DOI: 10.1002/ejoc.200700507

Functionalized 8 nm Long Aryleneethynylene Molecular Wire with Alkyne Termini

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Keywords: Molecular wires / Conjugation / Fluorene / Sonogashira reaction / Aryleneethynylene

The synthesis 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 is described. 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 observed for **16** ($\lambda_{\max}$ = 420, 443 nm in $CHCl_3$ solution) are consistent with a highly conjugated penta[(9,9-dihexyl-2,7-fluorenylene)-ethynylene] 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 through 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–aryl carbon 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 an Si–aryl carbon 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/

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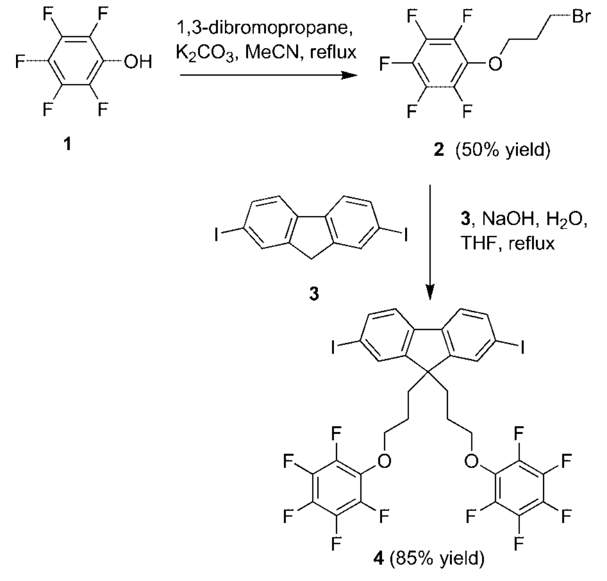
molecule/Si devices is in the field of sensor technology[14] where pendant units could act as molecular recognition sites.

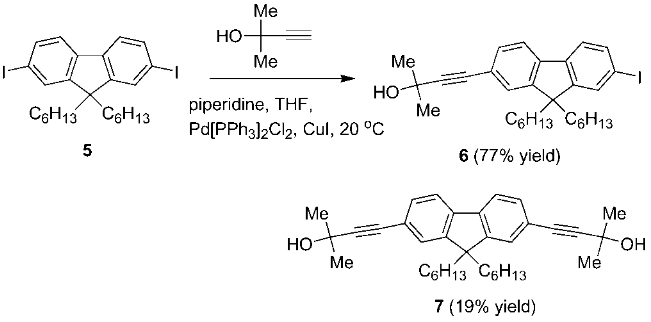
Results and Discussion

The symmetrical target molecule **16** was obtained by 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-hydroxy-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** (Scheme 4) 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**.

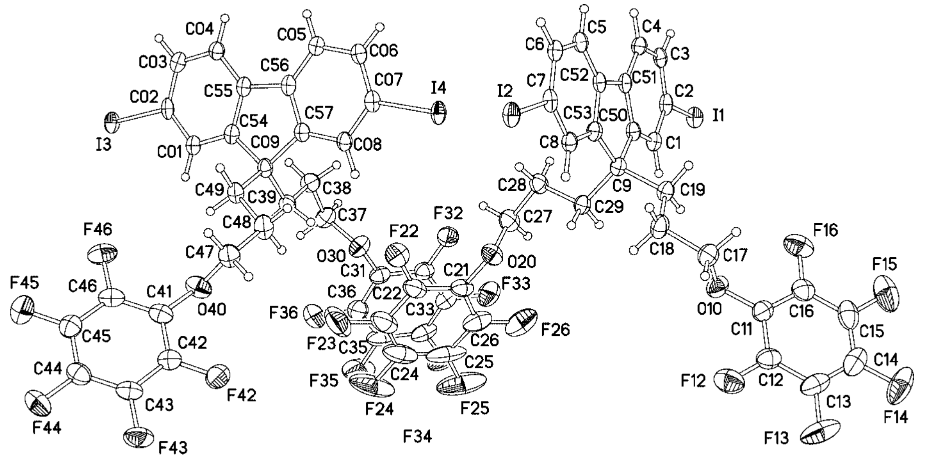
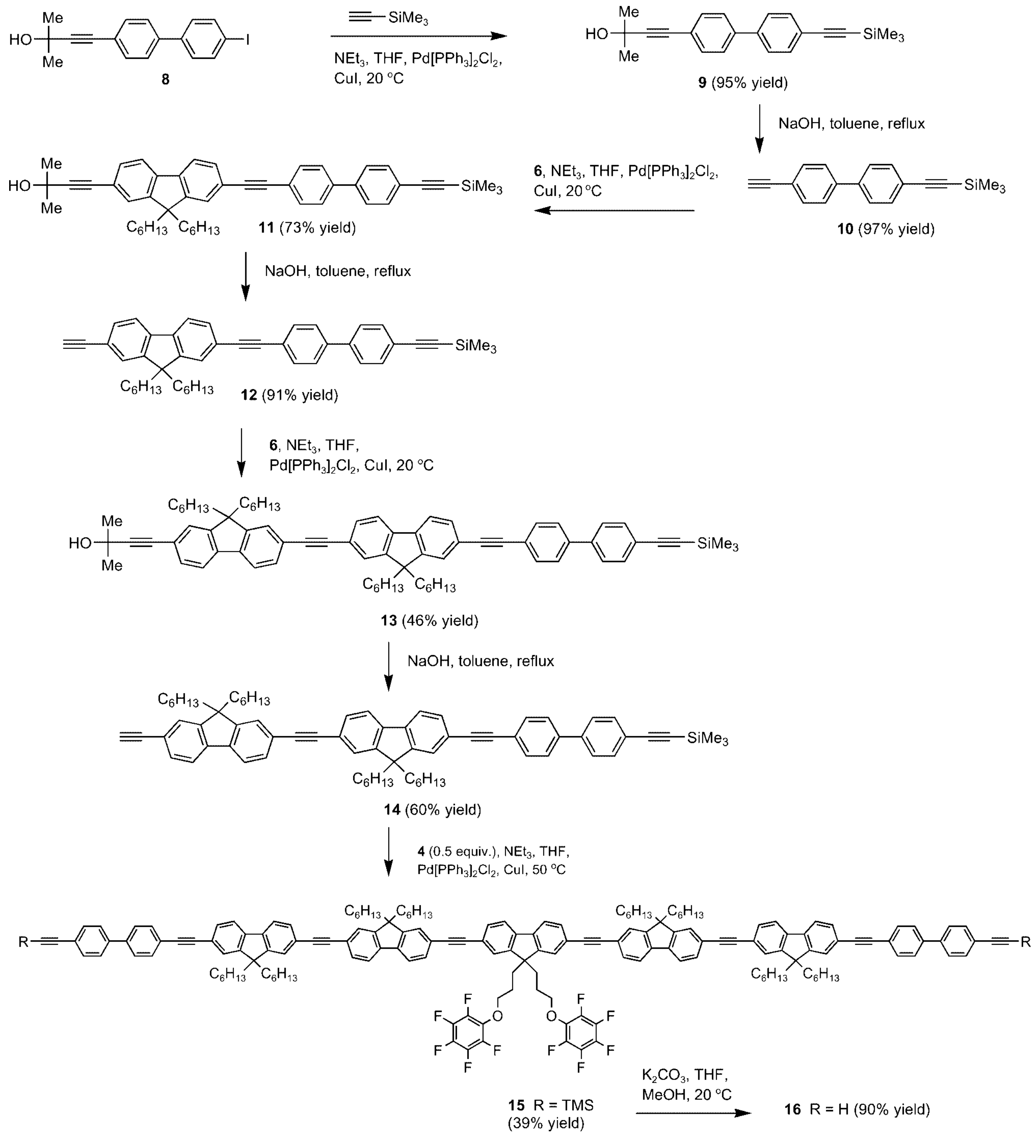
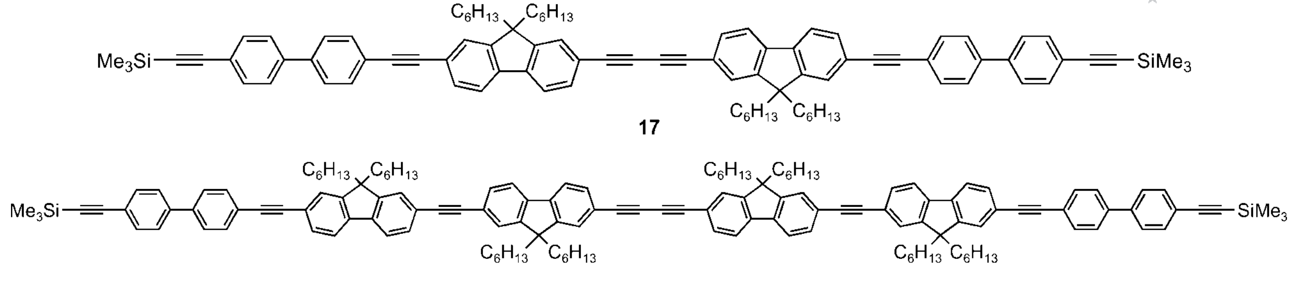


Figure 1. Two independent molecules of **4** in the crystal. Thermal ellipsoids are drawn at the 50% probability level.



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

In the crucial convergent step, twofold 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. Compound **16** was stable to storage at 5 °C in the dark for at least several months. Evidence for extended π-conjugation through the 2,7-fluorenyleneethynylene backbone of **16** was provided by the UV/Vis absorption and fluorescence spectra in chloroform solution (see Supporting Information, Figure S4) and DFT calculations (see below). In particular the absorption peak at λ_{max} = 385 nm and the strong blue fluorescence at λ_{max} = 420, 443 nm are consistent with literature data for penta[(9,9-dihexyl-2,7-fluorenylene)ethynylene] suggesting the same conjugation length in both structures.[15] Any additional conjugation in structure **16** would be limited by the twisting in the outer biphenyl systems.



Scheme 4. Self-coupled symmetrical butadiyne derivatives.

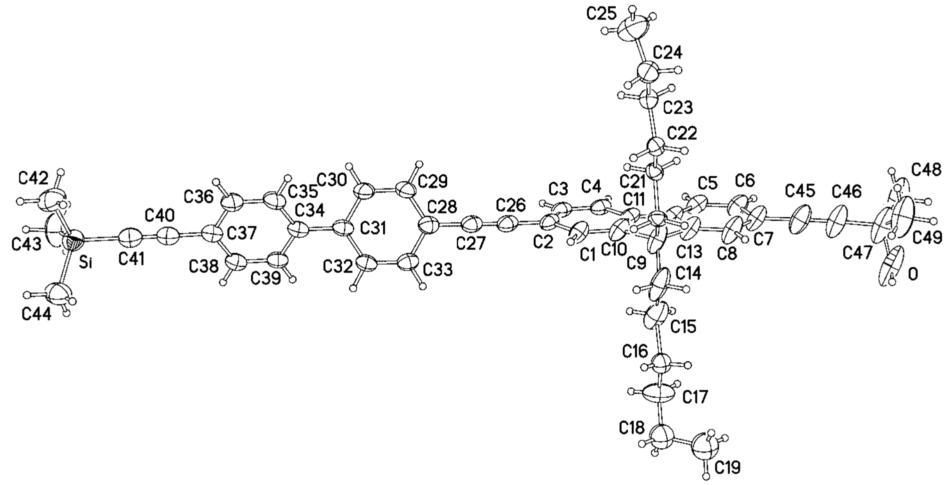


Figure 2. Molecule of **11** in the crystal. Thermal ellipsoids are drawn at the 50% probability level. Only the major conformations of the disordered *n*-hexyl chains are shown.

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]

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 76.8°; the angle between the latter ring and the C(34–39) ring equals 29.1°. For further discussion, see the Supporting Information.

To probe the structural and electronic properties of **16**, DFT calculations[21] 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. 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 alkyl chains, which, due to their insulating behavior, isolate the pentafluorophenoxy units from the backbone.

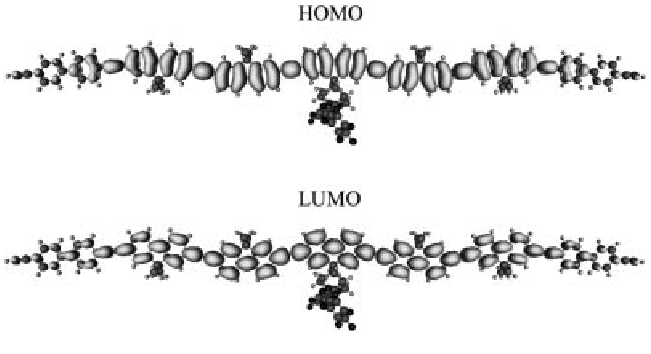


Figure 3. Spatial distribution of the HOMO and LUMO orbitals of molecule **16′**, where the methyl groups in the calculated structure replace the hexyl groups of the synthesized compound **16**. The calculated intramolecular terminal C···C′ distance is 7.84 nm.

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

General analytical/spectroscopic equipment have been described previously.[17]

2,7-Diiodo-9,9-bis(3-pentafluorophenoxypropyl)fluorene (4): NaOH (1.2 g, 30 mmol) in water (1.5 mL) was added in one portion to a suspension of 2,7-diiodofluorene (**3**; 1.78 g, 4.25 mmol) in THF (40 mL) under argon. 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 with 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); m.p. 112.3–112.9 °C. MS (MALDI-ToF): *m/z* = 865.9 [M$^+$]. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.71–7.68 (m, 4 H), 7.43 (d, J = 8.4 Hz, 2 H), 3.89 (t, J = 6.0 Hz, 4 H), 2.24–2.19 (m, 4 H), 1.08–1.03 (m, 4 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$, with C-F decoupling): δ = 150.7, 142.8, 140.3, 139.8, 139.2, 136.8, 133.4, 132.0, 121.8, 93.5, 75.3, 54.6, 36.0, 24.4 ppm. $C_{31}H_{18}F_{10}I_2O_2$ (866.27): calcd. C 42.98, H 2.09; found C 42.76, H 1.98.

9,9-Dihexyl-7-(3-hydroxy-3-methylbutynyl)-2-iodofluorene (6) and 9,9-Dihexyl-2,7-bis(3-hydroxy-3-methylbutynyl)fluorene (7): Pd(PPh$_3$)$_2$Cl$_2$ (0.75 g) and CuI (0.25 g) were added in one portion to a mixture of 9,9-dihexyl-2,7-diiodofluorene (**5**; 17.58 g, 30 mmol), 3-hydroxy-3-methylbutyne (2.10 g, 25 mmol) and piperidine (20 mL) in THF (150 mL) under argon. The reaction mixture was stirred at room temperature for 2 h. The solvent was removed under reduced pressure. The residue was dissolved in diethyl ether and filtered through a Celite column. The filtrate was concentrated 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$_3$): δ = 7.67–7.58 (m, 3 H), 7.41–7.38 (m, 3 H), 2.42 (s, 1 H), 1.94–1.88 (m, 4 H), 1.66 (s, 6 H), 1.17–0.97 (m, 12 H), 0.77 (t, J = 7.2 Hz, 6 H), 0.60–0.56 (m, 4 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 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 ppm. $C_{30}H_{39}IO$ (542.54): calcd. 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); m.p. 79–80 °C. MS (ES): *m/z* = 498.4 [M$^+$]. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.57 (d, J = 8.0 Hz, 2 H), 7.38 (dd, J = 8.0, 1.2 Hz, 2 H), 7.77 (d, J = 1.2 Hz, 2 H), 2.10 (br. s, 2 H), 1.95–1.88 (m, 4 H), 1.66 (s, 12 H), 1.15–0.96 (m, 12 H), 0.76 (t, J = 7.2 Hz, 6 H), 0.59–0.55 (m, 4 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 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 ppm. $C_{35}H_{46}O_2$ (498.74): calcd. C 84.29, H 9.30; found C 84.32, H 9.28.

4-(3-Hydroxy-3-methylbutynyl)-4′-(trimethylsilylethynyl)biphenyl (9): Trimethylsilylacetylene (3.0 mL, 21.0 mmol) was added in one portion to a solution of **8**[17] (5.25 g, 14.5 mmol) and triethylamine (20 mL) in THF (100 mL) under argon. To this solution Pd(PPh$_3$)$_2$Cl$_2$ (0.25 g) and CuI (0.1 g) were added in one portion. The mixture was stirred at room temperature for 3 h, then concentrated to dryness. The dark residue was dissolved in diethyl ether (200 mL) and filtered through a Celite column. The filtrate was concentrated 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); m.p. 169.6–170 °C. MS (ES): *m/z* = 332.3 [M$^+$]. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.53 (d, J = 8.4 Hz, 2 H), 7.52 (s, 4 H), 7.47 (d, J = 8.4 Hz, 2 H), 2.04 (br. s, 1 H), 1.64 (s, 6 H), 0.27 (s, 9 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 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 ppm. $C_{22}H_{24}OSi$ (332.51): calcd. C 79.47, H 7.28; found C 79.55, H 7.24.

4-Ethynyl-4′-(trimethylsilylethynyl)biphenyl (10): Finely powdered NaOH (600 mg) was added in one portion to a mixture of **9** (4.60 g, 13.83 mmol) in anhydrous toluene (190 mL) under argon. The reaction mixture was immersed in a preheated oil bath (140 °C) and refluxed for 15 min, then cooled to room temperature. Solids were removed by filtration, the filtrate was concentrated to dryness and purified by column chromatography (silica; eluent petroleum ether/dichloromethane, 1:1, v/v) to give **10** as a white powder (3.70 g, 97% yield); m.p. 126–127 °C. MS (ES): *m/z* = 274.2 [M$^+$]. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.54–7.53 (m, 8 H), 3.14 (s, 1 H), 0.28 (s, 9 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 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 ppm. $C_{19}H_{18}Si$ (274.43): calcd. C 83.15, H 6.61; found C 83.20, H 6.64.

Compounds 15 and 18: Pd(PPh$_3$)$_2$Cl$_2$ (0.03 g) and CuI (0.01 g) were added in one portion to a mixture of **4** (56 mg, 0.065 mmol) and triethylamine (1 mL) in THF (100 mL) under argon. A solution of **14** (160 mg, 0.162 mmol) in THF (40 mL) was added slowly. The mixture was stirred at 50 °C for 72 h, then concentrated to dryness and the residue was purified by column chromatography (silica; eluent petroleum ether/dichloromethane, 9:1, v/v) to give, as the first fraction, **18** as a yellow powder (25 mg, 8% yield) (see Supporting Information). The second product to elute was **15** as a yellow powder (65 mg, 39%) m.p. 283.1–283.5 °C. MS (MALDI-ToF): *m/z* = 2585.2 [M$^+$]; calcd. 2585.3. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.73–7.54 (m, 46 H), 3.93–3.88 (t, J = 6.0 Hz, 4 H), 2.34 (br. s, 4 H), 2.02 (br. s, 16 H), 1.16–1.01 (m, 52 H), 0.80–0.76 (m, 24 H), 0.64 (br. s, 16 H), 0.28 (s, 18 H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$, with C–F decoupling): δ = 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 ppm. $C_{177}H_{180}F_{10}O_2Si_2$ (2585.48): calcd. C 82.22, H 7.02; found C 82.42, H 7.22.

Compound 16: Finely powdered potassium carbonate (200 mg) was added in one portion to a solution of **15** (45 mg, 0.017 mmol) in THF (10 mL) and methanol (5 mL) under argon. The suspension was stirred for 2 h; solids were removed by filtration and the filtrate was concentrated 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); m.p. 172–173 °C. MS (MALDI-ToF): m/z = 2440.2 [M$^+$]; calcd. 2440.3. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74–7.54 (m, 46 H), 3.91 (t, J = 6.0 Hz, 4 H), 3.15 (s, 2 H), 2.30 (br. s, 4 H), 2.01 (br. s, 16 H), 1.18–1.01 (m, 52 H), 0.80–0.76 (m, 24 H), 0.63 (br. s, 16 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, with C–F decoupling): δ = 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 ppm. λ_{max} (abs.) ($CHCl_3$) = 385 nm; λ_{max} (photoluminescence) ($CHCl_3$) = 420, 443 nm. $C_{171}H_{164}F_{10}O_2$ (2441.12): calcd. C 84.13, H 6.77; found C 84.21, H 6.68.

Supporting Information (see footnote on the first page of this article): Synthetic details and characterization data for compounds **2**, **11**–**14**, **17** and **18**; X-ray crystallographic discussion of the structures of **4** and **11**. UV/Vis absorption and fluorescence spectra of **16**; details of the theoretical calculations.

Acknowledgments

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

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Received: June 1, 2007