Version 01/06/2007
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A Functionalized 8 nm Long Aryleneethynylene Molecular Wire with Alkyne Termini

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Supporting information for this article. Synthetic details and characterization data for compounds **2**, **11-14**, **17** and **18**; X-ray crystallographic file for **4** and **11** in CIF format and a discussion of the structures; UV-Vis absorption and fluorescence spectra of **16**; details of the theoretical calculations.

Keywords: molecular wires / conjugation / fluorene / Sonogashira reaction

Abstract: The synthesis is described of new conjugated aryleneethynylene derivatives of up to *ca*. 8 nm molecular length (compound **16**) with terminal alkyne substituents and 9,9-dihexylfluorene units in the backbone. Key synthetic steps are Pd-mediated Sonogashira coupling methodology combined with regioselective removal from the terminal alkyne units of 2-hydroxy-2-propyl protecting groups in the presence of trimethylsilyl groups. The structural and electronic properties of **16** were obtained from DFT calculations: the intramolecular terminal C…C' distance in its relaxed conformation was found to be 7.8 nm. The calculated distribution of HOMO and LUMO orbitals and the strong blue fluorescence of **16** (λ_{max} 420, 443 nm in $CHCl_3$ solution) are consistent with a highly conjugated aryleneethynylene structure. Molecule **16** possesses multifunctionality and is of interest for future molecular electronic device applications.

Introduction

Organic molecules with extended π–conjugated systems are of considerable current interest in molecular electronics due to their potential applications in electrical circuits, switches, light-emitting devices and sensors.[1] The synthesis of nanometer-length conjugated organic molecules which are suitably functionalized for assembly onto metal or semiconductor surfaces is a considerable challenge.[2] Various molecular wires of this type have been connected into hybrid organic/semiconductor architectures,[3] usually via terminal thiol-gold contacts,[4] although amines[5] can also effectively bond to gold.

For future practical applications the interfacing organic molecular wires with silicon[6] is an attractive alternative to assembly onto gold surfaces. The high thermodynamic and kinetic stability of the C-Si bond leads to a robust anchor point. Moreover, the potential problem of metal nanofilament formation[7] is removed thereby ensuring that molecular effects are measured. This research is in its very early stages and initial steps are being reported. For example, Tour *et al.* have exploited direct Si-arylcarbon bonding to short

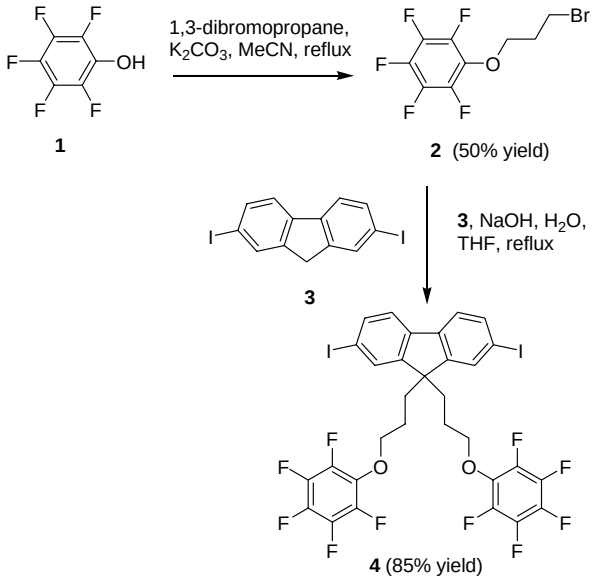
phenyleneethynylene oligomers (3 aryl rings) in the construction of a metal-free silicon–molecule–carbon nanotube architecture.[8] Direct linkage of a *para*-substituted benzene derivative to Si, again through a Si-arylcarbon bond, was a key step in assembling a multilayer nanoparticle film in a silicon nanogap device.[9]

Silicon nanogaps of 7-8 nm dimensions can be readily obtained by conventional lithographic and CMOS techniques which are amenable to mass production.[10] It is, therefore, timely to develop synthetic routes to organic molecular wires which are suitably functionalized at the termini to bridge a 7-8 nm gap. Terminal alkynes are attractive as there are precedents for their assembly onto hydride-terminated silicon surfaces by covalent Si–C≡C– bonding.[11] Linear aryleneethynylene oligomers, (aryl–C≡C–)$_n$, are well-suited for the wire component as they have conjugated rigid-rod structures[12] whose molecular lengths are well-defined, although the barrier to rotation about the aryl–ethynyl bond is low (typically < 1 kcal mol^{-1}).[13]

As the length of π–systems increase, synthetic endeavors often encounter problems with purification, chemical instability and poor solubility. The main aim of the present work was to establish an efficient route to alkyne-terminated aryleneethynylene derivatives of up to *ca*. 8 nm in length. To this end, molecule **16** has successfully been obtained and fully characterized. The 9,9-dialkylfluorene units in the backbone ensure good processability in organic solvents. To demonstrate that our methodology is compatible with more elaborate functional groups, electron-deficient bis(pentafluorophenoxypropyl) substituents were appended to the central fluorene unit of **16**. Such functionalization is relevant as a visionary future application of integrated Si/molecule/Si devices is in the field of sensor technology[14] where pendant units could act as molecular recognition sites.

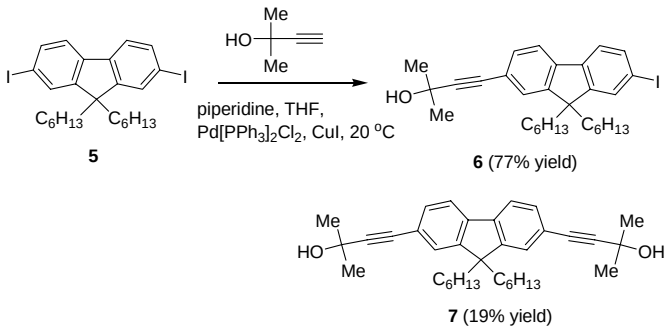
Results and Discussion

The symmetrical target molecule **16** was obtained via a convergent strategy using iterative palladium-mediated Sonogashira cross-coupling methodology. Scheme 1 shows the synthesis of **4** which was used as the reagent for the central unit of **16**. The reaction of pentafluorophenol **1** with 1,3-dibromopropane under basic conditions gave **2** in 50% yield. 2,7-Diiodofluorene **3** was then dialkylated at C9 using **2** under basic conditions to afford **4** in 85% yield. The X-ray molecular structure of **4** is shown in Figure 1.



Scheme 1. Synthesis of the core reagent **4**.

Another key building block **6** was obtained in 77% yield by reaction of **5**[15] with 3-hydroxyl-3-methylbutyne under standard Sonogashira cross-coupling conditions[16] [piperidine, $Pd(PPh_3)_2Cl_2$ and CuI in THF]. The disubstituted derivative **7** was also obtained as a minor byproduct (19% yield) in this reaction (Scheme 2). The polar 2-hydroxy-2-propyl protecting group(s) facilitated the clean chromatographic purification of the product mixture.

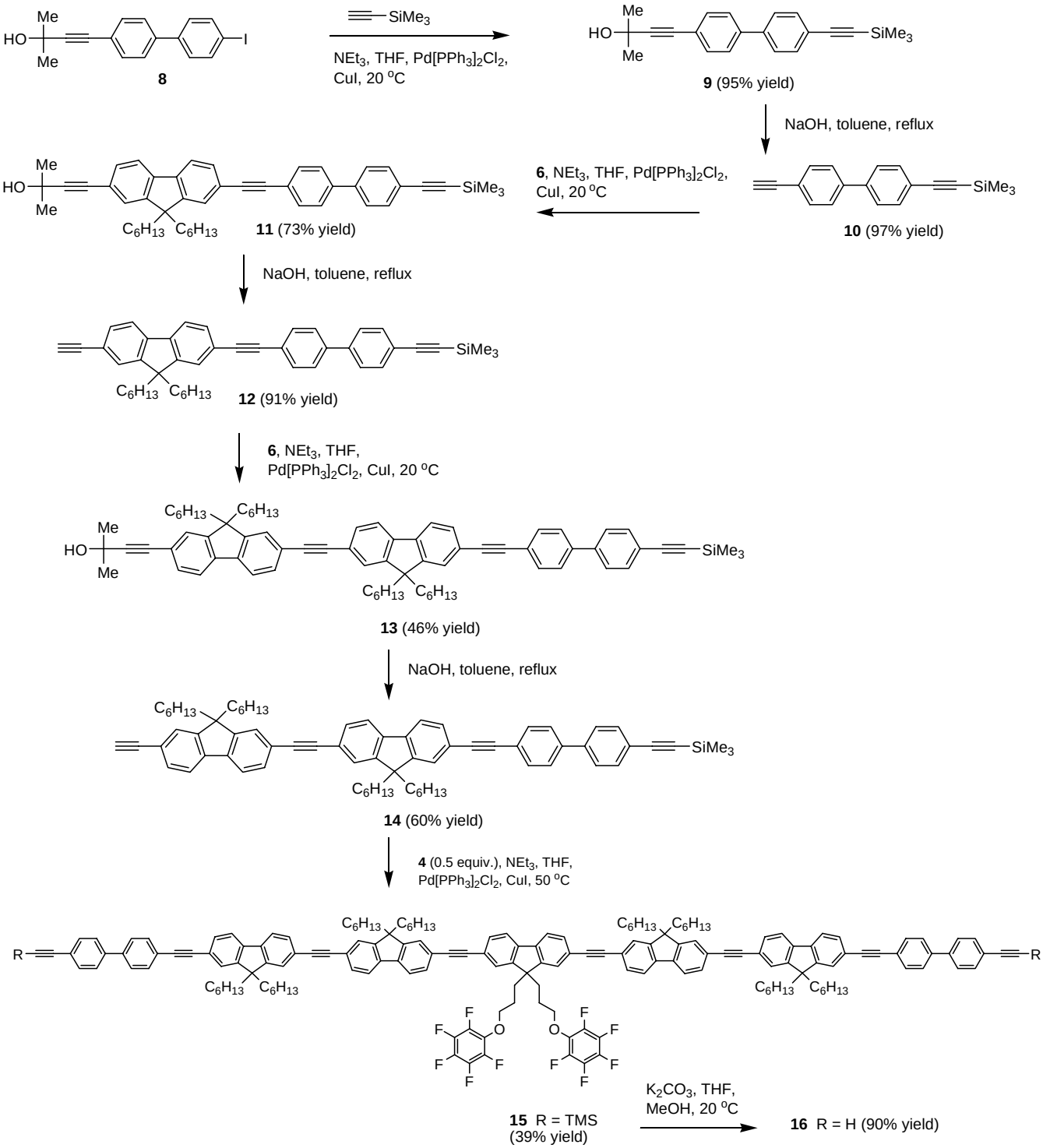


Scheme 2. Synthesis of the key reagent **6**.

To assemble the terminal biaryl segment of the wire, compound **8**[17] was converted into **9** by reaction with trimethylsilylacetylene [$Pd(PPh_3)_2Cl_2$, CuI, triethylamine] in 95% yield. Throughout Scheme 3 our strategy used the regioselective removal of a 2-hydroxy-2-propyl protecting group from terminal alkynes in the presence of a trimethylsilyl group[18] at the other terminus of the growing chain. Refluxing **9** in toluene in the presence of sodium hydroxide[19] gave **10** in 97% yield. The subsequent reactions to linearly extend the aryleneethynylene system were iterative cross-coupling/deprotection procedures. Thus, reaction of **10** with **6** gave **11** in 73% yield, followed by deprotection of **11** to give **12** (91% yield). The X-ray molecular structure of **11** is described below. By direct analogy, compounds **13** and **14** were obtained in 46 and 60% yields, respectively. The butadiyne derivative **17** (Chart 1) was obtained in 24% yield from oxidative self-coupling of **12**, alongside formation of the cross-coupled product **13**. The hexyl chains ensured good solubility and straightforward purification of the building blocks **11**-**14** and **17**.

In the crucial convergent step, two-fold Sonogashira reaction of **14** with reagent **4** yielded **15** (39% yield) along with the self-coupled butadiyne derivative **18** (8% yield). Deprotection of the terminal TMS groups of **15** with K_2CO_3 in THF/methanol gave the target wire **16** as a yellow solid in 90% yield. Evidence for extended π–conjugation through the backbone of **16** was provided by the UV-Vis absorption and fluorescence spectra in chloroform solution (see the Supporting Information; Figure S4) and DFT calculations (see below). In particular the

strong blue fluorescence at λ_{max} 420, 443 nm is consistent with a highly conjugated aryleneethynylene structure.[15]



Scheme 3. Synthesis of the target 8 nm wire **16**.

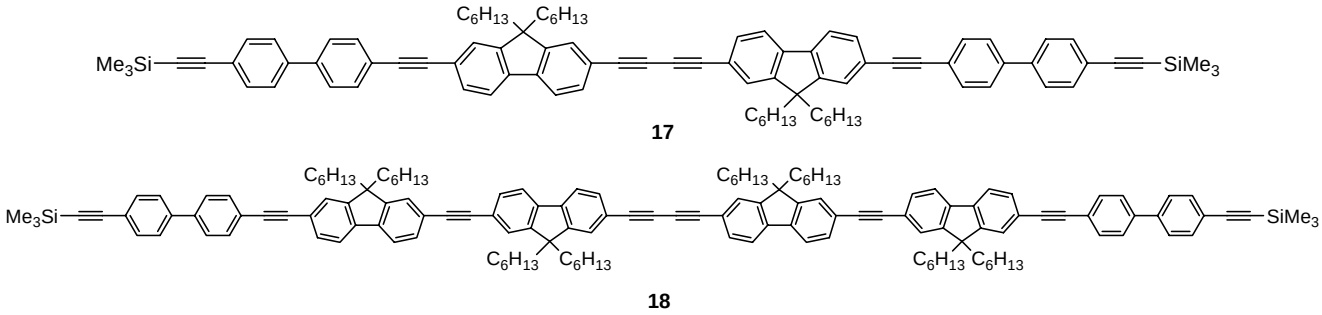


Chart 1. Self-coupled symmetrical butadiyne derivatives.

The asymmetric unit of **4** comprises two molecules (Figure 1). The crystal packing is highly unusual and is worthy of note. There are *segregated* stacks of fluorene and pentafluorophenyl moieties, whereas the common motif of such systems is a mixed stack of alternating arene and perfluoroarene moieties or molecules.[20]

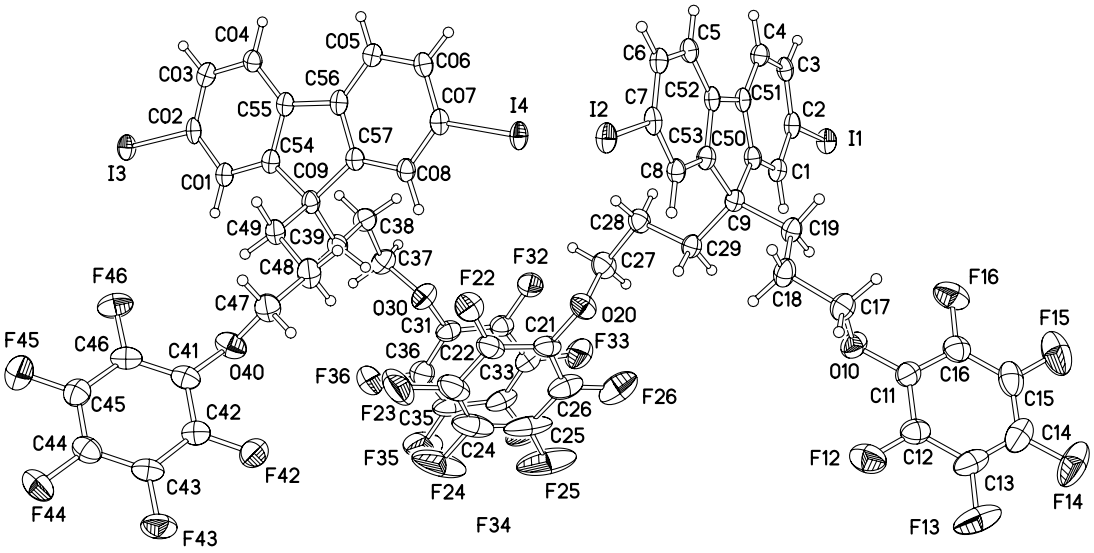


Figure 1**.** Two independent molecules of **4** in crystal. Thermal ellipsoids are drawn at the 50% probability level.

In the crystal structure of **11** both *n*-hexyl chains of the molecule are intensely disordered; the most probable conformations are shown in Figure 2. The dihedral angle between the (planar) fluorene moiety and the benzene ring C(28-33) equals 76.8º; the angle

between the latter ring and the C(34-39) ring equals 29.1º. For further discussion see the Supporting Information.

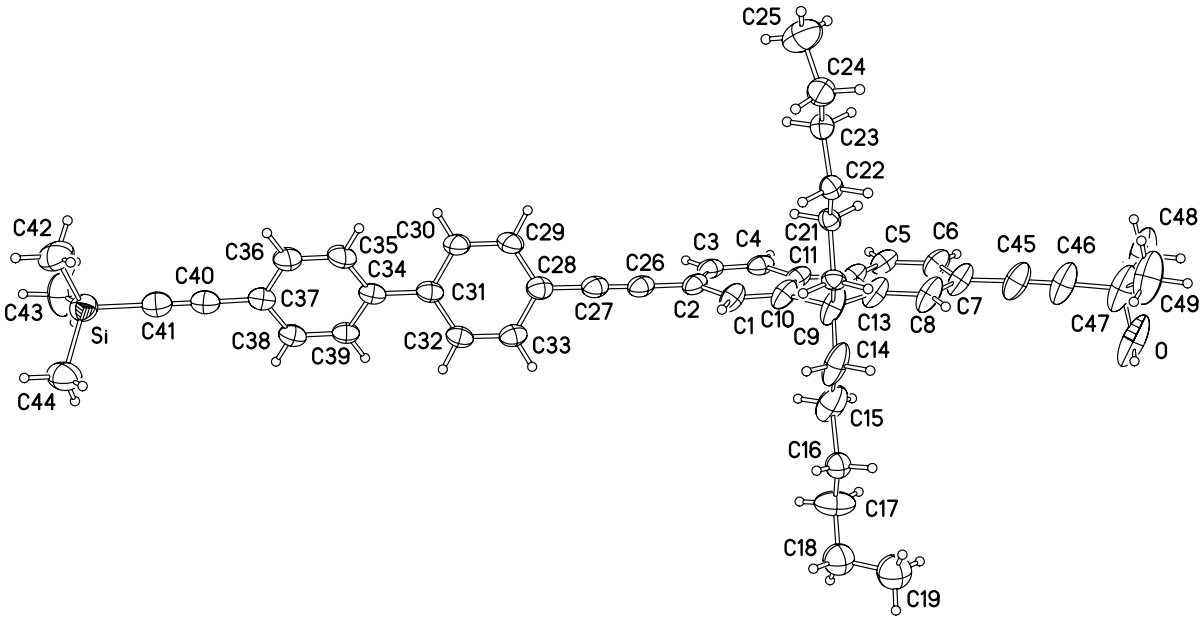


Figure 2. Molecule of **11** in the crystal. Thermal ellipsoids are drawn at the 50% probability level. Only the major conformations of the disordered *n*-hexyl chains are shown.

To probe the structural and electronic properties of **16**, Density Functional Theory (DFT) calculations were performed on the analogue **16'** with the four outer fluorene units substituted with methyl groups at C(9). The intramolecular terminal C…C' distance for this molecule in its relaxed conformation is calculated to be 7.8 nm with the outer phenyl rings of the biphenyl units twisted by 29° relative to the aryleneethynylene backbone (Figure 3). The relaxed structure possesses a "zigzag" conformation, with the 9,9-dimethylfluorene units alternately oriented "upwards" and "downwards". Figure 3 shows the spatial distribution of the modulus squared of the HOMO and LUMO orbitals for **16'** with extensive delocalization along the wire. The HOMO and LUMO peaks of the bis(pentafluorophenoxypropyl)fluorene units are located 1.40 eV below the HOMO and 1.26 eV above the LUMO of the whole molecule, respectively. This separation in energy is a consequence of the large electronegativity of the fluorine atoms which push the bonding and antibonding states downwards and upwards in energy, respectively, and the presence of the alkane chains,

which, due to their insulating behavior, isolate the pentafluorophenoxy units from the backbone.

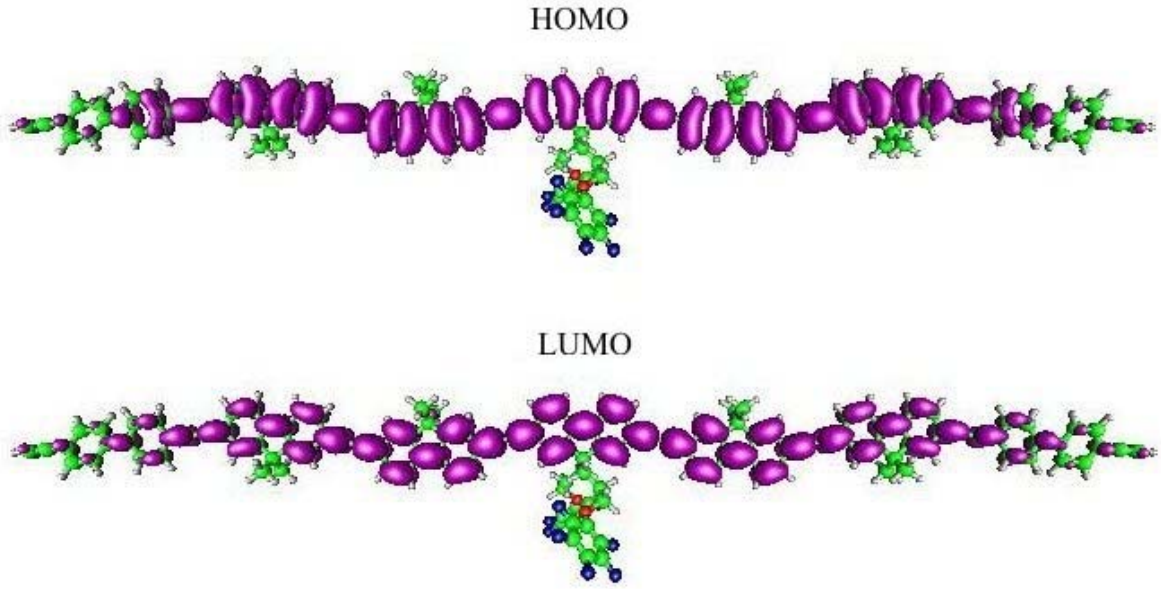


Figure 3. Spatial distribution of the HOMO and LUMO orbitals (purple contours) of molecule **16'**, where the methyl groups in the calculated structure replace the hexyl groups of the synthesized compound **16**. Gray, green, red and blue spheres correspond to hydrogen, carbon, oxygen and fluorine atoms, respectively. The calculated intramolecular terminal C…C' distance = 7.84 nm.

Conclusions

We have synthesized a range of new functionalized aryleneethynylene building blocks leading to molecular wires of up to ca. 8 nm in length which are amenable to full spectroscopic and analytical characterization. A key feature of the synthetic protocol is the clean removal from the terminal alkynes of a 2-hydroxy-2-propyl protecting group in the presence of a trimethylsilyl group at the other terminus. The alkyne termini of **16** make this molecule a candidate for future hard-wiring into hybrid silicon/molecule/silicon

nanostructures by covalent C-Si linkages. Moreover, the presence of bis(pentafluorophenoxypropyl) substituents on the central fluorene unit in **16** establishes that this methodology is applicable for the incorporation of more elaborate pendant groups into this class of molecular electronic materials.

Experimental Section

9,9-Bis(3-pentafluorophenoxypropyl)-2,7-diiodofluorene 4: To a suspension of 2,7-diiodofluorene **3** (1.78 g, 4.25 mmol) in THF (40 mL) under argon, NaOH (1.2 g, 30 mmol) in water (1.5 mL) was added in one portion. Compound **2** (2.9 g, 9.05 mmol) in THF (10 mL) was added dropwise and the mixture was heated at reflux for 24 h then diluted with water (100 mL). The organic phase was extracted with dichloromethane, separated and dried over $MgSO_4$. The solvent was removed in vacuo and the residue was crystallized from methanol to give **4** as colorless crystals (3.13 g, 85% yield); mp 112.3-112.9 ^{o}C. MS (MALDI-ToF) *m/z* 865.9 (M^+). ^{1}H NMR (400 MHz, $CDCl_3$): 7.71-7.68 (m, 4H), 7.43 (d, 2H, *J* = 8.4 Hz), 3.89 (t, 4H, *J* = 6.0 Hz), 2.24-2.19 (m, 4H), 1.08-1.03 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): 150.7, 142.8, 140.3, 139.8, 139.2, 138.4, 136.8, 136.0, 133.4, 132.0, 121.8, 93.5, 75.3, 54.6, 36.0, 24.4. Anal. calcd. for $C_{31}H_{18}F_{10}I_2O_2$: C, 42.98; H, 2.09. Found: C, 42.76; H, 1.98.

2-Iodo-7-(3-hydroxy-3-methylbutynyl)-9,9-dihexylfluorene 6 and 2,7-bis(3-hydroxy-3-methylbutynyl)-9,9-dihexylfluorene 7: To a mixture of 2,7-diiodo-9,9-dihexylfluorene **5** (17.58 g, 30 mmol), 3-hydroxyl-3-methylbutyne (2.10 g, 25 mmol) and piperidine (20 mL) in THF (150 mL) under argon, $Pd(PPh_3)_2Cl_2$ (0.75 g) and CuI (0.25 g) were added in one portion. The reaction was stirred for 2 h at room temperature. The solvent was removed under reduced pressure. The residue was dissolved in diethyl ether and filtered through a

celite column. The filtrate was evaporated to dryness and the residue was purified by column chromatography (silica; eluent dichloromethane). The first product to elute was **6** as a yellow oil (10.46 g, 77% yield). MS (ES) *m/z* 542.3 (M^+). ^{1}H NMR (400 MHz, $CDCl_3$): 7.67-7.58 (m, 3H), 7.41-7.38 (m, 3H), 2.42 (s, 1H), 1.94-1.88 (m, 4H), 1.66 (s, 6H), 1.17-0.97 (m, 12H), 0.77 (t, 6H, *J* = 7.2 Hz), 0.60-0.56 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): 153.3, 150.1, 140.3, 140.0, 136.0, 132.1, 130.8, 126.0, 121.7, 121.7, 119.7, 99.1, 93.1, 83.0, 65.7, 55.4, 40.3, 31.6, 31.5, 29.6, 23.7, 22.6, 14.0. Anal. calcd. for $C_{30}H_{39}IO$: C, 66.41; H, 7.25. Found: C, 66.36; H, 7.18.

The second product to elute was **7** which crystallized from ethanol as colourless crystals (2.85 g, 19% yield); mp 79-80 ^{o}C. MS (ES) *m/z* 498.4 (M^+). ^{1}H NMR (400 MHz, $CDCl_3$): 7.57 (d, 2H, *J* = 8.0 Hz), 7.38 (dd, 2H, *J* = 8.0 Hz, 1.2 Hz), 7.77 (d, 2H, *J* = 1.2 Hz), 2.10 (broad s, 2H), 1.95-1.88 (m, 4H), 1.66 (s, 12H), 1.15-0.96 (m, 12H), 0.76 (t, 6H, *J* = 7.2 Hz), 0.59-0.55 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): 150.9, 140.6, 130.8, 126.0, 121.4, 119.8, 93.9, 83.0, 65.8, 55.2, 40.3, 31.6, 31.5, 31.4, 29.7, 23.7, 22.6, 14.0. Anal. calcd. for $C_{35}H_{46}O_2$: C, 84.29; H, 9.30. Found: C, 84.32; H, 9.28.

4-(3-Hydroxy-3-methylbutynyl)-4'-(trimethylsilylethynyl)biphenyl 9: To a solution of **8**[17] (5.25 g, 14.5 mmol) and triethylamine (20 mL) in THF (100 mL) under argon, timethylsilylacetylene (3.0 mL, 21.0 mmol) was added in one portion. To this solution $Pd(PPh_3)_2Cl_2$ (0.25 g) and CuI (0.1 g) were added in one portion. The mixture was stirred for 3 h at room temperature then evaporated to dryness. The dark residue was dissolved in diethyl ether (200 mL) and filtered through a celite column. The filtrate was evaporated and the residue was purified by column chromatography (silica; dichloromethane-diethyl ether, 99:1 v/v) to obtain **9** as a white powder (4.60 g, 95% yield); mp 169.6-170 ^{o}C. MS (ES) *m/z* 332.3 (M^+). ^{1}H NMR (400 MHz, $CDCl_3$): 7.53 (d, 2H, *J* = 8.4 Hz), 7.52 (s, 4H), 7.47 (d, 2H, *J* = 8.4 Hz), 2.04 (broad s, 1H), 1.64 (s, 6H), 0.27 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$):

140.2, 140.0, 132.5, 132.1, 126.8, 126.7, 122.5, 122.1, 104.9, 95.3, 94.7, 82.0, 65.7, 31.5, 0.0. Anal. calcd. for $C_{22}H_{24}OSi$: C, 79.47; H, 7.28. Found: C, 79.55; H, 7.24.

4-Ethynyl-4'-(trimethylsilylethynyl)biphenyl 10: To a mixture of **9** (4.60 g, 13.83 mmol) in anhydrous toluene (190 mL) under argon, finely-powdered NaOH (600 mg) was added in one portion. The reaction mixture was immersed in a preheated oil bath (140 ^{o}C) and refluxed for 15 min, then cooled to room temperature. Solids were removed by filtration, the filtrate was evaporated to dryness and purified by column chromatography (silica; eluent petroleum ether-DCM, 1:1 v/v) to give **10** as a white powder (3.70 g, 97% yield); mp 126-127 ^{o}C. MS (ES) *m/z* 274.2 (M^{+}). ^{1}H NMR (400 MHz, $CDCl_3$): 7.54-7.53 (m, 8H), 3.14 (s, 1H), 0.28 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): 140.6, 140.14, 132.6, 132.5, 126.8, 125.9, 122.6, 121.4, 104.8, 95.3, 83.5, 78.1, 0.0. Anal. calcd. for $C_{19}H_{18}Si$: C, 83.15; H, 6.61. Found: C, 83.20; H, 6.64.

Compounds 15 and 18: To a mixture of **4** (56 mg, 0.065 mmol) and triethylamine (1 mL) in THF (100 mL) under argon, $Pd(PPh_3)_2Cl_2$ (0.03 g) and CuI (0.01 g) were added in one portion. A solution of **14** (160 mg, 0.162 mmol) in THF (40 mL) was added slowly. The mixture was stirred at 50 ^{o}C for 72 h then evaporated to dryness and the residue was purified by column chromatography (silica; eluent petroleum ether-DCM, 9:1 v/v) to give, as the first fraction, **18** as a yellow powder (25 mg, 8% yield). (See the Supporting Information). The second product to elute was **15** as a yellow powder (65 mg, 39%) mp 283.1-283.5 ^{o}C. MS (MALDI-ToF) *m/z* 2585.2 (M^{+}); (calcd. 2585.3). ^{1}H NMR (400 MHz, $CDCl_3$): 7.73-7.54 (m, 46H), 3.93-3.88 (t, 4H, J = 6.0 Hz), 2.34 (broad s, 4H), 2.02 (broad s, 16H), 1.16-1.01 (m, 52H), 0.80-0.76 (m, 24H), 0.64 (broad s, 16H), 0.28 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): 151.2, 149.2, 140.9, 140.8, 140.7, 140.6, 140.3, 140.0, 136.8, 132.5, 132.1, 131.4, 130.8, 126.9, 126.7, 126.0, 125.8, 123.0, 122.7, 122.5, 122.13, 122.08, 121.9, 121.8, 120.3, 120.1, 104.9, 95.3, 91.5, 90.9, 90.2, 89.7, 75.4, 55.3, 54.5, 54.4, 40.5, 36.1, 31.6, 30.0, 24.5, 24.0,

22.6, 14.01, 13.98, 0.0. Anal. calcd. for $C_{177}H_{180}F_{10}O_2Si_2$: C, 82.22; H, 7.02. Found: C, 82.42; H, 7.22.

Compound 16: To a solution of **15** (45 mg, 0.017 mmol) in THF (10 mL) and methanol (5 mL) under argon, finely-powdered potassium carbonate (200 mg) was added in one portion. The suspension was stirred for 2 h; solids were removed by filtration and the filtrate was evaporated to dryness. The residue was triturated with hexane (1 mL). The precipitate was collected by filtration, washed with hexane (2 × 1 mL) and dried under vacuum to give **16** as a yellow powder (38 mg, 90% yield); mp 172-173 ^{o}C. MS (MALDI-ToF) *m/z* 2440.2 (M^+); (calcd. 2440.3). ^{1}H NMR (400 MHz, $CDCl_3$): 7.74-7.54 (m, 46H), 3.91 (t, 4H, J = 6.0 Hz), 3.15 (s, 2H), 2.30 (broad s, 4H), 2.01 (broad s, 16H), 1.18-1.01 (m, 52H), 0.80-0.76 (m, 24H), 0.63 (broad s, 16H). ^{13}C NMR (100 MHz, $CDCl_3$): 151.2, 149.4, 140.9, 140.8, 140.69, 140.66, 140.6, 139.9, 132.7, 132.1, 131.4, 130.8, 127.0, 126.9, 126.0, 125.8, 122.84, 122.75, 122.1, 121.9, 121.8, 121.4, 120.3, 120.0, 91.6, 91.42, 90.9, 90.2, 89.6, 83.5, 78.1, 75.4, 55.3, 40.5, 36.1, 32.0, 29.8, 24.5, 23.8, 22.6, 14.00, 13.98. λ_{max} (abs.) ($CHCl_3$) 385 nm; λ_{max} (PL) ($CHCl_3$) 420, 443 nm; Anal. calcd. for $C_{171}H_{164}F_{10}O_2$: C, 84.13; H, 6.77. Found: C, 84.21; H, 6.68.

Acknowledgements

We thank the Department of Trade and Industry and QinetiQ for funding this work.

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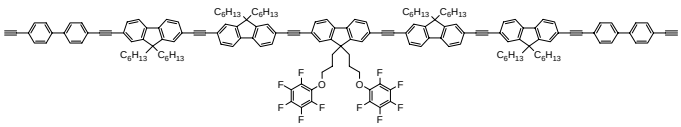
Table of Contents Graphic



Supporting Information for:

A Functionalized 8 nm Long Aryleneethynylene Molecular Wire with Alkyne Termini

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Contents

General. All synthetic reagents were used as supplied. Solvents were dried and distilled using standard procedures.

1-Bromo-3-(pentafluorophenoxy)propane 2. A mixture of pentafluorophenol **1** (5.0 g), potasium carbonate (2.0 g) and 1,3-dibromopropane (20 mL) in acetonitrile (40 mL) was refluxed for 24 h under argon. The solvent was removed under reduced pressure. The residue was purified by column chromatography (silica; eluent petroleum ether). The product co-eluted with the excess dibromopropane. After removal of dibromopropane under vacuum, **2** was obtained as a colorless liquid (4.15 g, 50% yield). ^{1}H NMR (400 MHz, $CDCl_3$): 4.31 (t, 2H, J = 6.0 Hz), 3.64 (t, 2H, J = 6.4 Hz), 2.30 (m, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): 143.0, 140.6, 139.3, 136.6, 133.5, 73.0, 32.8, 28.9. Anal. calcd. for $C_9H_6BrF_5O$: C, 35.44; H, 1.98. Found: C, 35.65; H, 2.03.

2-(3-Hydroxy-3-methylbutynyl)-7-[(4'-trimethylsilylethynyl)-4-biphenylethynyl]-9,9-dihexylfluorene 11. To a solution of **10** (2.20 g, 8.0 mmol), triethylamine (10 mL) and **6** (4.45 g, 8.0 mmol) in THF (100 mL) under argon was added $Pd(PPh_3)_2Cl_2$ (0.25 g) and CuI (0.07 g) in one portion. The reaction mixture quickly turned brown and was stirred for 3 h at room temperature. The dark mixture was then evaporated in vacuo; the residue was dissolved in diethyl ether and filtered. The filtrate was evaporated to dryness and the residue was purified by column chromatography (silica; eluent dichloromethane) to give **11** as a yellow powder, which was recrystallized from hexane and ether (4.0 g, 73 % yield); mp 218.5-219 ^{o}C; MS (ES) *m/z* 688.5 (M^+). ^{1}H NMR (400 MHz, $CDCl_3$): 7.67-7.51 (m, 12H), 7.41 (dd, 1H, J = 8.0 Hz, 1.6 Hz), 7.39 (d, 1H, J = 1.6 Hz), 2.06 (s, 1H), 1.99-1.94 (m, 4H), 1.67 (s, 6H), 1.41-0.99 (m, 12H), 0.77 (t, 6H, J = 7.2 Hz), 0.63-0.53 (m, 4H), 0.27 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): 151.09, 151.05, 140.8, 140.7, 140.3, 140.0, 132.5, 132.1, 130.8, 126.9, 126.7, 126.1, 126.0, 122.7, 122.5, 121.9, 121.5, 120.0, 119.9, 104.9, 95.3, 94.0, 91.5, 89.6, 83.01, 65.8, 55.3, 40.4, 31.60, 31.56, 29.7, 23.7, 22.6, 14.0, 0.0. Anal. calcd. for $C_{49}H_{56}OSi$: C, 85.41; H, 8.19. Found: C, 85.21; H, 8.10.

2-Ethynyl-7-[(4'-trimethylsilylethynyl)-4-biphenylethynyl]-9,9-dihexylfluorene 12. To a mixture of **11** (3.90 g, 5.66 mmol) in anhydrous toluene (100 mL) under argon, finely-powdered NaOH (600 mg) was added in one portion. The reaction mixture was refluxed in a preheated oil bath (140 ^{o}C) for 2.5 h. The reaction mixture was cooled to room temperature and filtered. The filtrate was evaporated to dryness and the residue was triturated with

hexane. The solid product was collected by filtration and washed with hexane to afford **12** as a yellow powder (3.25 g, 91% yield); mp 209.5-210.2 ^{o}C. MS (ES) *m/z* 630.5 (M^{+}). ^{1}H NMR (400 MHz, $CDCl_3$): 7.69-7.47 (m, 14H), 3.17 (s, 1H), 2.01-1.95 (m, 4H), 1.16-1.01 (m, 12H), 0.78 (t, 6H, *J* = 7.2 Hz), 0.63-0.55 (m, 4H), 0.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): 151.2, 151.1, 141.2, 140.6, 140.2, 140.0, 132.45, 132.1, 131.3, 130.8, 126.9, 126.7, 126.6, 126.0, 122.7, 122.5, 122.1, 120.8, 120.1, 119.9, 104.9, 95.3, 91.4, 89.7, 84.6, 55.3, 40.3, 31.5, 29.7, 23.7, 22.6, 14.0, 0.0. Anal. calcd. for $C_{46}H_{50}Si$: C, 87.56; H, 7.99. Found: C, 87.66; H, 7.92.

Compound 13 and **Compound 17.** To a solution of **12** (1.89 g, 3.0 mmol), **6** (1.63 g, 3.0 mmol) and triethylamine (1 mL) in THF (60 mL) was added $Pd(PPh_3)_2Cl_2$ (0.12 g) and CuI (0.04 g) in one portion. The reaction mixture was stirred for 3 h at room temperature. The solvent was removed under reduced pressure. The residue was purified by column chromatography (silica; eluent petroleum-ether/DCM, 50:50 to pure DCM). The first product obtained was **17** as a yellow powder (0.45 g, 24% yield): mp 284-285 ^{o}C (dec.). MS (MALDI-ToF) *m/z* 1259.8 (M^{+}+1). ^{1}H NMR (400 MHz, $CDCl_3$): 7.70-7.52 (m, 28H), 2.02-1.95 (m, 8H), 1.16-1.01 (m, 24H), 0.79 (t, 12H, *J* = 7.2 Hz), 0.66-0.57 (m, 8H), 0.28 (s, 18H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): 151.3, 151.2, 141.6, 140.5, 140.2, 140.0, 132.5, 132.1, 131.7, 130.9, 126.9, 126.7, 126.0, 122.7, 122.5, 122.3, 120.5, 120.2, 120.1, 104.9, 95.3, 91.4, 89.8, 83.2, 74.5, 55.3, 40.3, 31.5, 29.7, 23.8, 22.6, 14.0, 0.0. Anal. calcd. for $C_{92}H_{98}Si_2$: C, 87.70; H, 7.84. Found: C, 87.58; H, 7.88.

The second product obtained was **13** as a brown foamy solid (1.45 g, 46% yield): mp 112-113 ^{o}C. MS (MALDI-ToF) *m/z* 1044.9 (M^{+}). ^{1}H NMR (400 MHz, $CDCl_3$): 7.70-7.51 (m, 18H), 7.44-7.40 (m, 2H), 2.16 (s, 1H), 2.04-1.95 (m, 8H), 1.68 (s, 6H), 1.16-1.01 (m, 24H), 0.79 (two overlapping triplets, 12H, *J* = 7.2 Hz), 0.68-0.56 (m, 8H), 0.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): 151.2, 151.13, 151.08, 151.0, 140.8, 140.68, 140.67, 140.64, 140.2, 139.9, 132.5, 132.1, 130.84, 130.81, 130.8, 130.7, 126.9, 126.7, 126.04, 125.95, 122.7, 122.5, 122.1, 122.0, 121.9, 121.4, 120.03, 119.99, 119.8, 104.9, 95.2, 94.0, 91.5, 90.9, 90.8, 89.7, 83.1, 65.7, 55.3, 55.2, 40.5, 31.6, 29.8, 29.7, 23.8, 23.7, 22.6, 14.3, 14.0, 0.0. Anal. calcd. for $C_{76}H_{88}OSi$: C, 87.30; H, 8.48. Found: C, 87.36; H, 8.46.

Compound 14. To a mixture of **13** (1.30 g, 1.24 mmol) in toluene (100 mL) under argon, finely-powdered NaOH (300 mg) was added in one portion. The suspension was heated to reflux for 3 h with a preheated oil bath (140 ^{o}C). The solvent was removed under reduced pressure. The residue was dissolved in dichloromethane (30 mL) and the solid was removed

by filtration. The filtrate was evaporated under reduced pressure and the residue was purified by column chromatography (silica; eluent petroleum-ether/DCM, 9:1 v/v) to give **14** as a yellow powder (0.74 g, 60% yield): mp 153.1-154.2 ^{o}C. MS (MALDI-ToF) *m/z* 986.8061 (M^+). ^{1}H NMR (400 MHz, $CDCl_3$): 7.71-7.49 (m, 20H), 3.17 (s, 1H), 2.04-1.96 (m, 8H), 1.16-1.01 (m, 24H), 0.79 (t, 12H, J = 7.2 Hz), 0.67-0.56 (m, 8H), 0.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): 151.2, 151.1, 151.0, 141.2, 140.8, 140.7, 140.5, 140.2, 139.9, 132.5, 132.1, 131.3, 130.84, 130.77, 126.9, 126.7, 126.5, 126.0, 122.7, 122.5, 122.2, 122.0, 121.9, 120.7, 120.1, 120.03, 120.00, 119.9, 104.9, 95.3, 91.5, 90.9, 90.8, 89.7, 84.6, 55.30, 55.26, 40.5, 40.4, 31.59, 31.55, 29.8, 29.7, 23.8, 23.7, 22.9, 22.6, 14.00, 13.99, 0.0. Anal. calcd. for $C_{73}H_{82}Si$: C, 88.79; H, 8.37. Found: C, 88.82; H, 8.33.

Compound 18. mp 302.6-303.5 ^{o}C. MS (MALDI-ToF) *m/z* 1972.5 (M^+); (calcd. 1972.2). ^{1}H NMR (400 MHz, $CDCl_3$): 7.71-7.53 (m, 40H), 1.99 (broad s, 16H), 1.16-1.01 (m, 48H), 0.81-0.76 (m, 24H), 0.62 (broad s, 16H), 0.28 (s, 18H). Anal. calcd. for $C_{146}H_{162}Si_2$: C, 88.88; H, 8.28. Found: C, 88.80; H, 8.30.

Crystallographic studies. Single-crystal X-ray diffraction experiments (Table S1) for **4** and **11** were carried out on a Bruker 3-circle diffractometer with a SMART 6K CCD area detector, using graphite-monochromated Mo-K_α radiation (λ=0.71073 Å) and Cryostream (Oxford Cryosystems) open-flow N_2 cryostats. The structures were solved by direct methods and refined by full-matrix least squares against F^2 of all data, using SHELXTL 6.14 software (Bruker AXS, Madison, WI, USA, 2003). For **4** an absorption correction was made by numerical integration based on crystal face-indexing (transmission factors 0.5154 to 0.8968).

As shown in the text (Fig. 1) the asymmetric unit of **4** comprises two molecules. The crystal packing reveals *segregated* stacks of fluorene and pentafluorophenyl moieties rather than the usual mixed stack motif of alternating arene and perfluoroarene moieties or molecules.[1,2] Each iodine atom forms one or two short intermolecular I…C contacts (3.46 to 3.57 Å, cf. the sum of van der Waals radii[3] of 3.80 Å) with the outer (6-membered) rings of the fluorene moieties. In these contacts, the C-I bonds are roughly perpendicular to the fluorene planes.

The crystal packing of compound **11** is rather loose (21 Å^3 per non-hydrogen atom). Both *n*-hexyl chains of the molecule are intensely disordered; the most probable conformations are shown in the text. The dihedral angle between the (planar) fluorene moiety and the benzene ring C(28-33) equals 76.8º; the angle between the latter ring and the C(34-

39) ring equals 29.1º. The two molecules, related by an inversion centre (1 1.5 1), are linked by a pair of hydrogen bonds of type O-H…π{C(45)≡C(46)} between the hydroxyl group and the π-system of the alkyne bond.

Table S1. Crystal data

Compound	**4**	**11**
CCDC dep. no.	628780	628781
Formula	$C_{31}H_{18}F_{10}I_2O_2$	$C_{49}H_{56}OSi$
Formula weight	866.25	689.03
T, K	120	120
Symmetry	triclinic	triclinic
Space group	$P\bar{1}$ (# 2)	$P\bar{1}$ (# 2)
a, Å	8.0245(5)	10.359(1)
b, Å	17.6262(10)	12.820(1)
c, Å	21.6275(14)	17.950(2)
α, °	101.75(1)	96.43(1)
β, °	94.54(1)	99.59(1)
γ, °	90.25(1)	112.65(1)
V, Å^3	2984.9(3)	2128.2(4)
Z	4	2
μ, mm^{-1}	2.20	0.09
Refls collected	54827	22483
Unique refls	17409	9755
R_{int}	(0.082[a]) 0.063	0.043
Refls $F^2>2\sigma(F^2)$	11587	5065
$R[F^2>2\sigma(F^2)]$	0.038	0.060
w$R(F^2)$, all data	0.100	0.178

[a] Before absorption correction

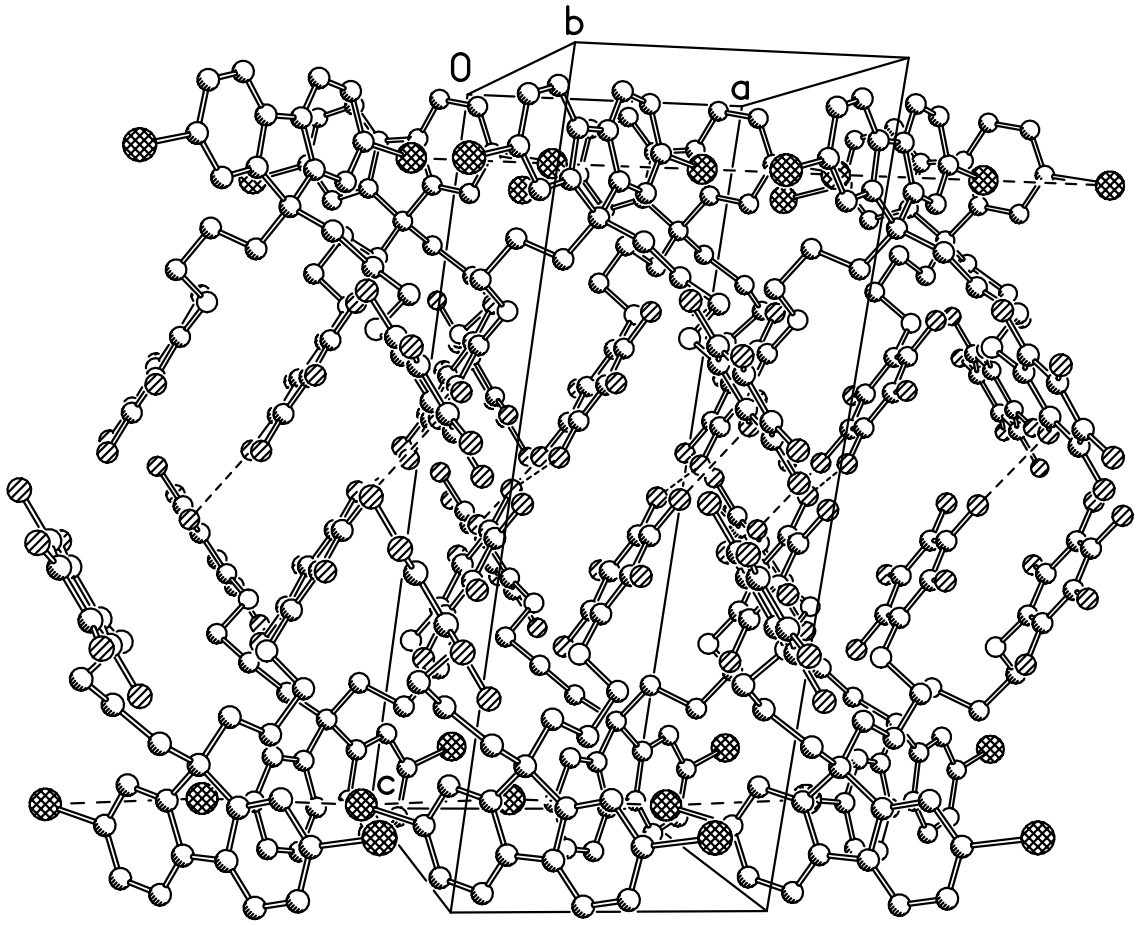


Figure S3. Crystal packing of compound **4**, showing shortest intermolecular contacts F…F and I…I . Hydrogen atoms are omitted.

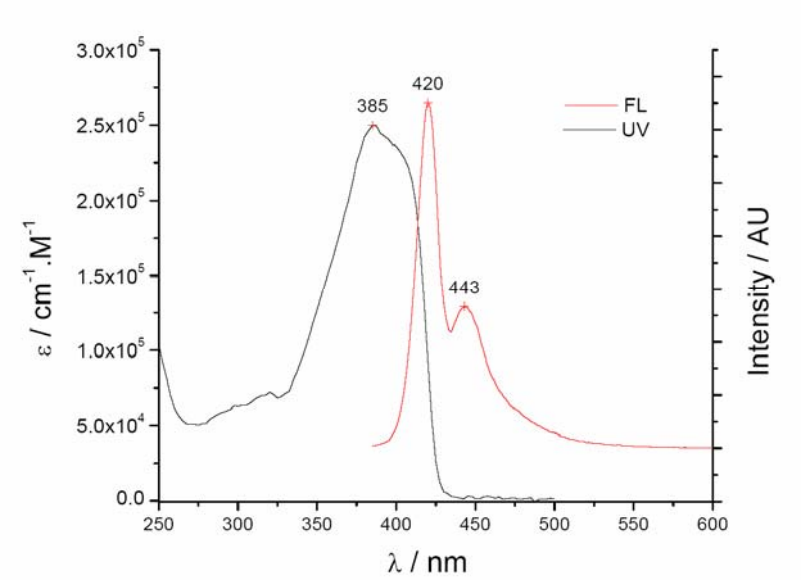


Figure S4. UV-Vis absorption and fluorescence spectra of **16** in chloroform solution.

Theoretical Studies

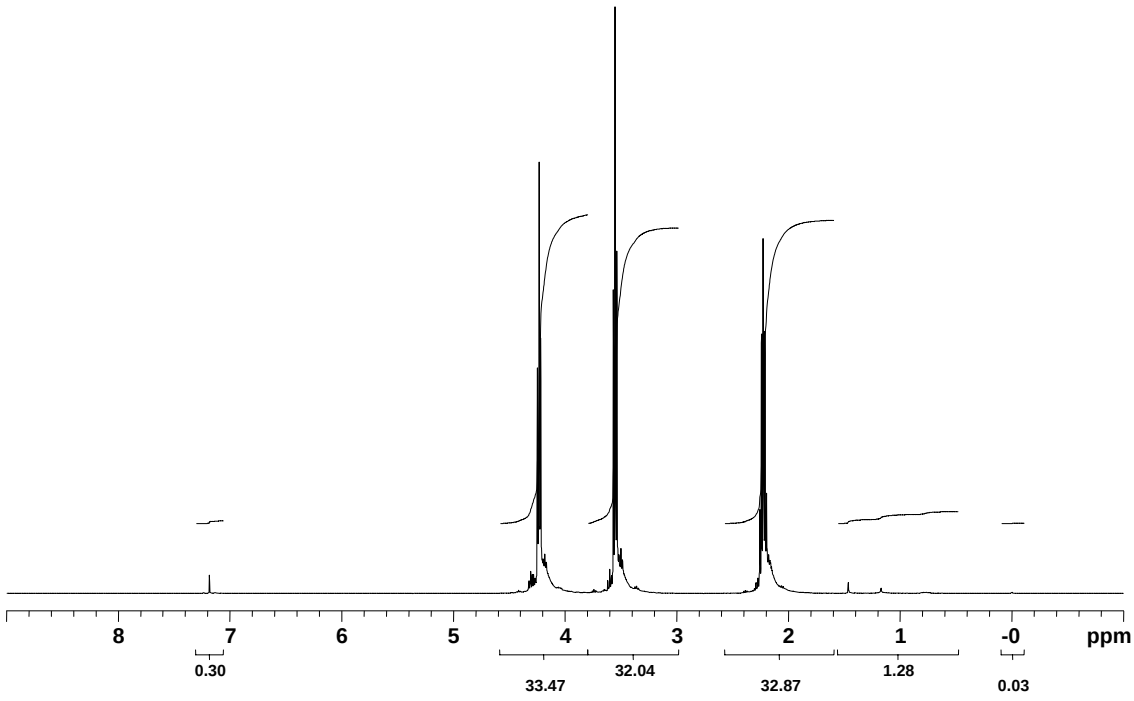
The theoretical structural and electronic properties were obtained using Density Functional Theory[4] as implemented in the SIESTA package.[5] The ionic cores were substituted by norm-conserving pseudopotentials parametrized with the recipe of Troullier and Martins.[6] The single particle molecular states were calculated using a linear combination of atomic orbitals. We employed a double-ζ polarized basis set: two atomic orbitals per valence quantum channel and one polarization shell, i.e. two *s* and three *p* for H and two *s*, six *p* and five *d* for C, O and F. The cutoff radii were determined using an energy shift of 0.02 Ry and the second ζ were generated with a split-norm of 0.15. The real space grid was defined with a plane-wave cutoff of 300 Ry. The exchange and correlation energy was calculated with the Local Density Approximation (LDA) as parametrized by Perdew and Zunger.[7] The Fermi distribution function was smeared with a temperature of 75 K and the density matrix was converged until the differences between consecutive iterations were smaller than 10^{-4}. The atomic coordinates were relaxed with a conjugated gradient method until all forces were smaller than 0.03 eV/Å.

To find the most stable structural conformation of **16** the conjugated backbone was initially relaxed with the central fluorene unit substituted with two hydrogen atoms at C(9) and the other four fluorene units substituted with methyl groups at C(9). The calculation started from a straight backbone conformation, where all the conjugated aryl groups were aligned along the *z* direction. However, after relaxation the structure moved to a "zigzag" conformation, with the 9,9-dimethylfluorene units alternately oriented "upwards" and "downwards", as can be seen in Figure 2. The intramolecular terminal C…C' distance for this hypothetical molecule was found to be 7.85 nm with the outer phenyl rings of the biphenyl units twisted by 29° relative to the aryleneethynylene backbone. The bis(pentafluorophenoxypropyl) substituents were then attached to the central fluorene unit and the whole structure was relaxed again. As expected, the backbone structure did not change appreciably and the intramolecular terminal C…C' distance was 7.84 nm. However, the bis(pentafluorophenoxypropyl) units moved to a open configuration, where their oxygen atoms were separated by a distance of 5.94 Å [cf. intramolecular O…O' distances of 6.49 and 6.62 Å in the X-ray crystal structure of **4** shown in Figure 1]. Figure 2 shows the spatial distribution of the modulus squared of the HOMO and LUMO orbitals for this analog of **16** (i.e. **16'**). We have checked that such a conformation corresponds to the absolute energy minimum by starting from different initial separations of the bis(pentafluorophenoxypropyl) units in a backbone of reduced length [namely, the model fragment 2,7-diethynyl-9,9-bis(3-

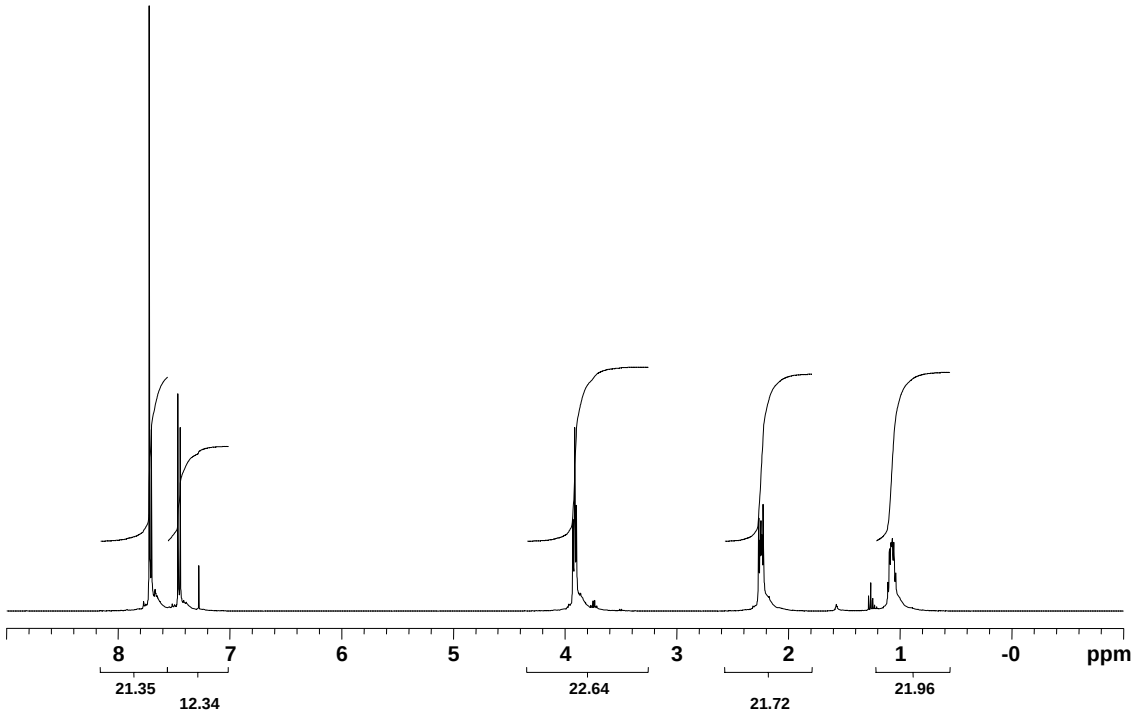
pentafluorophenoxypropyl)fluorene] and verifying that they either relax to higher-energy minima or relax to the above lowest-energy conformation.

By using the projected density of states or comparing the density of states of the isolated backbone with the density of states of **16'** it is possible to find out which states are associated with the main backbone and which are associated only with the 9,9-bis(pentafluorophenoxypropyl)fluorene units. The HOMO and LUMO peaks of the bis(pentafluorophenoxypropyl)fluorene units are located 1.40 eV below the HOMO and 1.26 eV above the LUMO of the whole molecule, respectively. This separation in energy is a consequence of the large electronegativity of the fluorine atoms which push the bonding and antibonding states downwards and upwards in energy, respectively, and the presence of the alkane chains, which, due to their insulating behavior, isolate the pentafluorophenoxy units from the backbone. As a consequence, the states of the backbone and the states associated with the bis(pentafluorophenoxypropyl)fluorene units can be considered to be spatially and energetically detached.

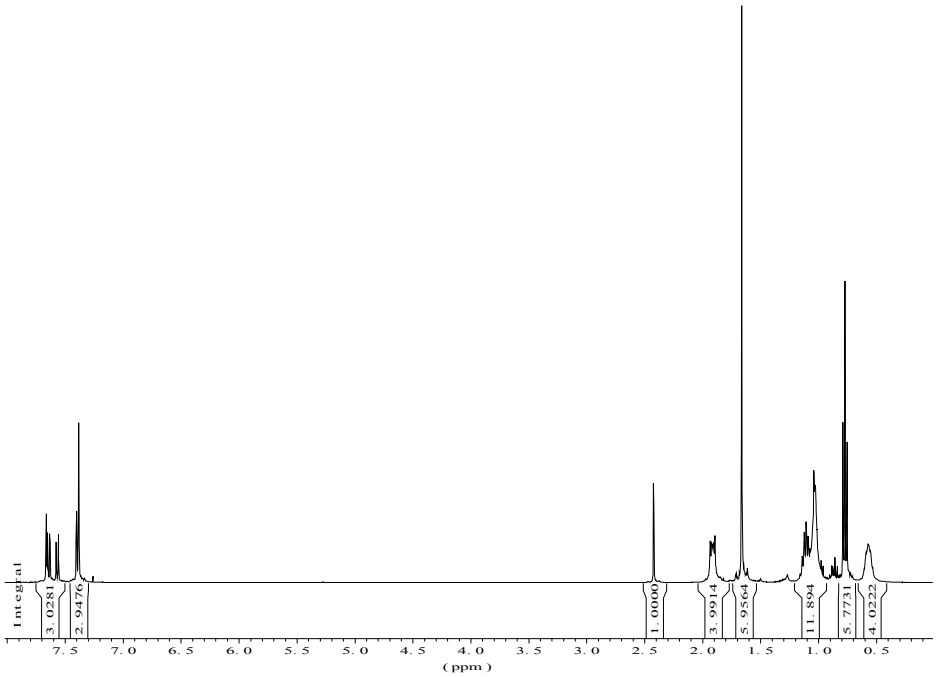
Copies of NMR Spectra



^{1}H NMR spectrum of compound **2** in $CDCl_3$ at 400 MHz.



^{1}H NMR spectrum of compound **4** in $CDCl_3$ at 400 MHz.



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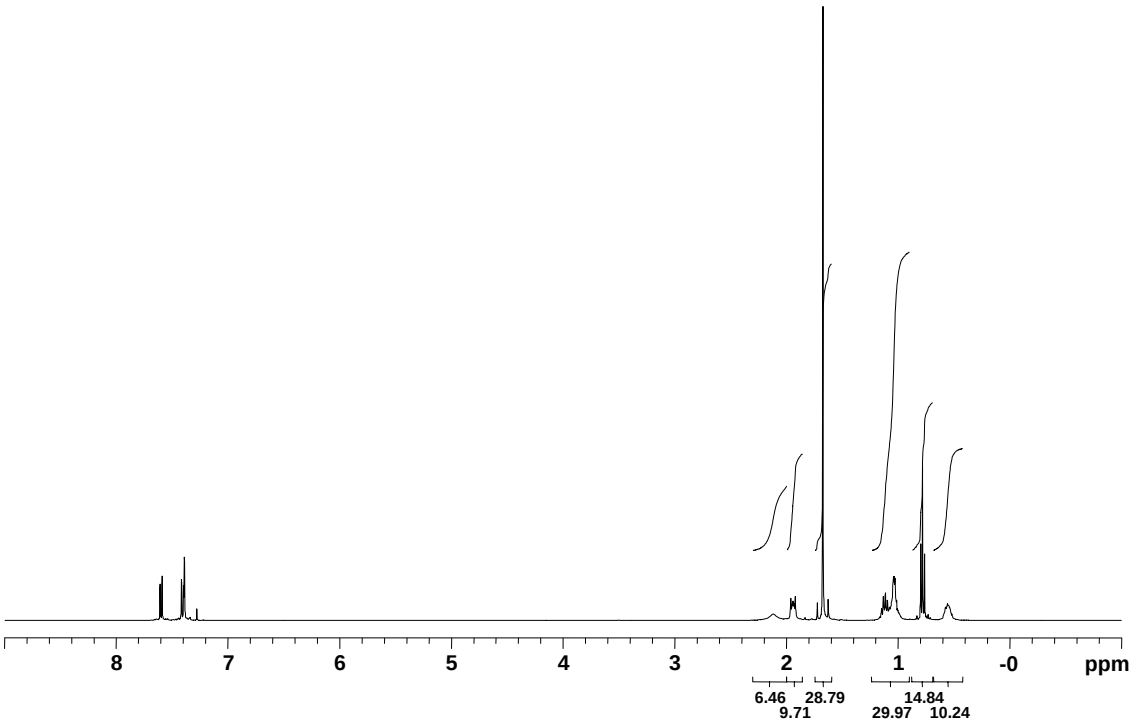

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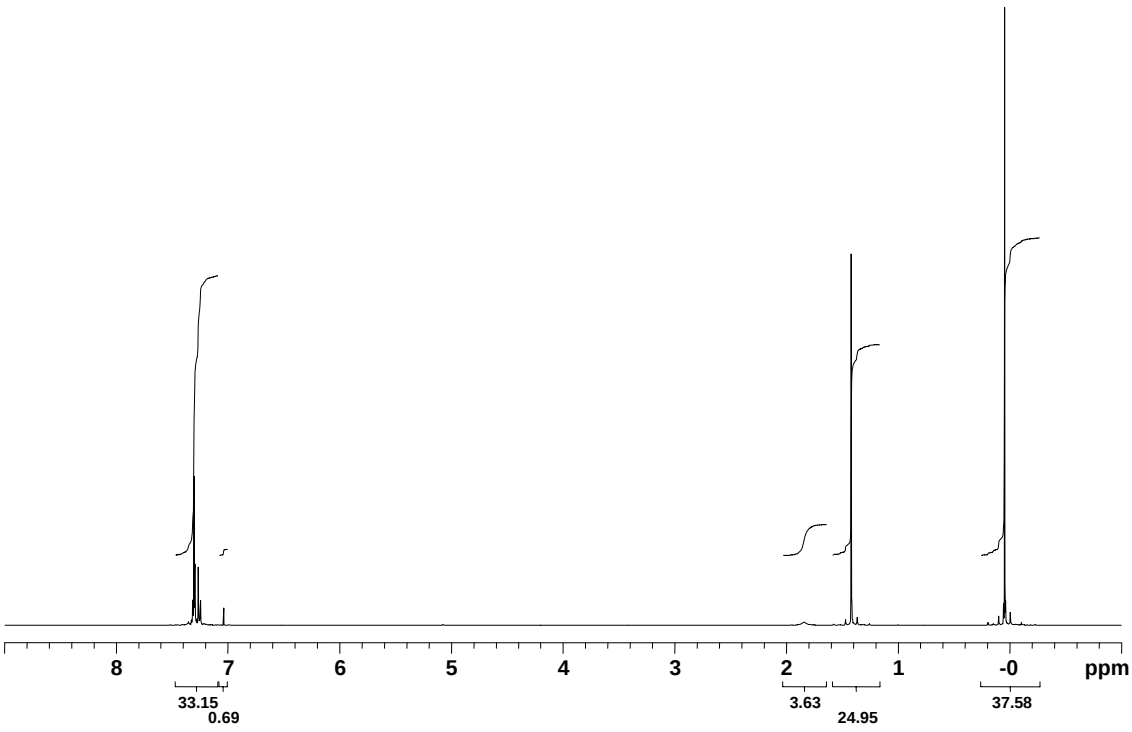

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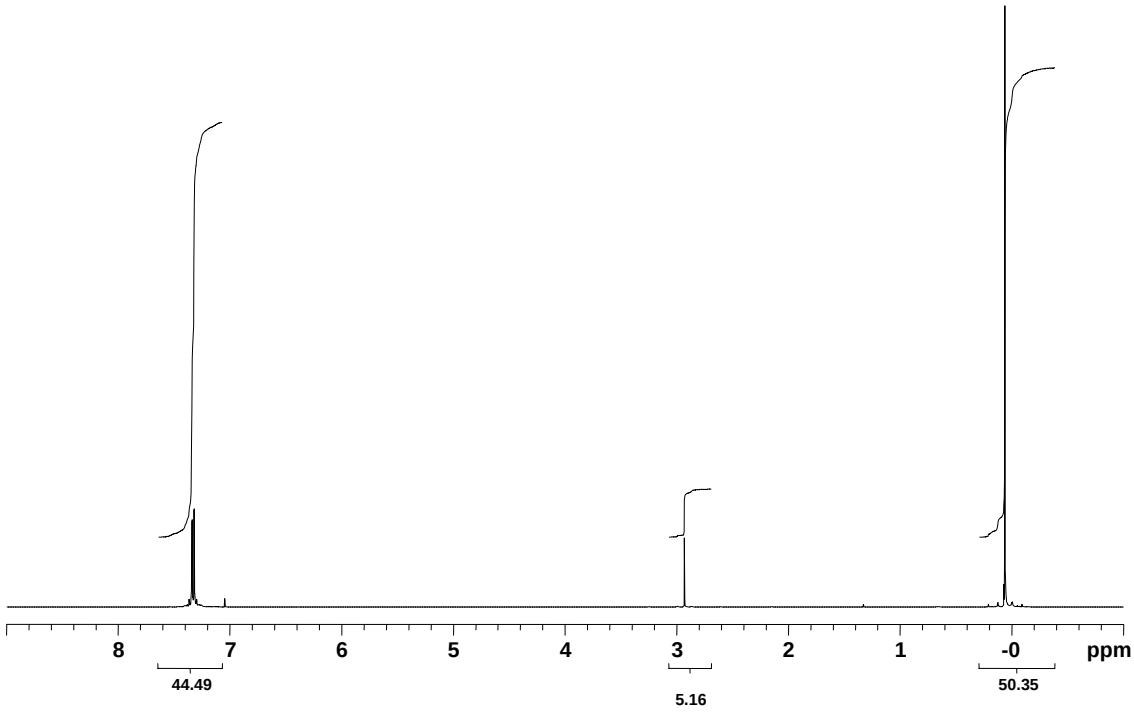
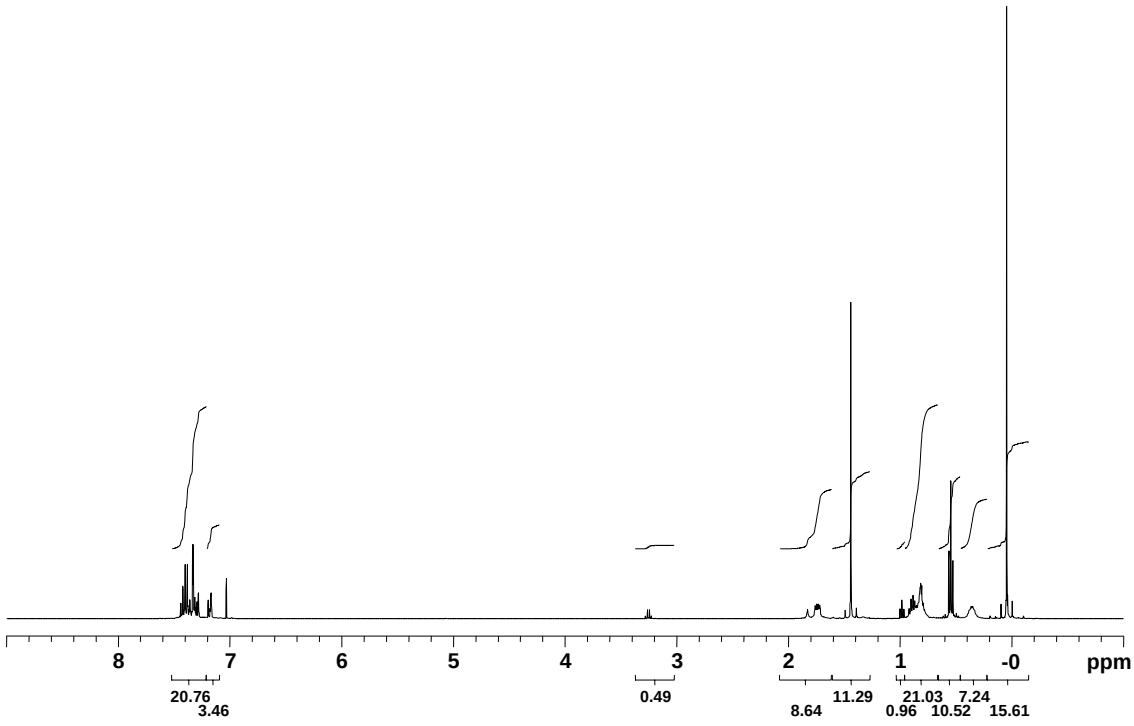
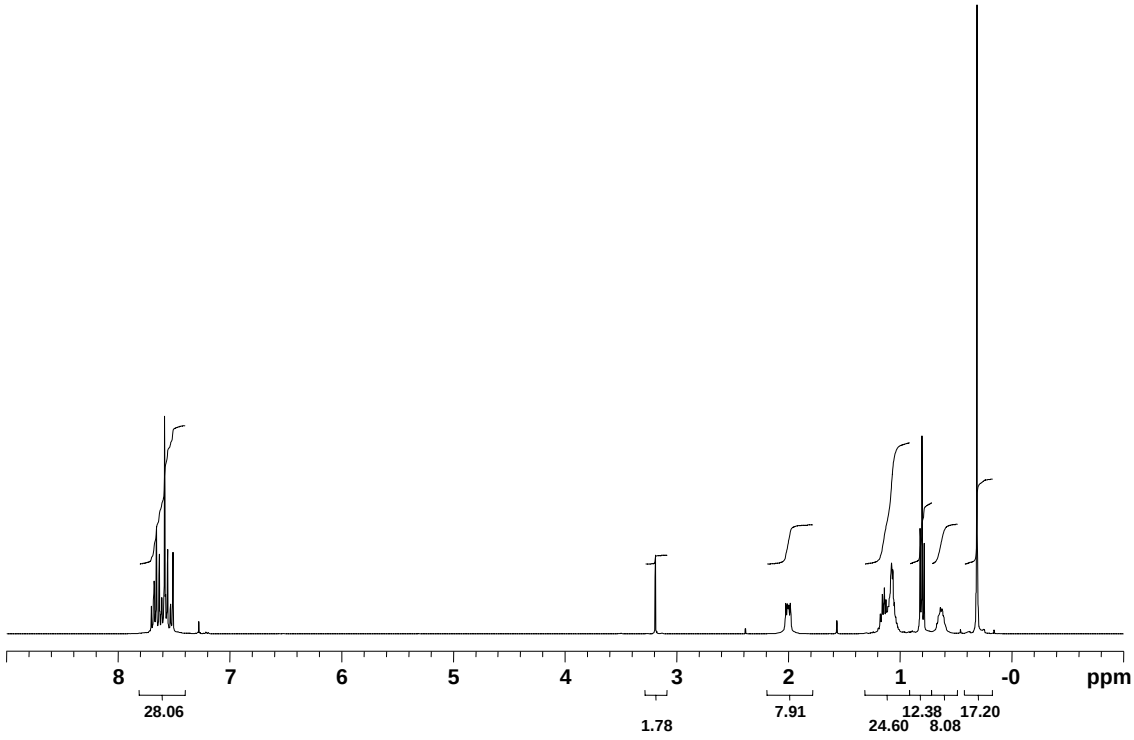


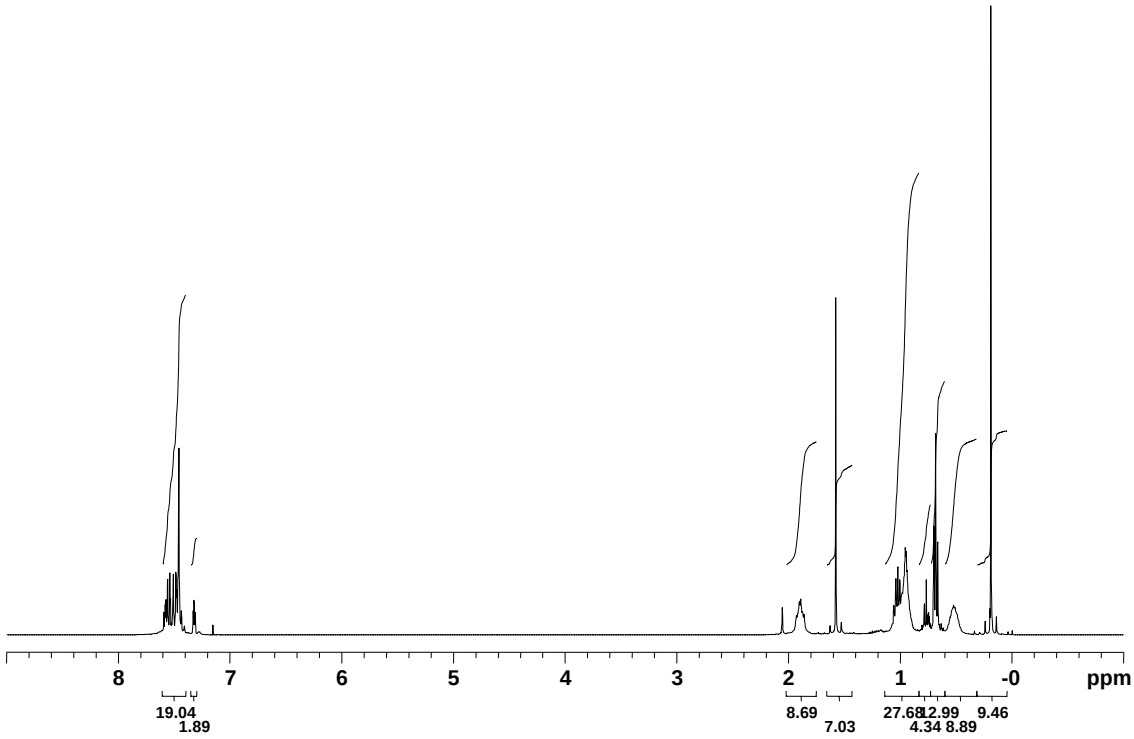
^{1}H NMR spectrum of compound **10** in $CDCl_3$ at 400 MHz.



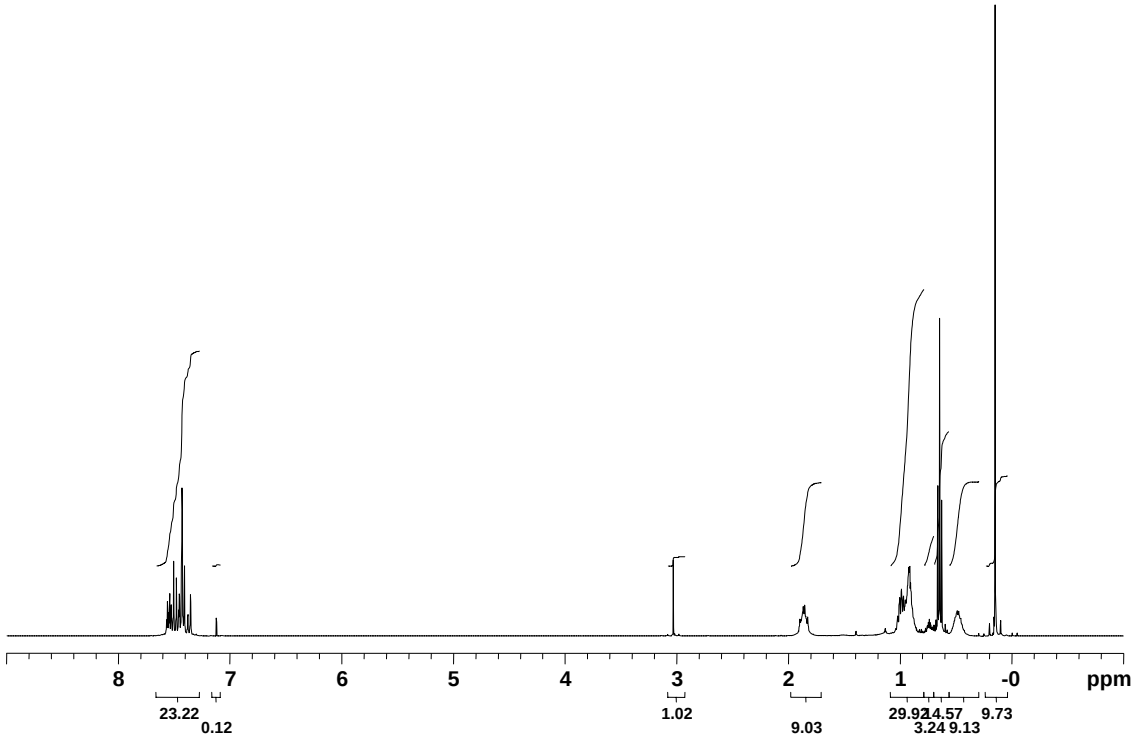
^{1}H NMR spectrum of compound **11** in $CDCl_3$ at 400 MHz.



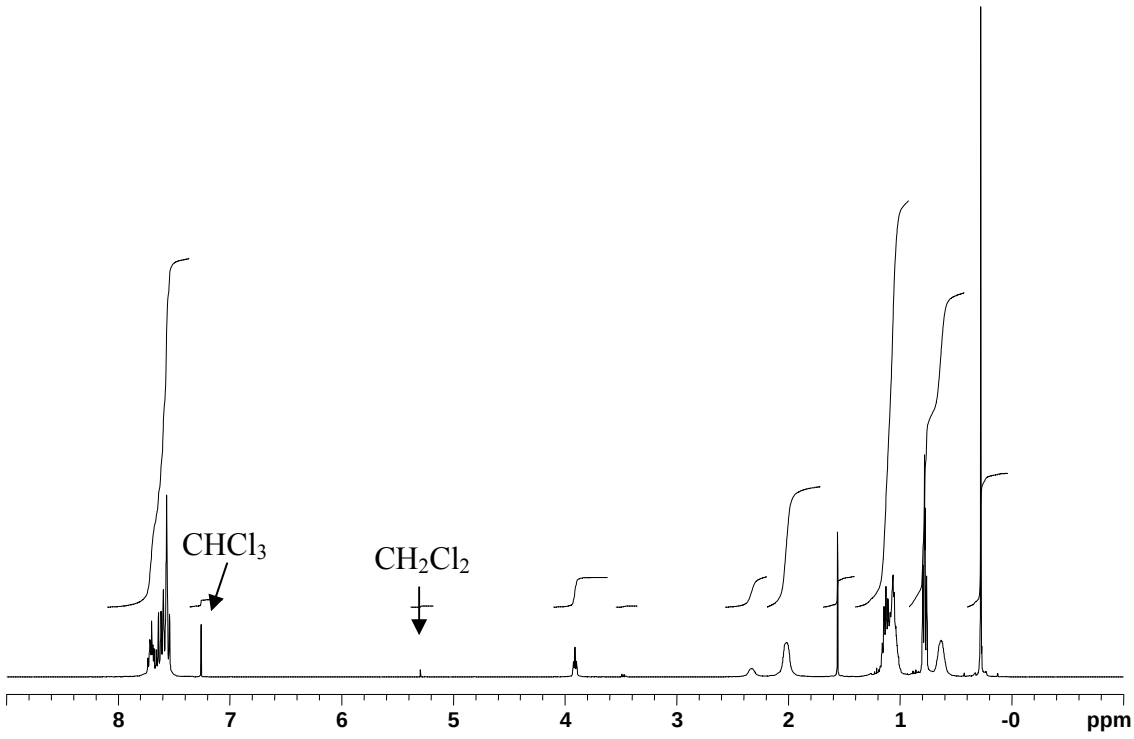
^{1}H NMR spectrum of compound **12** in $CDCl_3$ at 400 MHz.



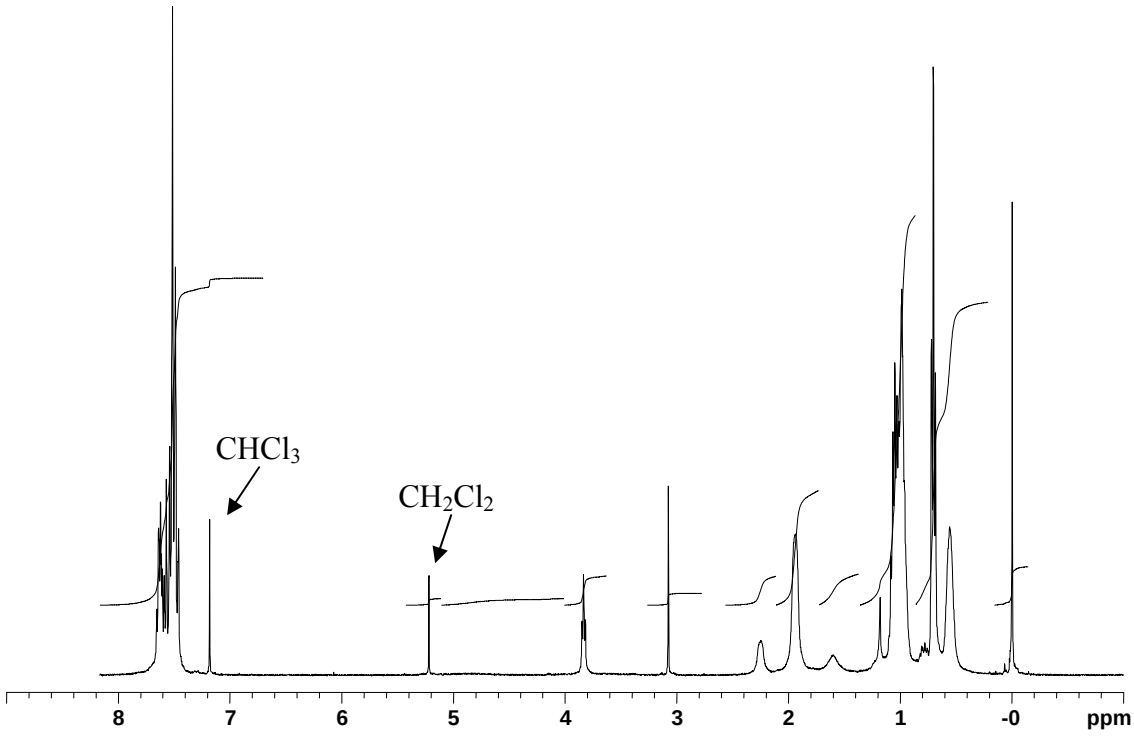
^{1}H NMR spectrum of compound **13** in $CDCl_3$ at 400 MHz.



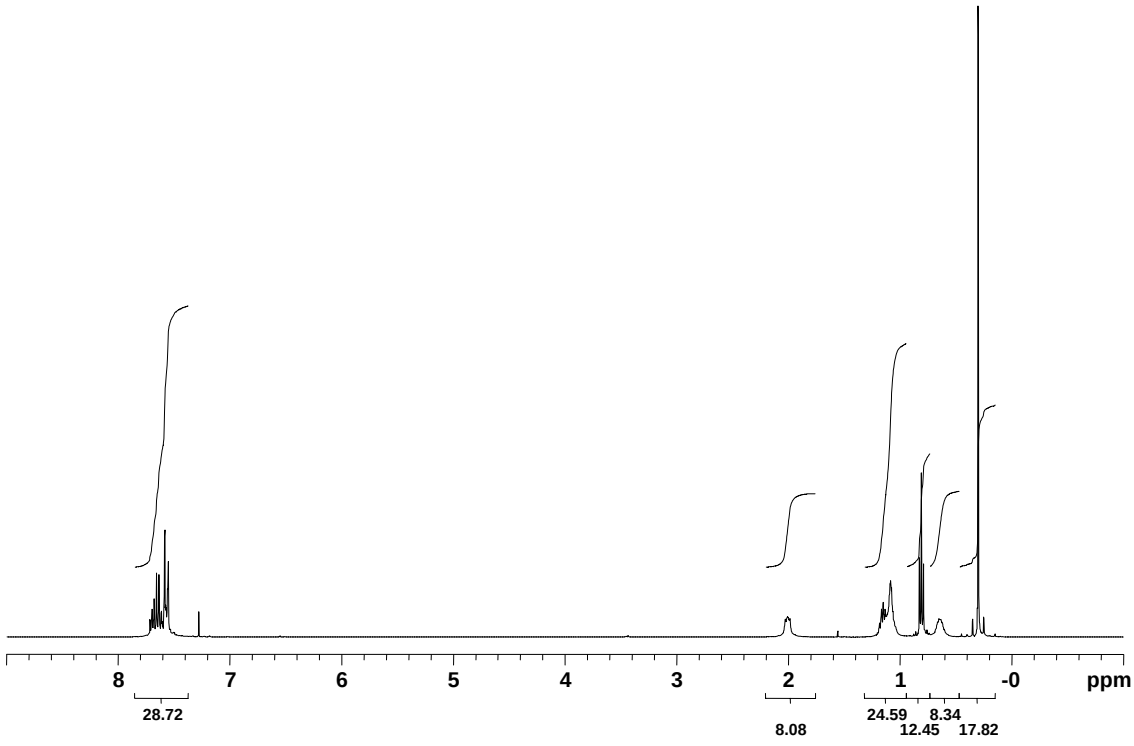
^{1}H NMR spectrum of compound **14** in $CDCl_3$ at 400 MHz.



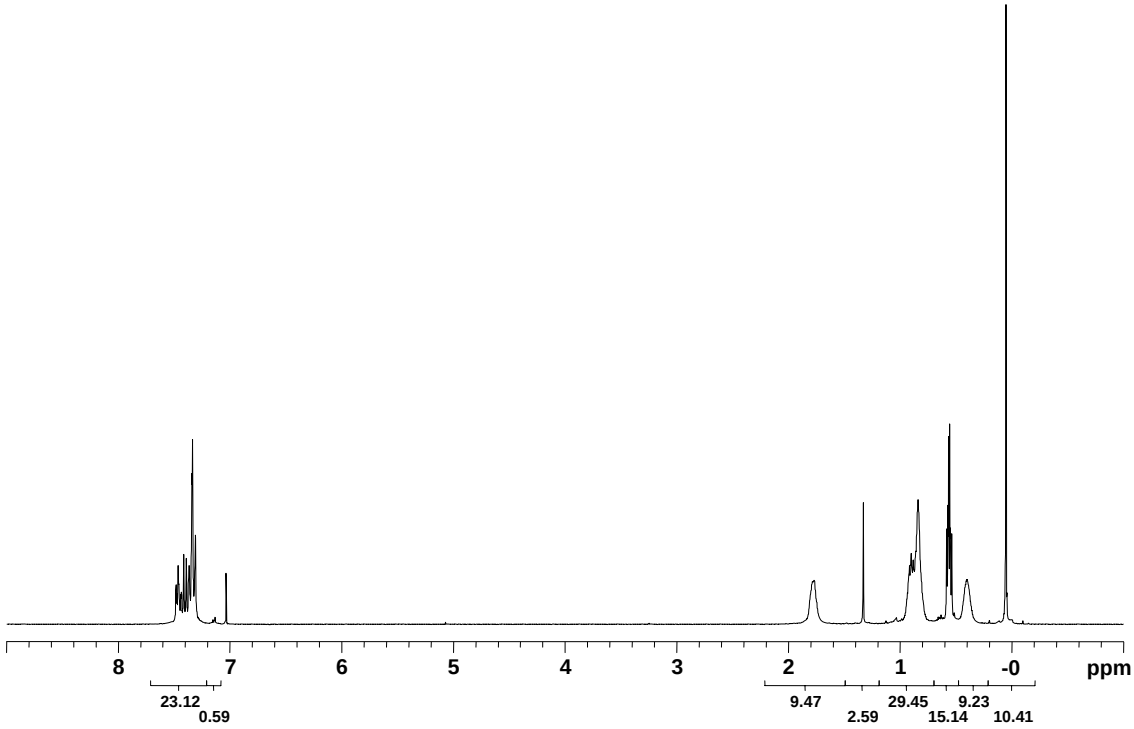
^{1}H NMR spectrum of compound **15** in $CDCl_3$ at 400 MHz.



^{1}H NMR spectrum of compound **16** in $CDCl_3$ at 400 MHz.



^{1}H NMR spectrum of compound **17** in $CDCl_3$ at 400 MHz.



^{1}H NMR spectrum of compound **18** in $CDCl_3$ at 400 MHz.

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