YES          | YES             |
| 25 | a | 100.72   | 3.34420     | YES          | YES             |
| 26 | a | 113.58   | 1.11297     | YES          | YES             |
| 27 | a | 133.52   | 0.44821     | YES          | YES             |
| 28 | a | 141.31   | 0.04947     | YES          | YES             |
| 29 | a | 150.73   | 0.39555     | YES          | YES             |
| 30 | a | 153.45   | 0.51829     | YES          | YES             |
| 31 | a | 187.02   | 0.01490     | YES          | YES             |
| 32 | a | 188.82   | 0.43593     | YES          | YES             |
| 33 | a | 211.43   | 0.40714     | YES          | YES             |
| 34 | a | 220.02   | 0.62549     | YES          | YES             |
| 35 | a | 221.22   | 0.56544     | YES          | YES             |
| 36 | a | 225.27   | 0.15296     | YES          | YES             |
| 37 | a | 227.91   | 0.94971     | YES          | YES             |
| 38 | a | 231.43   | 3.62865     | YES          | YES             |
| 39 | a | 232.51   | 1.65025     | YES          | YES             |
| 40 | a | 243.14   | 0.36457     | YES          | YES             |
| 41 | a | 243.57   | 1.34072     | YES          | YES             |
| 42 | a | 250.26   | 1.23045     | YES          | YES             |
|   |   |   |   |   |
|---|---|---|---|---|
| 43 | a | 261.80 | 3.25255 | YES | YES |
| 44 | a | 267.68 | 2.33423 | YES | YES |
| 45 | a | 286.85 | 0.39468 | YES | YES |
| 46 | a | 300.30 | 8.65023 | YES | YES |
| 47 | a | 311.09 | 5.19060 | YES | YES |
| 48 | a | 320.77 | 0.13197 | YES | YES |
| 49 | a | 321.33 | 0.28313 | YES | YES |
| 50 | a | 336.02 | 0.18493 | YES | YES |
$^{17}$Me-H

SCF Energy (au) BP86/SV(P)  -1767.072709752
SCF Energy (au) PBE0/def2-TZVPP -1766.765108985
Zero Point Energy (au) 0.5566944
Chemical potential (kJ mol$^{-1}$) 1257.75

xyz coordinates
71

Au  -0.8551331  -2.0693216  -2.0491215
C   0.0580902  -0.6865028  -0.9818862
N  -1.8066710  -3.5129863  -3.1635742
C  -2.6905703  -1.0889013  -2.3985436
C  -3.0718441  -3.2365794  -3.5943670
C   2.3845040  -5.7744154  -2.3759811
H   3.0441144  -6.6456038  -2.4982848
C   0.6563875  -3.5402259  -2.0790076
C  -3.5708447  -1.9144576  -3.1846066
C  -3.1203255   0.1718374  -1.9918320
H  -2.4681439   0.8276251  -1.3930543
C  -4.4108238   0.6488195  -2.3400676
C   1.9245422  -3.5272782  -1.5040214
H   2.277113   -2.6575577  -0.9272590
C  -3.7326852  -4.2211840  -4.3604164
H  -4.7531949  -4.0463434  -4.7303658
C  -1.083738   -5.7935783  -2.9564093
C   0.8032853  -6.6898874  -3.5225424
C   2.7987973  -4.6365810  -1.6447485
C  -3.0657939  -5.4248661  -4.6414117
H  -3.5751644  -6.193215  -5.2397605
C  -1.7625418  -5.6620240  -4.1752121
H  -1.2499706  -6.080807  -4.4012961
C   0.2305160  -4.6971325  -2.8237183
C  -1.1182450  -4.6652820  -3.4100526
C   4.8509653  -1.4292079  -3.5250022
H  -5.5413015  -2.044019  -4.1265444
C  -5.2782532  -0.1593946  -3.1137666
H  -6.2822215   0.186258  -3.3941149
O   4.0114338  -4.5141172  -1.0433012
O  -4.7245062   1.8923561  -1.8879756
C   0.6343146   0.1810651  -0.3139635
C   1.2980972  -1.1854827  -0.4595881
C   2.5896112  -3.1918538  -2.0084138
C   3.2792810  -2.5060217  -0.9949645
C   2.6578033   1.5096185  -0.2300493
C   0.5966390  -1.8761743  -1.4863628
C   1.2246561   2.8625924  -2.2654528
H   3.2158675   0.9786060  -0.5560804
H  -0.4530443   1.6035762   1.6631914
O   0.6249478   3.5622242  -3.2784844
C   4.9406569  -5.5810587  -1.1369609
C  -5.9932681  -2.4415989  -2.2025242
C  -6.1361719  -2.5460836  -3.3041284
H  -6.0164944   3.4476842  -1.7379333
H  -6.8249435   1.8268552  -1.7836031
H   5.2254805   -5.7885924  -2.1956112
H   4.5431408  -6.5161237  -0.6759649
H   5.8400585  -5.2549270  -0.5769033
C  -0.6843786   3.2000087   3.7294235
O   3.2697947   4.1094467   2.7683709
C   2.8500995   5.4816864   2.6762827
H   1.7876523   5.5780857   2.9961354
H   2.9264077   5.8153171   1.6127332
\begin{tabular}{cccc}
\textbf{C} & 3.7622445 & 6.3223518 & 3.5655707 \\
\textbf{C} & 3.6818294 & 5.9599749 & 5.0537784 \\
\textbf{H} & 3.4850774 & 7.3911922 & 3.4124137 \\
\textbf{H} & 4.8102166 & 6.2120442 & 3.2033113 \\
\textbf{C} & -0.6895313 & 1.9716770 & 4.6481377 \\
\textbf{H} & -1.3709922 & 3.0612453 & 2.8622040 \\
\textbf{H} & -1.0337497 & 4.0948361 & 4.2892953 \\
\textbf{H} & 0.3523641 & 1.0784338 & 4.0755602 \\
\textbf{H} & -1.7500704 & 2.1754374 & 4.9320463 \\
\textbf{H} & 0.1752771 & 2.1453410 & 5.9030469 \\
\textbf{H} & 4.3682234 & 6.5914179 & 5.6600716 \\
\textbf{H} & 3.9589804 & 4.8962502 & 5.2138768 \\
\textbf{H} & 2.6502940 & 6.1022041 & 5.4481526 \\
\textbf{H} & 0.1559852 & 1.2288113 & 6.5322155 \\
\textbf{H} & -0.1838777 & 2.9940404 & 6.5286353 \\
\textbf{H} & 1.2327560 & 2.3523175 & 5.6315609 \\
\textbf{H} & 4.3349473 & 2.7743600 & 0.8295126 \\
\end{tabular}

$\text{vibrational spectrum (first 50 lines)}$

\begin{tabular}{cccccc}
# & \textbf{mode} & \textbf{symmetry} & \textbf{wave number} & \textbf{IR intensity} & \textbf{selection rules} \\
& & & \textbf{cm**(-1)} & \textbf{km/mol} & \textbf{IR} & \textbf{Raman} \\
1 & & 0.00 & 0.00000 & - & - \\
2 & & 0.00 & 0.00000 & - & - \\
3 & & 0.00 & 0.00000 & - & - \\
4 & & 0.00 & 0.00000 & - & - \\
5 & & 0.00 & 0.00000 & - & - \\
6 & & 0.00 & 0.00000 & - & - \\
7 & a & 3.03 & 0.22581 & YES & YES \\
8 & a & 10.71 & 0.14395 & YES & YES \\
9 & a & 13.93 & 0.41903 & YES & YES \\
10 & a & 20.68 & 0.03337 & YES & YES \\
11 & a & 24.34 & 1.49901 & YES & YES \\
12 & a & 33.47 & 0.63235 & YES & YES \\
13 & a & 36.21 & 0.52816 & YES & YES \\
14 & a & 42.28 & 0.74933 & YES & YES \\
15 & a & 56.24 & 0.00511 & YES & YES \\
16 & a & 58.96 & 0.07864 & YES & YES \\
17 & a & 73.09 & 1.43194 & YES & YES \\
18 & a & 78.86 & 0.79286 & YES & YES \\
19 & a & 84.64 & 0.42560 & YES & YES \\
20 & a & 86.20 & 0.00311 & YES & YES \\
21 & a & 100.50 & 3.67395 & YES & YES \\
22 & a & 105.16 & 0.37083 & YES & YES \\
23 & a & 118.38 & 1.04580 & YES & YES \\
24 & a & 122.34 & 0.27419 & YES & YES \\
25 & a & 141.29 & 0.06132 & YES & YES \\
26 & a & 149.83 & 0.65771 & YES & YES \\
27 & a & 157.64 & 1.03772 & YES & YES \\
28 & a & 168.92 & 1.59676 & YES & YES \\
29 & a & 186.99 & 0.01480 & YES & YES \\
30 & a & 189.84 & 1.76420 & YES & YES \\
31 & a & 202.04 & 0.37153 & YES & YES \\
32 & a & 212.12 & 0.50631 & YES & YES \\
33 & a & 221.10 & 0.41503 & YES & YES \\
34 & a & 225.11 & 0.02593 & YES & YES \\
35 & a & 227.39 & 0.91412 & YES & YES \\
36 & a & 231.75 & 0.75058 & YES & YES \\
37 & a & 237.55 & 5.68215 & YES & YES \\
38 & a & 243.37 & 0.00491 & YES & YES \\
39 & a & 248.32 & 0.20801 & YES & YES \\
40 & a & 269.94 & 5.22572 & YES & YES \\
41 & a & 274.81 & 2.45840 & YES & YES \\
42 & a & 286.78 & 0.42487 & YES & YES \\
\end{tabular}
|   | a  |       |       |       | YES | YES |
|---|-----|-------|-------|-------|-----|-----|
| 43| 299.32 | 6.38706 | YES | YES |
| 44| 300.46 | 2.29804 | YES | YES |
| 45| 315.00 | 4.53361 | YES | YES |
| 46| 320.92 | 0.05952 | YES | YES |
| 47| 335.80 | 0.18074 | YES | YES |
| 48| 352.98 | 1.66252 | YES | YES |
| 49| 369.74 | 0.39468 | YES | YES |
| 50| 376.54 | 1.49694 | YES | YES |
**18Me-F**

SCF Energy (au) BP86/SV(P)  
-2852.672642047

SCF Energy (au) PBE0/def2-TZVPP  
-2852.569716431

Zero Point Energy (au)  
0.5772148

Chemical potential (kJ mol⁻¹)  
1260.38

xyz coordinates

| 81 |
|---|
| **Au**  | 1.6554606 | -2.4625321 | -1.9945194 |
| **C**   | -0.7471317 | 1.1062442 | -0.8890718 |
| **N**   | -2.6014515 | 3.8769626 | -3.1493694 |
| **C**   | -3.4660740 | -1.4482182 | -2.3763297 |
| **C**   | -3.8512385 | -3.5748894 | -3.6074836 |
| **C**   | 1.5309802 | -6.2171804 | -2.2851198 |
| **H**   | 2.1786124 | -7.0981388 | -2.4011095 |
| **C**   | -0.1668156 | -3.9580111 | -2.0051717 |
| **C**   | -4.3394982 | -2.2502187 | -3.1936256 |
| **C**   | -3.8859919 | -1.8609399 | -1.9637667 |
| **H**   | -3.2391692 | -0.4523866 | -1.3409866 |
| **C**   | -5.1604557 | 0.3155916 | -2.3365363 |
| **C**   | 1.0862207 | -9.3730989 | -1.3982960 |
| **H**   | -1.4386692 | -3.171955 | -0.8008500 |
| **C**   | -4.5083787 | -4.5395363 | -4.4016615 |
| **H**   | -5.5164652 | -4.3436641 | -4.7945098 |
| **C**   | 0.2698807 | -6.2078536 | -2.8978244 |
| **C**   | -0.0356478 | -7.0923771 | -3.4818369 |
| **C**   | 1.9454449 | -5.0952759 | -1.5300633 |
| **C**   | -3.8540398 | -5.7503395 | -4.6810669 |
| **H**   | -4.3608545 | -5.5083671 | -5.3008891 |
| **C**   | -2.5665356 | -6.0140353 | -4.1861327 |
| **H**   | -2.0637207 | -6.9654934 | -4.412083 |
| **C**   | -5.9266007 | -5.0984302 | -2.7742168 |
| **C**   | -1.9257146 | -5.0375046 | -3.3932250 |
| **H**   | -5.6034020 | -1.7404190 | -3.5584193 |
| **C**   | -6.2884411 | -2.3371653 | -4.1840882 |
| **H**   | -6.0210257 | -0.4694151 | -3.1388457 |
| **H**   | -7.0124189 | -0.1023468 | -3.4409882 |
| **O**   | 3.1442662 | -5.0002043 | -0.8966059 |
| **O**   | -5.4652938 | 1.5574127 | -1.8759119 |
| **C**   | -0.1757555 | -0.2538255 | -0.1980994 |
| **C**   | 0.4861765 | 0.7325933 | 0.5992039 |
| **C**   | 1.7984632 | 2.6793756 | 2.1884590 |
| **C**   | 2.4709101 | 2.0691093 | 1.0991697 |
| **C**   | 1.8285575 | 1.0931652 | 0.3167453 |
| **C**   | -0.1966310 | 1.3547418 | 1.6751822 |
| **C**   | 0.4529885 | 2.3247135 | 2.4620933 |
| **O**   | 3.7536771 | 2.5013777 | 0.9022054 |
| **H**   | 2.3308262 | 0.6018605 | -0.5226177 |
| **H**   | -1.2387728 | 1.0641625 | 1.8640473 |
| **O**   | -0.1171546 | 3.0073192 | 3.5001866 |
| **C**   | 4.0532913 | -6.0865002 | -0.9710312 |
| **C**   | -6.7178184 | 2.1314598 | -2.2128955 |
| **H**   | -6.8323767 | 2.2525564 | -3.3159728 |
| **H**   | -6.7358652 | 3.1314897 | -1.7348862 |
| **H**   | -7.5684470 | 1.5246496 | -1.8217710 |
| **H**   | 4.3652968 | -6.2922903 | -2.022952 |
| **H**   | 3.6220428 | -7.0158197 | -0.5295232 |
| **H**   | 4.9420860 | -5.7841410 | -0.3815104 |
| **C**   | 4.5057643 | 1.9387820 | -0.1608166 |
| **C**   | -1.4218783 | 2.6649752 | 3.9471027 |
| **O**   | 2.4561575 | 3.5827467 | 2.9806774 |
| **C**   | 2.3489076 | 4.9465470 | 2.5623676 |
| # | mode | symmetry | wave number | IR intensity | selection rules |
|---|------|----------|-------------|--------------|-----------------|
| 1 | 0.00 | 0.00000   | -           | -            |
| 2 | 0.00 | 0.00000   | -           | -            |
| 3 | 0.00 | 0.00000   | -           | -            |
| 4 | 0.00 | 0.00000   | -           | -            |
| 5 | 0.00 | 0.00000   | -           | -            |
| 6 | 0.00 | 0.00000   | -           | -            |
| 7 | 2.70 | 0.00598   | YES         | YES          |
| 8 | 6.77 | 0.18495   | YES         | YES          |
| 9 | 9.91 | 0.16590   | YES         | YES          |
| 10 | 11.46 | 0.28179 | YES         | YES          |
| 11 | 12.76 | 0.28717 | YES         | YES          |
| 12 | 16.74 | 0.60748 | YES         | YES          |
| 13 | 21.13 | 0.11437 | YES         | YES          |
| 14 | 23.22 | 0.77900 | YES         | YES          |
| 15 | 25.60 | 0.16708 | YES         | YES          |
| 16 | 28.47 | 0.99798 | YES         | YES          |
| 17 | 32.64 | 0.56703 | YES         | YES          |
| 18 | 34.45 | 1.17445 | YES         | YES          |
| 19 | 39.98 | 1.79878 | YES         | YES          |
| 20 | 48.59 | 1.36510 | YES         | YES          |
| 21 | 56.21 | 0.00428 | YES         | YES          |
| 22 | 56.67 | 0.63014 | YES         | YES          |
| 23 | 66.01 | 0.83649 | YES         | YES          |
| 24 | 75.54 | 0.17560 | YES         | YES          |
| 25 | 80.66 | 0.65910 | YES         | YES          |
| 26 | 85.94 | 0.88522 | YES         | YES          |
| 27 | 86.35 | 0.05486 | YES         | YES          |
| 28 | 98.71 | 1.84037 | YES         | YES          |
| 29 | 100.74 | 3.70079 | YES         | YES          |
| 30 | 113.22 | 0.60468 | YES         | YES          |
| 31 | 116.37 | 0.57680 | YES         | YES          |
| 32 | 141.34 | 0.04939 | YES         | YES          |
|   |   |               |               |   |   |
|---|---|---------------|---------------|---|---|
| 33| a | 143.89        | 0.48299       | YES| YES|
| 34| a | 147.55        | 0.51692       | YES| YES|
| 35| a | 160.68        | 0.20504       | YES| YES|
| 36| a | 181.09        | 0.94894       | YES| YES|
| 37| a | 187.08        | 0.01447       | YES| YES|
| 38| a | 193.06        | 0.31269       | YES| YES|
| 39| a | 215.61        | 2.22448       | YES| YES|
| 40| a | 221.10        | 0.56232       | YES| YES|
| 41| a | 223.38        | 0.61395       | YES| YES|
| 42| a | 225.05        | 0.22703       | YES| YES|
| 43| a | 225.24        | 0.90741       | YES| YES|
| 44| a | 229.71        | 1.42549       | YES| YES|
| 45| a | 231.42        | 3.37635       | YES| YES|
| 46| a | 239.96        | 1.45631       | YES| YES|
| 47| a | 243.18        | 0.00374       | YES| YES|
| 48| a | 249.30        | 0.54208       | YES| YES|
| 49| a | 250.61        | 0.15340       | YES| YES|
| 50| a | 268.26        | 1.17348       | YES| YES|
18Me-H

SCF Energy (au) BP86/SV(P) -1960.07790301
SCF Energy (au) PBE0/def2-TZVPP -1959.766407787
Zero Point Energy (au) 0.6430347
Chemical potential (kJ mol⁻¹) 1464.55

xyz coordinates
81

Au  -1.6536401  -2.4593383  -2.0053295
C   -0.7463100  -1.0847510  -0.9226739
N   -2.6002739  -3.8942872  -3.1352095
C   -3.4903256  -1.4796359  -2.3477182
C   -3.8655092  -3.6163387  -3.5649395
C   -1.5931559  -6.1559944  -2.3603003
H   2.2541648   -7.0252010  -2.4890282
C   -0.1389561  -3.9269623  -2.0469935
C   -4.3676733  -2.2927479  -3.1431501
C   -3.9229112  -0.2237038  -1.9294543
H   1.4776903   -3.0531914  -0.8823073
C   -4.5233809  -4.5951895  -4.3410058
H   -5.5437597  -4.4189223  -4.7106695
C   0.3182267  -6.1717257  -2.9436078
H   0.0154605  -7.0635591  -3.5179802
C   2.0041501   -5.0252010  -1.6179050
C   -3.8538587  -5.7949225  -4.6321464
H   -4.3611340  -6.5640032  -5.2378719
C   -2.5506185  -6.0338077  -4.1665210
H   -2.0358772  -6.9766927  -4.4007852
C   -0.5613815  -5.0772500  -2.8030219
C   -1.9094284  -5.0431835  -3.3913640
H   -5.6842989  -1.8132312  -3.4808069
H   -6.3365817  -2.4239306  -4.0892613
C   -6.0785859   -5.5482221  -3.0555426
H   -7.0828500  -0.1995167  -3.3362563
O   3.2157450  -4.9057032  -1.0126246
O   -5.5304100  -1.4926392  -1.8119705
C   -0.1764484  -0.2224089  -0.2428019
C   0.4832596   -0.7757015  -0.5432650
C   1.7915169   2.7442092  -2.1097007
C   2.4885860   2.0799315  -1.0649443
C   1.8430257  -1.0929600  -0.2961440
C   -0.2196549  -1.4486384  -1.5740492
C   0.4288178   2.4270742  -2.3512298
O   3.7868284   2.4626376  -0.8957600
H   2.3678074   -0.5615364  -0.5083703
H   -1.2708822  -1.1834142  -1.7474569
O   -0.1577509  -3.1465704  -3.3570410
C   4.1440357  -5.9730790  -1.1098844
C   -6.8001267   -2.422341  -2.1220512
H   -6.9424970  -2.1570902  -3.2226986
H   -6.8257432   -3.0436761  -1.6471693
H   -7.6307305  -1.4216849  -1.7096560
H   4.4332515  -6.1373250  -2.1687201
H   3.7434698   -6.9108938  -0.6572226
H   5.0415035  -5.6522556  -0.5436135
C   4.5713082   -1.8126314  -0.1013176
C   -1.4657938  -2.7929257  -3.8195078
O   2.4564648   -3.6492478  -2.8933335
C   2.2010573   -5.0334556  -2.6066283
$vibrational spectrum (first 50 lines)
#  mode     symmetry     wave number   IR intensity    selection rules
#  cm**(-1)        km/mol         IR     RAMAN
1                        0.00         0.00000
2                        0.00         0.00000
3                        0.00         0.00000
4                        0.00         0.00000
5                        0.00         0.00000
6                        0.00         0.00000
7        a               3.07         0.01034       YES     YES
8        a              10.22         0.12702       YES     YES
9        a              13.80         0.42040       YES     YES
10        a              20.82         0.28738       YES     YES
11        a              22.12         0.03118       YES     YES
12        a              24.29         1.86400       YES     YES
13        a              31.30         0.21234       YES     YES
14        a              38.61         0.18366       YES     YES
15        a              42.80         1.96198       YES     YES
16        a              44.91         0.36195       YES     YES
17        a              48.55         0.07757       YES     YES
18        a              56.26         0.00478       YES     YES
19        a              59.99         0.72482       YES     YES
20        a              76.97         0.66874       YES     YES
21        a              82.88         0.67368       YES     YES
22        a              86.24         0.03777       YES     YES
23        a              94.43         0.32569       YES     YES
24        a             100.49         3.65739       YES     YES
25        a              102.47         0.39400       YES     YES
26        a              109.94         0.64615       YES     YES
27        a              120.44         0.54030       YES     YES
28        a              140.28         1.17123       YES     YES
29        a              141.31         0.06240       YES     YES
30        a              148.93         0.55902       YES     YES
31        a              154.13         0.08944       YES     YES
32        a              168.22         0.56197       YES     YES
|   |   |   |   |   |   |
|---|---|---|---|---|---|
| 33 | a | 182.71 | 0.51325 | YES | YES |
| 34 | a | 187.02 | 0.01736 | YES | YES |
| 35 | a | 193.31 | 0.27799 | YES | YES |
| 36 | a | 208.76 | 1.36899 | YES | YES |
| 37 | a | 219.72 | 0.29065 | YES | YES |
| 38 | a | 221.13 | 0.39686 | YES | YES |
| 39 | a | 223.74 | 0.57738 | YES | YES |
| 40 | a | 225.71 | 0.30248 | YES | YES |
| 41 | a | 231.55 | 1.08568 | YES | YES |
| 42 | a | 237.35 | 5.74408 | YES | YES |
| 43 | a | 243.53 | 0.00843 | YES | YES |
| 44 | a | 245.75 | 0.20150 | YES | YES |
| 45 | a | 250.12 | 1.09078 | YES | YES |
| 46 | a | 269.51 | 4.20942 | YES | YES |
| 47 | a | 275.34 | 2.53375 | YES | YES |
| 48 | a | 281.78 | 1.33063 | YES | YES |
| 49 | a | 287.05 | 0.28483 | YES | YES |
| 50 | a | 295.51 | 3.71741 | YES | YES |

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