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Convergent Synthesis of 10 nm Aryleneethynylene Molecular Wires by an Iterative Regioselective Deprotection/Sonogashira Coupling Protocol

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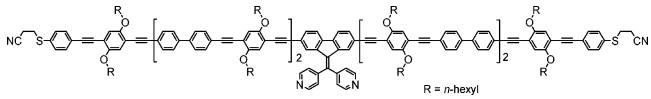

The synthesis of a new series of rigid-rod aryleneethynylene derivatives of up to ca. 10 nm molecular length (compounds **16** and **17**) is reported using iterative Pd-mediated Sonogashira coupling methodology combined with regioselective removal of the different protecting groups (namely, trimethylsilyl and 2-hydroxyprop-2-yl groups) from the terminal alkyne units. Additionally, the TMS−acetylene unit has been cleanly deprotected to afford a terminal alkyne in the presence of a cyanoethylsulfanyl group. Some of these molecular wires are functionalized with terminal protected thiophenol units for attachment to metal surfaces (compounds **16** and **17**). Internal electron-acceptor units have been incorporated into their structures, namely, 9-[di(4-pyridyl)methylene]fluorene (compound **17**) or fluorenone (compounds **19**−**22**). Optical absorption and photoluminescence spectra reveal a red shift in the value of λ_{max} with increasing molecular length, which approaches saturation at an effective conjugation length of ca. 15−20 π-units in the molecules, where each phenyl ring or a triple bond is counted as one π-unit.

Introduction

Functional π-conjugated systems which are available in incremental lengths from ca. 1 to 10 nm are of particular interest from experimental and theoretical viewpoints as advanced electronic and photonic materials.[1] For example, new fabrication methods and probes allow these "molecular wires" to be connected in a controlled manner into hybrid organic/semiconductor device architectures,[2] thereby paving the way for studies of single-molecule devices.[3] To enable the covalent anchoring of wire molecules to metal surfaces, thiols (or protected thiols) are the most widely used terminal groups.[4]

Ethynylated aromatic/heteroaromatic systems, with the generic structure (aryl−C≡C−)$_n$, are versatile, shape-persistent, rigid-rod molecules.[5] An attraction compared to that of their arylenevinylene counterparts is the lack of possible *Z*/*E* isomerism. Specific examples include: (a) 2,5-thienylethynylene oligomers with protected thiol termini;[6] (b) *p*-phenyleneethynylene oligomers with 5,5′-diethynyl-2,2′-bipyridine moieties in the backbone;[7] (c) 5,5′-diethynyl-2,2′-bipyridine-derived systems as metal-binding scaffolds;[8,9] (d) phenyleneethynylene pentamers[10] and oligo(9,9-dihexyl-2,7-fluorenylethynylenes)[11] as fluorophores for organic light-emitting devices; (e) co-oligomers possessing phenylene- and heterocyclic-enediyne units in the backbone which are fluorescent;[12] (f) a poly(*p*-phenyleneethynylene) derivative bearing macromolecular polyester

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substituents;[13] (g) oligomers containing 1,3,5-ethynylphenyl units; and[14,15] (h) fluorenone-containing aryleneethynylene oligomers which are electron dopable.[16]

We now report the synthesis using iterative Pd-mediated Sonogashira coupling methodology[17] of new, linearly conjugated aryleneethynylenes, notably the ca. 10 nm molecular wires, **16** and **17**. Our route differs from Tour's iterative approaches to oligo(aryleneethynylene) wires in the following ways. Iodinated thiophenes are the key building blocks for Tour's 2,5-thienylethynylene oligomers.[6] However, because most phenyl derivatives cannot be iodinated by a lithiation/iodination protocol, this route has limited applicability to systems other than thiophene. The second route of Tour's is rather tedious, involving consecutive hydrogenation, Friedel Craft's acylation, diazotization, and Sonogashira reactions, which limited the incorporation of functionality into the oligomer/polymer.[18] An aspect which is crucial to the success of our syntheses is the functionalization of terminal alkynes with different protecting groups (namely, trimethylsilyl and 2-hydroxy-2-propyl groups) and the regioselective removal of each one in the presence of the other. The methodology is versatile and has many attractive features, as illustrated by the end capping of the wires with cyanoethyl-protected thiophenol derivatives (compounds **16** and **17**) and the inclusion of redox-active moieties, either di(4-pyridyl)-methylene-9-fluorene (compound **17**) or fluorenone (compounds **19**−**22**), in the backbone.

Results and Discussion

Synthesis. Scheme 1 shows the protocol based on the selective removal[9,14] of the 2-hydroxy-2-propyl protecting group (as acetone) from the unsymmetrical intermediates **3**, **5**, **7**, **9**, and **11**, followed at each stage by a Sonogashira cross-coupling reaction. Starting reagents **1** and **2** were obtained from 1,4-dihexyloxy-2,5-diiodobenzene[19] and 4,4′-diiodobiphenyl, respectively, in 50% and 43% yields by reaction with one equivalent of 3-hydroxy-3-methylbutyne under standard Sonogashira conditions ($Pd[PPh_3]_2Cl_2$, CuI, piperidine). The hexyl substituents in **1** prevent solubility problems at later stages of the synthesis. Initial attempts at preparing **1** using triethylamine or triisopropylamine instead of the stronger base piperidine were unsuccessful: only starting materials were recovered. On the basis of this result, the conditions for the synthesis of **2** were formulated: for **2**, either neat piperidine or piperidine/THF can be used. Compound **1** was converted into the key reagent **3** by reaction with trimethylsilylacetylene ($Pd[PPh_3]_2Cl_2$, CuI, triethylamine) in 95% yield. Refluxing **3** in toluene in the presence of sodium hydroxide[20] removed the 2-hydroxy-2-propyl unit to give **4** in 77% yield. The subsequent reactions which linearly extended the aryleneethynylene system are iterative cross-coupling/deprotection procedures, leading to derivatives with alternating dihexyloxyphenyl and biphenyl units in the backbone. Thus, reaction of **4** with **2** gave **5**. The deprotection of **5** proceeded smoothly, as above, to afford **6** in 93% yield. Following these procedures, compounds **7**−**12** were obtained with good yields (69−99%) at each step. A benefit of the 2-hydroxy-2-propyl protecting group is that its high polarity facilitates the chromatographic separation of any unreacted starting material or byproducts which do not contain this unit.

Apart from **1** and **2** which require monocouplings to diiodo reagents, we tried to avoid using piperidine because of its toxicity and unpleasant smell. Triethylamine was, therefore, used in some steps. However, as the chain length increased, solubility in triethylamine was reduced, and THF was needed to dissolve the building blocks. In some cases, we had to use piperidine, such as in, for example, the cross-couplings of **10** and **14** with the corresponding iodides. The molar concentrations of the terminal alkynes varied for solubility reasons, although the reactions were very similar and iterative. The extended reaction times at later stages of the synthesis ensured the complete consumption of the precious alkynes and suppressed competing self-coupling reactions. Further optimization of the conditions might give a higher yield of **17**.

To obtain an oligomeric unit end capped with a protected thiol group, a Sonogashira reaction of **12** with 4-(2-cyanoethylsulfanyl)iodobenzene[16] gave **13** in 84% yield. In the next step, deprotection of the TMS−acetylene fragment of **13** with potassium carbonate gave **14**, without competing removal of the cyanoethyl group (which would be cleaved under more strongly basic conditions, typically sodium alkoxide or TBAF at room temperature).[16] In the final convergent step, a 2-fold Sonogashira reaction of **14** with the difunctional reagent **15** yielded **17** (18% yield) along with the self-coupled butadiyne derivative **16** (27% yield). The intramolecular S···S′ distances for **16** and **17** (MM^+ calculated values using Hyperchem 6.03) are 9.9 and 10.4 nm, respectively.

Scheme 2 illustrates how the selective removal of the TMS group in **3** has been used to furnish a different series of extended aryleneethynylene derivatives. Compound **18** was obtained in 96% yield by reaction of **3** with potassium carbonate in DCM/MeOH at room temperature. Two-fold cross-coupling of **18** with 2,7-diiodo-9-fluorenone gave the symmetrical product **19** in 92% yield, from which the terminal alkyne units were liberated upon treatment with sodium hydroxide in refluxing toluene (as in Scheme 1). Iterative reactions using reagent **2** gave compound **21**, and subsequent deprotection gave the π-extended system **22**. This family of molecular wires with terminal alkyne substituents could be suitable for the fabrication of devices using silicon electrodes.[21]

The X-ray crystal structure of **21** is shown in Figure 1. The asymmetric unit of **21**·$2CDCl_3$ contains one formula unit. The molecular rod of **21** has a slightly S-shaped conformation. The bonds C(23)−C(24), C(27)−C(30), C(37)−C(38), and C(76)−C(77) are inclined to the plane of the fluorenone moiety by 16.2, 13.1, 4.2, and 13.2°, respectively. The maximum length of the molecule (by the van der Waals shape) is ca. 56 Å. Two deuteriochloroform molecules (one of which is disordered by rotation around its 3-fold axis) are linked to **21** via C−D···O hydrogen bonds. Molecules of **21**, related by an inversion center,

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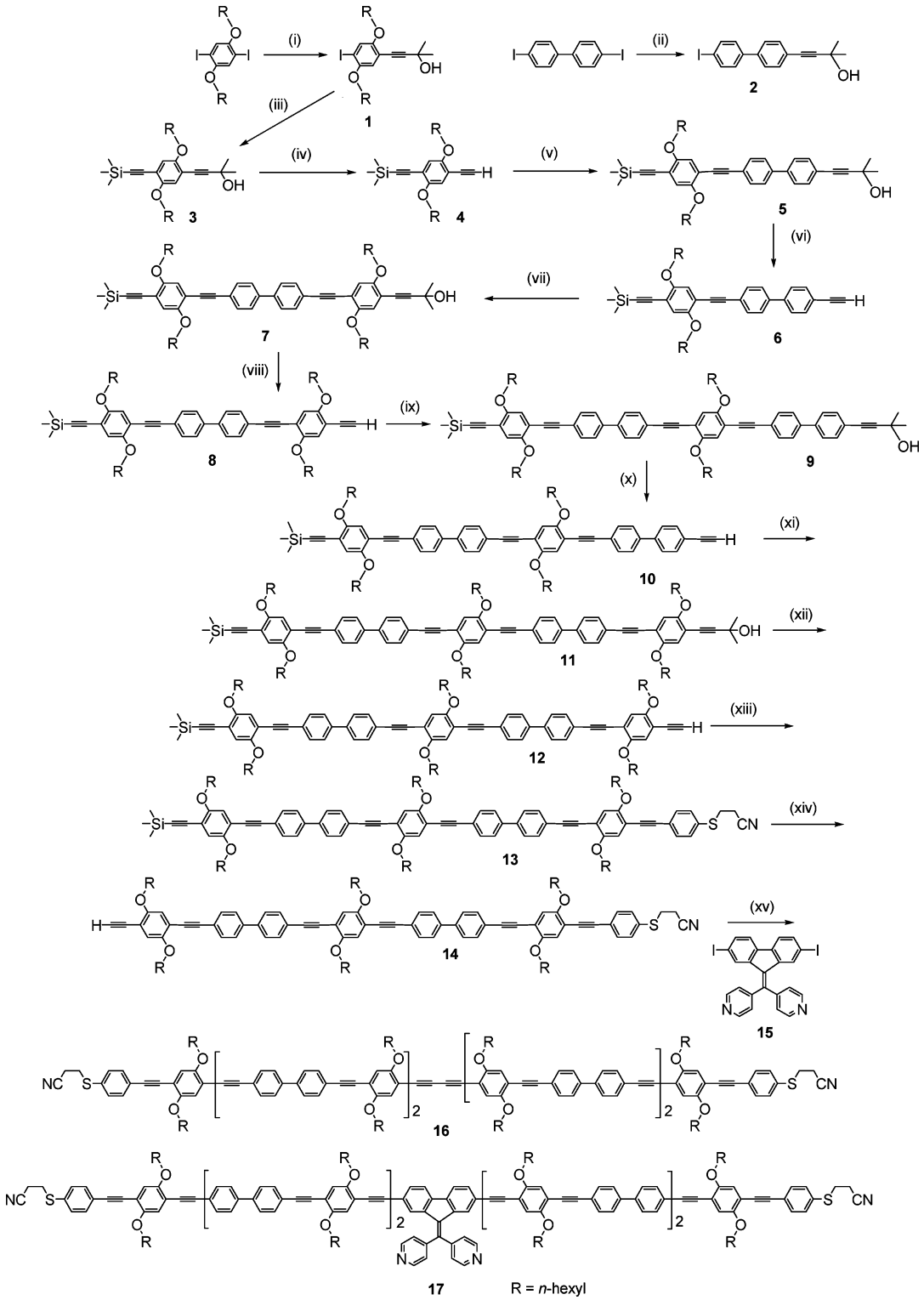
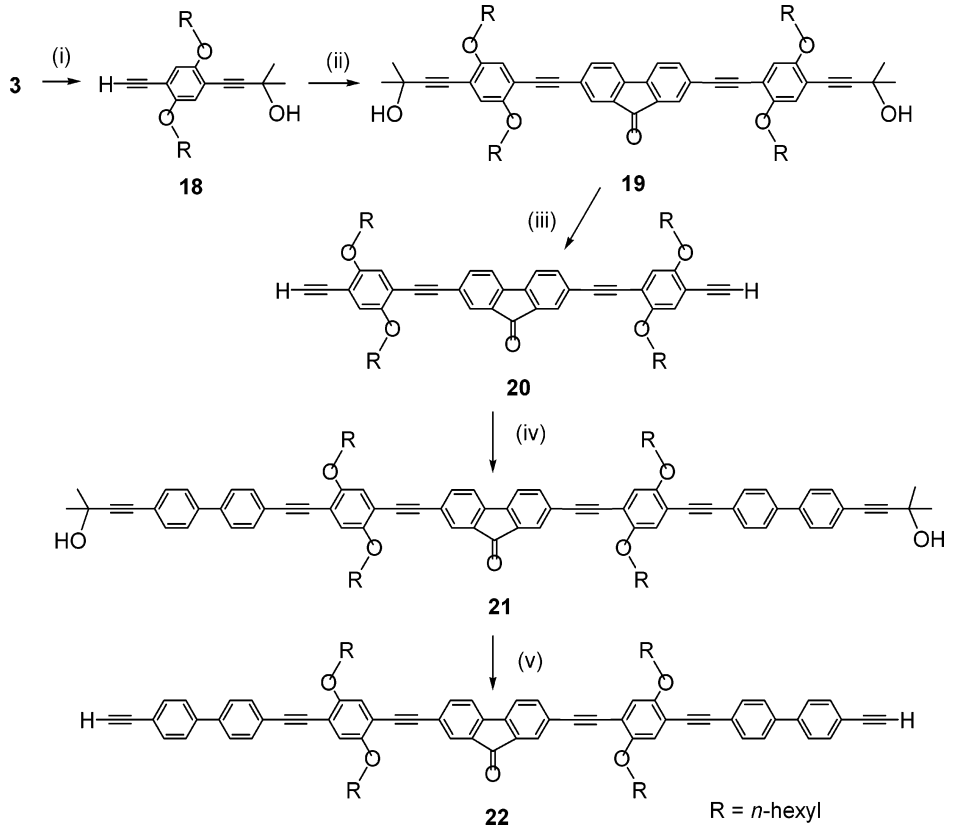
SCHEME 1[a]



[a] Reagents and conditions: (i) piperidine, $Pd[PPh_3]_2Cl_2$, CuI, HC≡$CCMe_2OH$ (1.1 equiv), 50 °C (50% yield); (ii) THF, piperidine, $Pd[PPh_3]_2Cl_2$, CuI, HC≡$CCMe_2OH$ (1.2 equiv), 50 °C (43% yield); (iii) THF, NEt_3, $Pd[PPh_3]_2Cl_2$, CuI, TMSC≡CH, 50 °C (95% yield); (iv) toluene, NaOH, reflux (77% yield); (v) **2**, NEt_3, $Pd[PPh_3]_2Cl_2$, CuI, 60 °C (86% yield); (vi) toluene, NaOH, reflux (93% yield); (vii) **1**, NEt_3, $Pd[PPh_3]_2Cl_2$, CuI, 60 °C (69% yield); (viii) toluene, NaOH, reflux (77% yield); (ix) **2**, NEt_3, $Pd[PPh_3]_2Cl_2$, CuI, 80 °C (85% yield); (x) toluene, NaOH, reflux (99% yield); (xi) **1**, THF, piperidine, $Pd[PPh_3]_2Cl_2$, CuI, 50 °C (80% yield); (xii) toluene, NaOH, reflux (97% yield); (xiii) 4-(2-cyanoethylsulfanyl)iodobenzene, NEt_3, $Pd[PPh_3]_2Cl_2$, CuI, THF, 50 °C (84% yield); (xiv) K_2CO_3, THF, MeOH, 20 °C (62% yield); (xv) **15** (0.5 equiv), THF, piperidine, $Pd[PPh_3]_2Cl_2$, CuI, 50 °C, **16** (27% yield) + **17** (18% yield).

form a dimer linked at both ends by intermolecular hydrogen bonds O(7)−H···O(4′) [O···O 2.775(2), O−H 0.82(3), H···O 1.96(3) Å, O−H···O angle 178(2)°] and its equivalent O(7′)−H···O(4), whereas the hydroxyl group O(4)−H is hydrogen

SCHEME 2[a]



[a] Reagents and conditions: (i) K_2CO_3, DCM, MeOH, 20 °C (96% yield); (ii) 2,7-diiodo-9-fluorenone (0.5 equiv), THF, NEt_3, $Pd[PPh_3]_2Cl_2$, CuI, 50 °C (92% yield); (iii) toluene, NaOH, reflux (96% yield); (iv) **2** (2.2 equiv), THF, NEt_3, $Pd[PPh_3]_2Cl_2$, CuI, 55 °C (64% yield); (v) toluene, NaOH, reflux (92% yield).

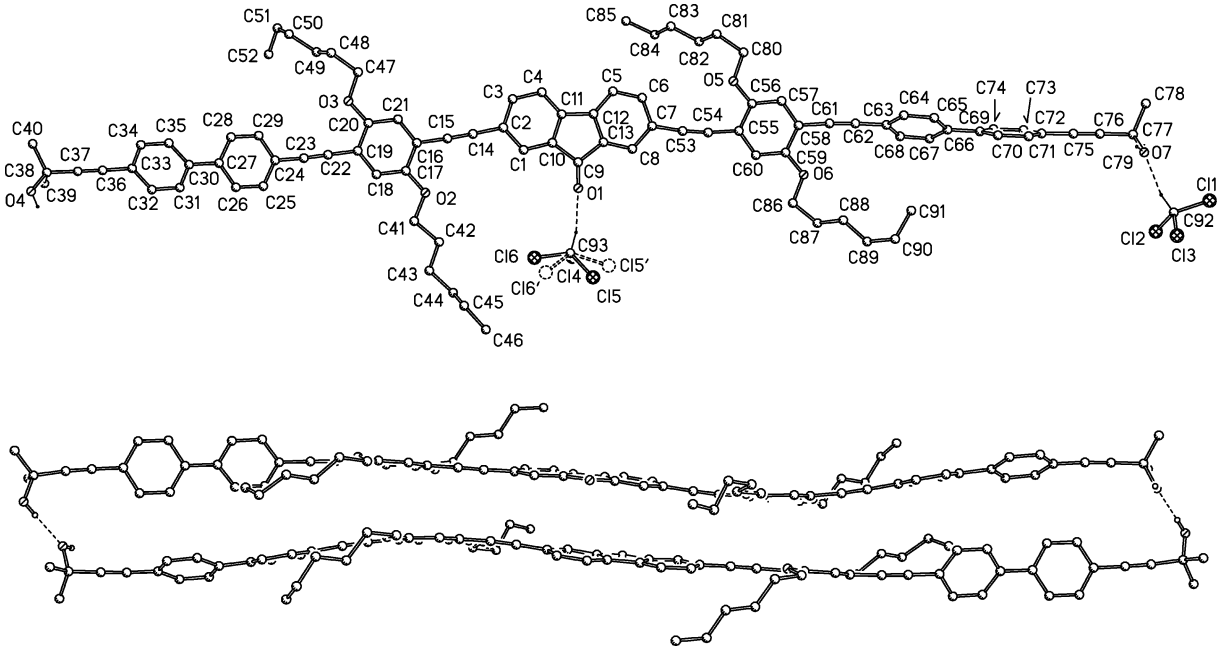


FIGURE 1. Molecular structure of **21**·2$CDCl_3$ showing hydrogen bonds (other H atoms are omitted) (top) and a dimer $(\mathbf{21})_2$ linked by O−H···O bonds (bottom).

bonded to the triple bond, C(61)≡C(62), of another dimer, related by the translation 2*a*−*c*.

Electrochemical Properties. The di(4-pyridyl)methylene-9-fluorene and fluorenone units impart electron-acceptor characteristics to molecules **17** and **19**−**22**. Cyclic voltammograms (CVs) of the two symmetrical fluorenone derivatives **20** and **22** are given Figure 2, where two reversible redox waves were observed when the reduction potentials were limited between

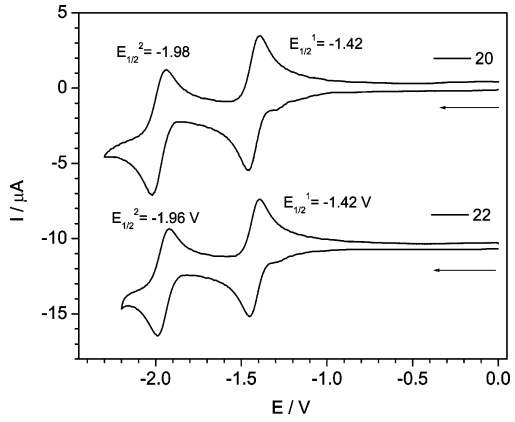


FIGURE 2. Cyclic voltammograms of **20** and **22** in THF vs Ag/Ag^+.

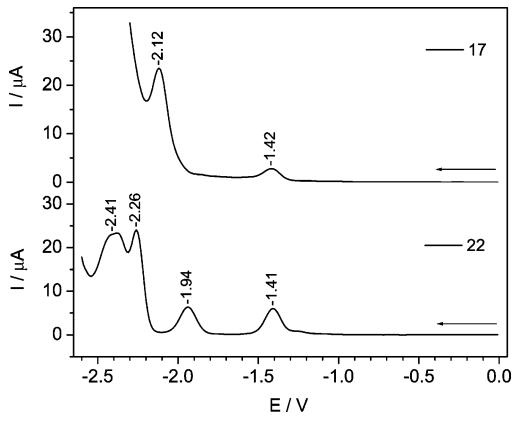


FIGURE 3. Differential pulse voltammograms of compounds **17** and **22** in THF vs Ag/Ag^+.

0 and −2.3 V. This type of twin-wave reversible redox chemistry is in agreement with that of 2,7-diethynyl-9-fluorenone, the smallest analogue of this class of compounds.[22] When the potential was scanned further down to −2.6 V, another pair of irreversible waves was observed for **22**. In the meantime, the first two redox waves also became irreversible, which is consistent with a chemical reaction occurring under the strongly reducing conditions. A differential pulse voltammogram (DPV) (Figure 3, lower) clearly shows the four reduction waves of compound **22**. No further reduction waves of **20** could be clearly observed on scanning to more negative potentials; presumably, these waves (if present) would appear at more cathodic potentials outside the solvent window because of the smaller number of triple bonds and the absence of the biphenylene units. For compound **17**, an irreversible fluorenone-type reduction (−1.42 V) due to the di(4-pyridyl)methylene-9-fluorene moiety was observed, followed by more intense irreversible reduction waves (−2.12 V) ascribed to the −C≡C− units (Figure 2, upper). For the butadiyne analogue **16**, only the irreversible alkyne-related reduction wave was observed at −2.20 V (data not shown).

Optical Properties. The availability of a series of arylene-ethynylene oligomers gives us the opportunity to assess the extent of electronic delocalization along the backbone by comparing their optical spectra. The solution UV−vis absorption and photoluminescence spectra of the terminal alkynes with different conjugation lengths, namely, compounds **4**, **6**, **8**, **10**, **12**, and **14**, were obtained and compared with those of molecules **16** and **17** (Table 1 and Figure 4). As the length of the molecules increased, both the wavelength and the intensity of the primary λ_{max} (the low-energy bands for **4** and **6**) increased. However, the λ_{max} red shifts were not linearly proportional to the increase in the molecular length. A plot of the red shift values against the number of the conjugated π-units (Figure 5) reveals that the red shift approaches saturation at an effective conjugation length of ca. 15−20 π-units in the molecules, where each phenyl ring or a triple bond is counted as one π-unit. (See the

TABLE 1. UV−Vis Absorption and Photoluminescence Data in Chloroform Solution

compound	absorption λ_{max}/nm (log ϵ)				PL λ_{max}/nm
4	267(4.36)	280(4.58)	340(4.05)		380
6		321(4.72)	368(4.63)		411
8	272(4.60)	325(4.85)	374(4.99)		415
10		329(4.85)	388(5.03)		431
12		330(4.91)	390(5.15)		433
14		330(4.95)	391(5.18)		434
16		330(5.25)	405(5.53)		451
17		332(5.29)	401(5.58)		451
20		305(4.86)	381(4.84)	452(3.92)	589
22	268(3.78)	325(4.99)	396(5.10)	465(4.23) sh	597

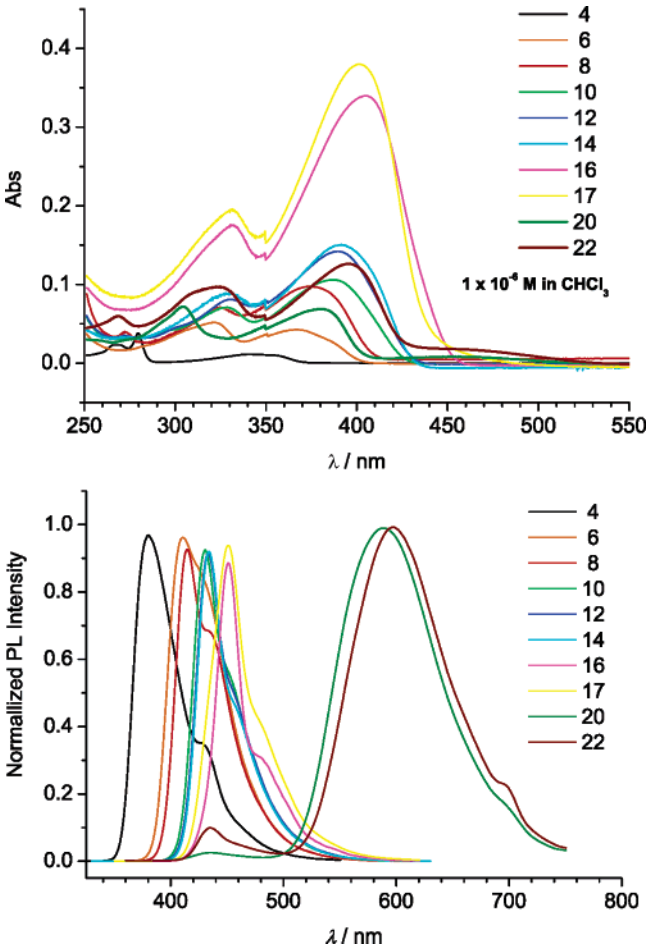


FIGURE 4. UV−vis absorption spectra (top) and photoluminescence spectra (bottom) of compounds **16** and **17** compared with those of other terminal ethynyl building blocks in chloroform solution. For PL measurements, the excitation wavelength λ_{exc} = 320 nm for all the compounds, except for **4** (λ_{exc} = 280 nm).

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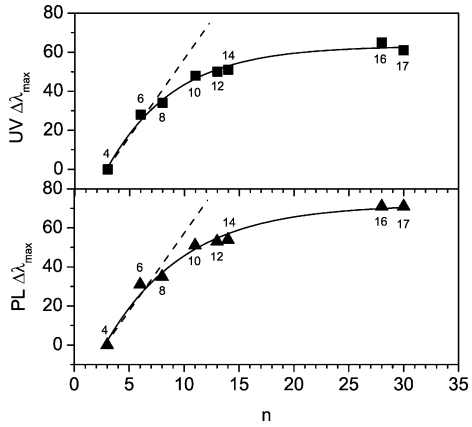

FIGURE 5. UV−vis and PL red shift values of compounds **4**, **6**, **8**, **10**, **12**, **14**, **16**, and **17** plotted against the number of conjugated π-units in the molecules. Each phenyl ring or a triple bond is counted as one π-unit.

Supporting Information for further discussion.) A similar convergence of λ_{max} with increasing conjugation length has been observed in previous phenyleneethynylene oligomers[10,23] and oligo(9,9-dihexyl-2,7-fluorenylethynylenes).[11] The broad, low-intensity emission from **20** and **22** is typical of that of fluorenone derivatives.[24]

Conclusions

We have presented the synthesis of a range of new highly functionalized aryleneethynylene reagents and building blocks up to 10 nm in length which are amenable to full spectroscopic and analytical characterization. These molecular wires are endowed with terminal functionality suitable for further reactions or for attachment to metal surfaces (compounds **16** and **17**). Moreover, internal electron-acceptor units have been incorporated into their structures (compounds **16** and **19**−**22**). A key aspect of the synthetic strategy is the judicious choice of terminal alkyne protecting groups (namely, trimethylsilyl and 2-hydroxy-2-propyl groups) and their regioselective removal. We have also established that the TMS−acetylene unit can be cleanly deprotected to afford a terminal alkyne in the presence of a cyanoethylsulfanyl group. These oligomers show well-defined optical absorption and emission properties, and electrochemical studies have established that compounds **16** and **19**−**22** are n dopable. These reagents and procedures should be valuable and highly versatile in molecular electronics applications related to supramolecular assembly and nanocircuits.

Experimental Section

General. Melting points were determined in open-end capillaries, and the temperatures were ramped at 5 °C min^{-1} near the melting temperatures, without calibration. Solution ^{1}H NMR and ^{13}C NMR spectra were recorded on a 300, 400, or 500 MHz spectrometer operating at (^{1}H) 299.91, 400.13, and 499.99 and (^{13}C) 75.42, 100.62, and 124.99 MHz, respectively. Chemical shifts are reported in ppm downfield of TMS. MALDI-TOF spectra were obtained using a dithranol matrix operating in reflector mode. Cyclic voltammograms (CVs) and differential pulse voltammograms (DPVs) were recorded in THF−TBA·PF_6 (0.1 M) solution, and the potentials quoted were referenced to the Ag/Ag^+ nonaqueous reference electrode, which contained a solution of 0.01 M $AgNO_3$ and 0.1 M $TBAPF_6$ in acetonitrile. Pt disk (Φ = 1.6 mm) and Pt wire were used as the working and counter electrodes, respectively. For CVs, the potentials were scanned at 100 mV/sec, and for DPVs, the potential was scanned at the rate of 50 mV/sec (pulse amplitude 50 mV; pulse width 50 ms). THF was purified with a commercial solvent purification system and then bubbled with argon through the solutions for 5 min prior to CV and DPV measurements. Under these conditions, the background from 0 to −2.50 V was transparent to reductions and ferrocene was oxidized at a half-wave potential of 0.22 V.

All the palladium-catalyzed coupling reactions were carried out under argon atmosphere. THF, used for those reactions, and toluene, used for the deprotection reactions, were purified using a solvent purification system. Triethylamine (TEA) was purchased from a commercial supplier and then refluxed and distilled over sodium in argon atmosphere. $Pd[PPh_3]_2Cl_2$ was prepared in our laboratory using a reported method.[25] Piperidine was purchased from a commercial supplier, dried over sodium hydroxide pellets for a week, and then distilled under argon. Other chemicals and routine solvents were used as purchased, without further purification.

X-ray Crystallography. The X-ray diffraction experiment was carried out on a three-circle diffractometer with a 6 K CCD area detector, using graphite-monochromated Mo K_α radiation ($\bar{\lambda}$ = 0.71073 Å) and an open-flow N_2 cryostat. The structure was solved by direct methods and refined by full-matrix least squares against F^2 of all reflections, using SHELXTL software (version 6.12, Bruker AXS, Madison WI, 2001). Crystal data: $C_{91}H_{92}O_7$_(**21**)·$2CDCl_3$; M = 1538.39; T = 120 K; triclinic; space group $P\bar{1}$ (No. 2); a = 12.985(1), b = 14.504(1), c = 23.877(2) Å; α = 91.64(1), β = 100.62(1), γ = 111.35(1)°; V = 4094.1(6) Å^3; Z = 2; D_c = 1.248 g cm^{-3}; μ = 0.27 mm^{-1}; 46 302 reflns with $2\theta \leq 55°$, 18 788 unique; R_{int} = 0.058, final R = 0.049 [11 599 data with $F^2 \geq 2\sigma(F^2)$], w$R(F^2)$ = 0.133 (all data). CCDC-280163.

1,4-Dihexyloxy-2-(3-hydroxy-3-methylbutynyl)-5-iodobenzene (1). 1,4-Dihexyloxy-2,5-diiodobenzene[26] (26.5 g, 50 mmol) was dissolved in freshly distilled piperidine (250 mL). $Pd[PPh_3]_2Cl_2$ (1.8 g) and CuI (0.6 g) were added to the solution followed by the addition of 3-hydroxy-3-methylbutyne (4.4 g, 52.3 mmol) in one portion. The mixture was stirred at room temperature for 1 h and then at 50 °C for an additional 1 h. The solvent was removed by vacuum evaporation. Diethyl ether (200 mL) was added to the brown residue followed by a suction filtration through a Celite pad. The filtrate was concentrated and then chromatographed (silica gel, DCM−diethyl ether, 99:1 v/v) to afford **1** (12.2 g, 50%) as a pale-yellow oil which solidified upon storage: mp 48.9−50.7 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (s, 1H), 6.80 (s, 1H), 3.93 (t, J = 6.3 Hz, 4H), 2.23 (s, 1H), 1.78 (m, 4H), 1.62 (s, 6H), 1.49 (m, 4H), 1.34 (m, 8H), 0.91 (m, 6H); ^{13}C NMR (75 Hz, $CDCl_3$) δ 154.3, 151.7, 123.6, 116.1, 112.9, 98.5, 87.4, 78.1, 70.0, 69.7, 65.7, 31.5, 31.44, 31.36, 29.2, 29.1, 25.7, 25.6, 22.59, 22.55, 14.0; MS (ES+) (m/z) 509.2 (M^+ + 23, 100%). Anal. Calcd for $C_{23}H_{35}IO_3$: C, 56.79; H, 7.25. Found: C, 56.90; H, 7.35.

4-(3-Hydroxy-3-methylbutynyl)-4′-iodobiphenyl (2). By analogy to the synthesis of **1**, 4,4′-diiodobiphenyl (8.12 g, 20 mmol) reacted with 3-hydroxy-3-methylbutyne (2.0 g, 23.7 mmol) in a mixture of THF (80 mL) and piperidine (20 mL), in the presence of $Pd[PPh_3]_2Cl_2$ (0.5 g) and CuI (0.25 g). The mixture was stirred at 50 °C for 2 h to yield an orange suspension. The crude product was chromatographed (silica gel, DCM−diethyl ether mixture, 95:5 v/v) and then crystallized from an ethanol−water mixture to afford **2** as pale-yellow needles (3.08 g, 43%, mp 179.6−180.1 °C): ^{1}H

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NMR (300 MHz, $CDCl_3$) δ 7.76 (d, J = 8.4 Hz, 2H), 7.49 (m, 4H), 7.31 (d, J = 8.4 Hz, 2H), 2.14 (s, 1H), 1.65 (s, 1H); ^{13}C NMR (75 Hz, $CDCl_3$) δ 139.72, 139.70, 137.9, 132.1, 128.8, 126.6, 122.1, 94.7, 93.4, 81.8, 65.6, 31.5. Anal. Calcd for $C_{17}H_{15}IO$: C, 56.37; H, 4.17. Found: C, 56.45; H, 4.17.

1,4-Dihexyloxy-2-(3-hydroxy-3-methylbutynyl)-5-(trimethylsilylethynyl)benzene (3). A mixture of compound **1** (4.86 g, 10 mmol), $Pd[PPh_3]_2Cl_2$ (0.35 g), and CuI (0.12 g) in THF (150 mL) and triethylamine (20 mL) was degassed with argon followed by the addition of trimethylsilylacetylene (3 mL, 21 mmol). The flask was sealed with a glass stopper, reacted at room temperature for 1.5 h, and then at 50 °C for an additional 1.5 h to afford a brown suspension. The mixture was vacuum evaporated to dryness, and the solid residue was boiled with hexane (100 mL). The solution was suction filtered through a Celite pad, and the filtrate was concentrated in vacuo. The oily residue was column chromatographed (silica gel, DCM) to afford **3** as a pale-yellow oil which turned into an amorphous solid upon standing (4.32 g, 95%, mp 67.1−69.5 °C): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (s, 1H), 6.84 (s, 1H), 3.93 (t, J = 6.4 Hz, 4H), 2.23 (s, 1H), 1.77 (m, 4H), 1.60 (s, 6H), 1.53 (m, 4H), 1.33 (m, 8H), 0.89 (m, 6H), 0.25 (s, 9H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 154.1, 153.5, 117.2, 117.1, 113.7, 113.6, 101.0, 99.8, 99.2, 78.4, 69.4, 65.7, 31.6, 31.5, 31.4, 29.3, 25.7, 22.6, 14.01, 13.99, −0.1; MS (ES+) (m/z) 935.8 ($2M^+$ + 23, 100%). Anal. Calcd for $C_{17}H_{15}IO$: C, 73.63; H, 9.71. Found: C, 73.60; H, 9.75.

1-Ethynyl-2,5-dihexyloxy-4-(trimethylsilylethynyl)benzene (4). Compound **3** (4.60 g, 10.07 mmol) was dissolved in dry toluene (100 mL). NaOH powder (2.0 g) was added, and the mixture was stirred and refluxed under argon for 1 h (oil bath at 138 °C). The resultant light-brown mixture was cooled and suction filtered through a Celite pad. The filtrate was vacuum evaporated to dryness, and the yellow solid was purified by column chromatography (silica gel, petroleum ether−DCM mixture, 2:1 v/v, bp 40−60 °C) to afford **4** as a yellow solid (3.05 g, 77%, mp 61.1−62.5 °C): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.92 (s, 2H), 3.96 (t, J = 6.6 Hz, 2H), 3.94 (t, J = 6.6 Hz, 2H), 3.32 (s, 1H), 1.79 (m, 4H), 1.49 (s, 4H), 1.34 (m, 8H), 0.90 (m, 6H), 0.25 (s, 9H); ^{13}C NMR (75 Hz, $CDCl_3$) δ 153.94, 153.92, 117.6, 117.1, 114.3, 112.7, 100.8, 100.2, 82.3, 79.9, 69.5, 69.4, 31.6, 31.5, 29.2, 29.1, 25.7, 25.5, 22.61, 22.56, 14.1, 14.0, −0.1; MS (EI) (m/z) 398 (M^+, 100%). Anal. Calcd for $C_{17}H_{15}IO$: C, 75.32; H, 9.61. Found: C, 75.60; H, 9.70.

Compound 5. Compounds **2** (3.00 g, 8.28 mmol) and **4** (3.10 g, 7.78 mmol) were dissolved in triethylamine (120 mL) with stirring and heating at 50 °C. $Pd[PPh_3]_2Cl_2$ (0.30 g) and CuI (0.10 g) were added to the solution, which was stirred at 50 °C for 0.5 h and then at 60 °C for an additional 3 h to yield a dark-yellow suspension. The mixture was evaporated in vacuo, and diethyl ether (150 mL) was added. The mixture was suction filtered through Celite, and the filtrate was dried of solvent. The residual yellow oil was column chromatographed (silica gel, DCM) to obtain **5** as a yellow solid (4.23 g, 86%, mp 97.9−99.9 °C): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (m, 8H), 6.98 (s, 1H), 6.96 (s, 1H), 4.01 (t, J = 5.1 Hz, 2H), 3.99 (t, J = 5.1 Hz, 2H), 2.08 (s, 1H), 1.82 (m, 4H), 1.64 (s, 6H), 1.55 (m, 4H), 1.36 (m, 8H), 0.91 (m, 6H), 0.27 (s, 9H); ^{13}C NMR (75 Hz, $CDCl_3$) δ 154.1, 153.4, 140.0, 139.9, 132.1, 132.0, 126.8, 126.7, 122.7, 122.0, 117.2, 116.7, 114.1, 113.7, 101.1, 100.1, 94.7, 86.9, 81.9, 69.5, 69.4, 65.7, 31.60, 31.58, 31.48, 29.3, 25.7, 22.6, 14.1, 14.0, −0.1; MS (EI) (m/z) 632 (M^+, 100%), 614 (M^+ − 18, 21%). Anal. Calcd for $C_{42}H_{52}O_3Si$: C, 79.70; H, 8.28. Found: C, 79.54; H, 8.25.

Compound 6. By analogy to the synthesis of **4**, compound **5** (3.43 g), toluene 80 (mL), and NaOH (2.0 g) were refluxed for 1 h to afford **6** as off-white/pale-yellow crystals (2.88 g, 93%, mp 87.7−88.4 °C) after column chromatography (silica gel, chloroform−hexane mixture, 3:2 v/v) and recrystallization from chloroform−ethanol: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.6 (m, 8H), 6.98 (s, 1H), 6.96 (s, 1H), 4.01 (t, J = 6.4 Hz, 2H), 3.99 (t, J = 6.4 Hz, 2H), 3.15 (s, 1H), 1.82 (m, 4H), 1.55 (m, 4H), 1.35 (m, 8H), 0.90 (m, 6H), 0.27 (s, 9H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 154.2, 153.6, 140.7, 139.9, 132.6, 132.1, 126.9, 126.8, 122.9, 121.4, 117.4, 116.9, 114.2, 113.9, 101.2, 100.1, 94.6, 87.0, 83.4, 78.0, 69.6, 69.6, 31.61, 31.59, 29.3, 25.73, 25.70, 22.6, 14.1, 14.0, −0.05; MS (EI) (m/z) 574 (M^+, 100%). Anal. Calcd for $C_{39}H_{46}O_2Si$: C, 81.48; H, 8.07. Found: C, 81.49; H, 8.07.

Compound 7. To the stirred mixture of **1** (2.92 g, 6 mmol), $Pd[PPh_3]_2Cl_2$ (0.18 g), CuI (0.06 g), and TEA (80 mL) was added a solution of **6** (2.88 g, 5 mmol) in TEA (50 mL) dropwise within 1.5 h at 60 °C. Heating and stirring were maintained for an additional 2 h to yield a yellow suspension. The mixture was dried of solvent by vacuum evaporation, and the residual dark-yellow solid was dissolved in ethanol (100 mL) with boiling. The solid which precipitated from the cooled solution was column chromatographed (silica gel, DCM). Subsequent recrystallization from ethanol yielded **7** as a pale-yellow solid (3.23 g, 69%, mp 141.7−142.3 °C): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (s, 8H), 6.99 (s, 1H), 6.98 (s, 1H), 6.96 (s, 1H), 6.92 (s, 1H), 4.00 (m, 8H), 2.09 (s, 1H), 1.82 (m, 8H), 1.64 (s, 6H), 1.54 (m, 8H), 1.36 (m, 16H), 0.90 (m, 12H), 0.27 (s, 9H); ^{13}C NMR (75 Hz, $CDCl_3$) δ 154.1, 153.6, 153.53, 153.46, 140.0, 132.0, 126.8, 122.7, 117.2, 117.0, 116.74, 116.69, 114.1, 113.8, 113.7, 113.3, 101.1, 100.1, 99.2, 94.7, 94.6, 86.91, 86.86, 78.5, 69.6, 69.5, 69.44, 69.40, 65.8, 31.61, 31.58, 31.42, 29.3, 25.7, 22.6, 14.07, 14.05, −0.06; MS (EI) (m/z) 932 (M^+, 0.4%), 660 (100%). Anal. Calcd for $C_{62}H_{80}O_5Si$: C, 79.78; H, 8.64. Found: C, 79.99; H, 8.64.

Compound 8. By analogy to the synthesis of **6**, compound **7** (3.37 g), toluene (70 mL), and NaOH (1.75 g) were refluxed for 1 h to yield compound **8** as a pale-yellow solid (2.47 g, 77%, mp 54.6−56.6 °C) after column chromatography (silica gel, chloroform−hexane, 3:2 v/v) and recrystallization from ethanol: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (s, 4H), 7.60 (s, 4H), 7.01 (s, 1H), 7.00 (s, 1H), 6.98 (s, 1H), 6.96 (s, 1H), 4.01 (m, 8H), 3.35 (s, 1H), 1.84 (m, 8H), 1.54 (m, 8H), 1.36 (m, 16H), 0.90 (m, 12H), 0.27 (s, 9H); ^{13}C NMR (75 Hz, $CDCl_3$) δ 154.1, 153.5, 153.4, 140.05, 139.96, 132.06, 132.05, 126.8, 122.7, 122.6, 117.7, 117.2, 116.8, 114.5, 114.1, 113.7, 112.6, 101.1, 100.1, 94.8, 94.7, 86.9, 86.7, 82.3, 80.0, 69.6, 69.5, 69.4, 31.61, 31.58, 31.51, 29.3, 29.1, 25.7, 25.6, 22.63, 22.58, 14.07, 14.04, 14.02, −0.1; MS (ES+) (m/z) 874.5 (M^+ − 14). Anal. Calcd for $C_{60}H_{76}O_4Si$: C, 81.03; H, 8.61. Found: C, 80.89; H, 8.53.

Compound 9. By analogy to the synthesis of **5**, compound **8** (2.47 g, 2.78 mmol), compound **2** (1.26 g, 3.48 mmol, 1.25 equiv), TEA (100 mL), $Pd[PPh_3]_2Cl_2$ (100 mg), and CuI (35 mg), at 80 °C for 3 h gave a thick yellow suspension. Ethanol (100 mL) was added, and a bright yellow solid was obtained by suction filtration. The solid was column chromatographed (silica gel, DCM) and then crystallized from chloroform−ethanol to afford **9** as an off-white solid (2.61 g, 85%, mp 187.1−187.8 °C): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (m, 12H), 7.57 (d, J = 8.2 Hz, 2H), 7.50 (d, J = 8.4 Hz, 2H), 7.05 (s, 2H), 6.99 (s, 1H), 6.96 (s, 1H), 3.98−4.08 (m, 8H), 2.08 (s, 1H), 1.85 (m, 8H), 1.65 (s, 6H), 1.56 (m, 8H), 1.37 (m, 16H), 0.91 (m, 12H), 0.27 (s, 9H); ^{13}C NMR (75 Hz, $CDCl_3$) δ 154.1, 153.6, 153.5, 140.02, 139.97, 139.9, 132.1, 132.0, 126.8, 126.7, 122.7, 122.0, 117.2, 116.8, 116.7, 114.1, 114.0, 113.7, 101.1, 100.1, 94.78, 94.74, 94.70, 94.66, 87.0, 86.9, 81.9, 69.6, 69.5, 69.4, 65.7, 31.6, 31.5, 29.3, 25.74, 25.71, 25.69, 22.6, 14.07, 14.05, −0.1; HR MALDI-TOF (m/z) (M^+) $C_{76}H_{88}O_5Si$ requires 1108.63955, found 1108.63971. Anal. Calcd for $C_{76}H_{88}O_5Si$: C, 82.27; H, 7.99. Found: C, 82.08; H, 7.93.

Compound 10. By analogy to the synthesis of **8**, compound **9** (2.61 g, 2.35 mmol), toluene (30 mL), and NaOH (1.20 g) were refluxed for 1 h to give a product which was purified by column chromatography (silica gel, DCM−hexane, 1:1 v/v) and crystallization from chloroform−ethanol to afford **10** as an off-white solid (2.46 g, 99%, mp 181.3−182.1 °C): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62−7.58 (m, 16H), 7.05 (s, 2H), 6.99 (s, 1H), 6.96 (s, 1H), 4.06 (t, J = 6.5 Hz, 4H), 4.01 (m, 4H), 3.15 (s, 1H), 1.85 (m, 8H), 1.56 (m, 8H), 1.37 (m, 16H), 0.91 (m, 12H), 0.27 (s, 9H); ^{13}C NMR

(125 Hz, $CDCl_3$) δ 154.2, 153.7, 153.5, 140.6, 140.0, 139.9, 132.6, 132.1, 126.88, 126.84, 126.82, 122.88, 122.74, 122.72, 121.3, 69.62, 69.56, 69.46, 31.61, 31.59, 29.32, 29.29, 25.75, 25.72, 25.70, 22.65, 22.64, 14.08, 14.06, −0.1; MALDI-TOF (*m*/*z*) 1050.6 (M^+). Anal. Calcd for $C_{73}H_{82}O_4Si$: C, 83.38; H, 7.86. Found: C, 83.62; H, 7.93.

Compound 11. Compound **1** (0.58 g, 1.19 mmol), $Pd[PPh_3]_2Cl_2$ (30 mg), and CuI (10 mg) were dissolved in freshly distilled piperidine (100 mL). A solution of compound **10** (0.63 g, 0.6 mmol) in THF (10 mL) was added, and the mixture was stirred at 50 °C for 36 h to obtain a clear yellow solution. Solvents were removed by vacuum evaporation, and ethanol (50 mL) was added to the residue. A yellow solid was collected by suction filtration, which after column chromatography (silica gel, DCM) and crystallization from chloroform−ethanol afforded **11** as a yellow solid (0.68 g, 80%, mp 179.0−180.1 °C): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (s, 8H), 7.61 (s, 8H), 7.06 (s, 2H), 7.00 (s, 1H), 6.99 (s, 1H), 6.97 (s, 1H), 6.93 (s, 1H), 4.07−3.98 (m, 12H), 2.19 (s, br, 1H), 1.91−1.79 (m, 12H), 1.65 (s, 6H), 1.60−1.50 (m, 12H), 1.37 (m, 24H), 0.92 (m, 18H), 0.28 (s, 9H); MALDI-TOF (*m*/*z*) 1409.9 (M^+). Anal. Calcd for $C_{96}H_{116}O_7Si$: C, 81.77; H, 8.29. Found: C, 81.86; H, 8.32.

Compound 12. By analogy to the synthesis of **10**, compound **11** (0.77 g, 0.543 mmol), toluene (40 mL), and NaOH (0.5 g) were refluxed for 1.5 h to give a product which was purified by column chromatography (silica gel, chloroform−hexane 85:15 v/v) and crystallization from chloroform−ethanol to afford **12** as a pale-yellow solid (0.71 g, 97%, mp 140.3−141.0 °C): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.632 (s, 8H), 7.628 (s, 4H), 7.622 (s, 4H), 7.07 (s, 2H), 7.03 (s, 1H), 7.00 (s, 2H), 6.98 (s, 1H), 4.08−4.00 (m, 12H), 3.36 (s, 1H), 1.85 (m, 12H), 1.56 (m, 12H), 1.36 (m, 24H), 0.92 (m, 18H), 0.28 (s, 9H); MALDI-TOF (*m*/*z*) 1351.7 (M^+). Anal. Calcd for $C_{93}H_{110}O_6Si$: C, 82.62; H, 8.20. Found: C, 82.80; H, 8.25.

Compound 13. To the stirred mixture of 4-(2-cyanoethylsulfanyl)iodobenzene[14] (0.40 g, 1.38 mmol, 4 equiv), $Pd[PPh_3]_2Cl_2$ (25 mg), CuI (10 mg), and TEA (20 mL) was added a solution of compound **12** (0.47 g, 0.349 mmol) in THF (15 mL) at 50 °C. The mixture was heated at 50 °C with stirring for 60 h to obtain a pale-yellow suspension. Vacuum evaporation gave a residual solid. Column chromatography (silica gel, chloroform then DCM) yielded compound **13** as a yellow solid (0.44 g, 84%, mp 184.5−485.6 °C): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 14H), 7.61 (s, 2H), 7.50 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 7.05 (s, 2H), 7.04 (s, 1H), 7.02 (s, 1H), 6.99 (s, 1H), 6.96 (s, 1H), 4.08−3.98 (s, 12H), 3.17 (t, J = 7.2 Hz, 2H), 2.63 (t, J = 7.2 Hz, 2H), 1.86 (m, 12H), 1.57 (m, 12H), 1.37 (m, 24H), 0.91 (m, 18H), 0.27 (s, 9H); MALDI-TOF (*m*/*z*) 1511.7 (M^+). Anal. Calcd for $C_{102}H_{117}NO_6SSi$: C, 80.96; H, 7.79; N, 0.93. Found: C, 81.22; H, 7.89; N, 0.80.

Compound 14. To a solution of compound **13** (0.28 g, 0.186 mmol) in THF (15 mL) was added K_2CO_3 powder (0.3 g), followed by methanol (6 mL) dropwise. The resultant yellow suspension was stirred at room temperature for 1 h. Solvents were removed in vacuo and yellow solid residue was chromatographed (silica gel, chloroform then chloroform−DCM, 2:1 v/v) to afford **14** as a yellow solid (0.17 g, 62%, mp 167.3−168.2 °C): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (s, 16H), 7.50 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 7.06 (s, 2H), 7.05 (s, 1H), 7.03 (s, 2H), 7.00 (s, 1H), 4.08−3.99 (m, 12H), 3.37 (s, 1H), 3.15 (t, J = 7.2 Hz, 2H), 2.62 (t, J = 7.2 Hz, 2H), 1.86 (m, 12H), 1.56 (m, 12H), 1.38 (m, 24H), 0.92 (m, 18H); MALDI-TOF (*m*/*z*) 1440.8 (M^+). Anal. Calcd for $C_{99}H_{109}NO_6S$: C, 82.52; H, 7.62; N, 0.97. Found: C, 82.02; H, 7.53; N, 0.83.

2,7-Diiodo-9-[di(4-pyridyl)methylene]fluorene 15. To the solution of 2,7-diiodofluorene[27] (4.18 g, 10 mmol) in dry THF (50 mL) was added potassium *tert*-butoxide (1.0 M solution in 2-methyl-propanol) (10.5 mL) at room temperature, and the mixture was stirred for 20 min. Solid di(4-pyridyl)ketone[28] (1.93 g, 10.5 mmol) was added in one portion to the resultant dark-red solution followed by stirring at room temperature for 0.5 h and then at 50 °C for 1 h. Acetic acid (1 mL) was added to the dark-green suspension, and the mixture was stirred for an additional 1 h. The yellow suspension was cooled and then suction filtered to afford a yellow solid which was crystallized from pyridine−ethanol to afford **15** as yellow crystals (3.66 g, 63%, mp 316.2−317.8 °C): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.92 (d, J_{13} = 1.2 Hz, 2H), 7.28 (m, 4H), 7.38 (d, J_{12} = 8.1 Hz, 2H), 7.61 (dd, J_{12} = 8.1 Hz, J_{13} = 1.2 Hz, 2H), 8.76 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 92.4, 121.2, 123.7, 134.1, 134.2, 137.8, 138.6, 139.4, 140.2, 148.2, 150.9; MS (ES+) (*m*/*z*) 585 (M^+ + 1, 100%). Anal. Calcd for $C_{24}H_{14}I_2N_2$: C, 49.34; H, 2.42; N, 4.80. Found: C, 49.40; H, 2.39; N, 4.82.

Compounds 16 and 17. By analogy to the synthesis of **13**, the solution of compound **14** (53 mg, 0.037 mmol) in THF was added to the stirred solution of **15** (10 mg, 0.017 mmol), $Pd[PPh_3]_2Cl_2$ (2 mg), CuI (1 mg), and piperidine (10 mL) at 50 °C. The reaction mixture was stirred for 50 h at 50 °C followed by a vacuum evaporation. Ethanol (50 mL) was added to the dark-yellow solid residue, and the mixture was boiled for 5 min and then cooled to room temperature, followed by a suction filtration to give a yellow solid. Preparative thin-layer chromatography (silica gel, chloroform−diethyl ether, 4:1 v/v) gave compound **16** as a yellow solid (14 mg, 27%, mp 202.0−205.0 °C, R_f = 0.84) followed by **17** as an orange-yellow solid (11 mg, 18%, mp 195.3−197 °C, R_f = 0.42).

16: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.79 (s, 2H), 7.67 (d, J = 7.5 Hz, 1H), 7.62 (s, 16H), 7.53 (d, J = 8 Hz, 1H), 7.50 (d, J = 8.0 Hz, 2H), 7.42 (s, 2H), 7.37 (d, J = 8.5 Hz), 7.05 (s, 2H), 7.04 (s, 1H), 7.02 (s, 1H), 7.01 (s, 1H), 6.93 (s, 1H), 6.84 (s, 1H), 4.06 (m, 12H), 3.18 (t, J = 7.5 Hz, 2H), 2.64 (t, J = 7.3 Hz, 2H), 1.87 (m, 12H), 1.57 (m, 12H), 1.38 (m, 24H), 0.91 (m, 18H); MALDI-TOF (*m*/*z*) 3210.1 (M^+). Anal. Calcd for $C_{222}H_{230}N_4O_{12}S_2$: C, 83.06; H, 7.22; N, 1.75. Found: C, 82.14; H, 7.24; N, 1.50.

17: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (s, 16H), 7.50 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 7.05 (s, 2H), 7.04 (s, 1H), 7.02 (s, 2H), 7.01 (s, 1H), 4.05 (m, 12H), 3.17 (t, J = 7.1 Hz, 2H), 2.63 (t, J = 7.2 Hz, 2H), 1.86 (m, 12H), 1.56 (m, 12H), 1.38 (m, 24H), 0.91 (m, 18H); MALDI-TOF (*m*/*z*) 2878.4 (M^+). Anal. Calcd for $C_{198}H_{216}N_2O_{12}S_2$: C, 82.57; H, 7.56; N, 0.97. Found: C, 82.08; H, 7.53; N, 0.94.

2,5-Dihexyloxy-4-(3-hydroxy-3-methylbutynyl)phenylacetylene (18). Compound **3** (4.32 g, 9.46 mmol) was dissolved in a mixture of DCM and methanol (50 mL, 1:1 v/v). Powdered K_2CO_3 (2.0 g) was added, and the mixture was stirred at room temperature for 3 h. The solid was removed by suction filtration through Celite, and the filtrate was evaporated to dryness. The crystalline yellow solid was chromatographed on a silica gel column (eluent DCM−diethyl ether, 98:2 v/v) to yield **18** as pale-yellow crystals (3.49 g, 96%, mp 42.0−43.8 °C): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (s, 1H), 6.87 (s, 1H), 3.95 (m, 4H), 3.32 (s, 1H), 2.19 (s, 1H), 1.78 (m, 4H), 1.62 (s, 6H), 1.47 (m, 4H), 1.33 (m, 8H), 0.90 (m, 6H); ^{13}C NMR (100 Hz, $CDCl_3$) δ 154.1, 153.5, 117.7, 117.1, 114.0, 112.6, 99.3, 82.1, 79.9, 78.3, 69.6, 69.5, 65.7, 31.6, 31.5, 31.4, 29.3, 29.1, 25.7, 25.6, 22.6, 22.5, 14.00, 13.97; MS (ES+) *m*/*z* 407.3 (M^+ + 23, 100%). Anal. Calcd for $C_{25}H_{36}O_3$: C, 78.08; H, 9.44. Found: C, 78.28; H, 9.53.

Compound 19. The mixture of **18** (1.27 g, 3.29 mmol), 2,7-diiodo-9-fluorenone[29] (0.70 g, 1.62 mmol), $Pd[PPh_3]_2Cl_2$ (120 mg), CuI (40 mg), THF (25 mL), and TEA (25 mL) was stirred at room temperature for 3 h and then at 50 °C for 4.5 h to afford an orange suspension. The liquids were removed by vacuum evaporation, and

(27) Okumoto, K.; Shirota, Y. *Chem. Mater*. **2003**, *15*, 699.

(28) Di(4-pyridyl)ketone was synthesized in 60% yield using a modification of the reported method: Minn, F. L.; Trichilo, C. L.; Hurt, C. R.; Filipescu, N. *J. Am. Chem. Soc*. **1970**, *92*, 3600.

(29) Merkushev, E. B.; Simakhina, N. D.; Koveshnikova, G. M. *Synthesis* **1980**, 486.

diethyl ether (100 mL) was added to the solid residue. The mixture was sonicated, followed by suction filtration through Celite. The filtrate was evaporated to dryness, and the residual solid was column chromatographed (silica gel, DCM−diethyl ether, 9:1 v/v) to afford **19** as an orange solid (1.41 g, 92%, mp 129.8−131.1 °C): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, J_{13} = 1.5 Hz, 1H), 7.60 (dd, J_{12} = 7.8 Hz, J_{13} = 1.5 Hz, 1H), 7.47 (d, J_{12} = 7.8 Hz, 1H), 6.92 (s, 1H), 6.88 (s, 1H), 3.97 (m, 4H), 2.39 (s, 1H), 1.81 (m, 4H), 1.63 (s, 6H), 1.53 (m, 4H), 1.35 (m, 8H), 0.90 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.1, 153.6, 153.5, 143.1, 137.7, 134.4, 127.2, 124.6, 120.4, 116.8, 116.6, 113.7, 113.2, 99.5, 93.8, 88.1, 78.4, 69.5, 69.4, 65.7, 31.6, 31.5, 31.4, 29.25, 29.23, 25.71, 25.68, 22.62, 14.0. Anal. Calcd for $C_{63}H_{76}O_7$: C, 80.05; H, 8.10. Found: C, 79.79; H, 7.98.

Compound 20. By analogy to the synthesis of **6**, a mixture of **18** (1.00 g, 1.06 mmol), toluene (40 mL), and NaOH (0.2 g) was refluxed for 50 min to yield compound **20** as a pale-yellow solid (0.84 g, 96%, mp 100.6−101.6 °C), which was purified by column chromatography (silica gel, DCM−petroleum ether, bp 40−60 °C, 2:1 v/v) and recrystallization from ethanol: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J_{13} = 1.2 Hz, 1H), 7.64 (dd, J_{12} = 6.0 Hz, J_{13} = 1.2 Hz, 1H), 7.49 (d, J_{12} = 6.0 Hz, 1H), 6.983 (s, 1H), 6.975 (s, 1H), 4.00 (m, 4H), 3.36 (s, 1H), 1.85 (m, 4H), 1.52 (m, 4H), 1.36 (m, 8H), 0.91 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.1, 154.1, 153.6, 143.2, 137.7, 134.5, 127.3, 124.6, 120.5, 117.7, 116.9, 114.0, 113.1, 94.0, 87.9, 82.5, 79.9, 69.7, 69.6, 31.55, 31.51, 29.2, 29.1, 25.7, 25.6, 22.62, 22.56, 13.99, 13.98; HR MALDI-TOF MS (*m*/*z*) $C_{57}H_{64}O_5$ requires 828.47483, found 828.47394. Anal. Calcd for $C_{57}H_{64}O_5$: C, 82.57; H, 7.78. Found: C, 82.80; H, 7.83.

Compound 21. By analogy to the synthesis of compound **5**, a mixture of compound **2** (0.40 g, 1.01 mmol), compound **19** (0.42 g, 0.5 mmol), $Pd[PPh_3]_2Cl_2$ (40 mg), CuI (15 mg), THF (5 mL), and TEA (25 mL) was stirred at room temperature for 2 h and at 55 °C for 3 h. Purification by column chromatography (silica gel, DCM−diethyl ether, 9:1 v/v) and recrystallization from chloroform−ethanol gave **21** as orange crystals (0.42 g, 64%, mp 207.5−208.6 °C, the sample for elemental analysis was dried under high vacuum at 1.5×10^{-2} mbar for 24 h). A single crystal for X-ray analysis was grown by slow evaporation of its deuterated chloroform−ethanol solution: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.63−7.44 (m, 10H), 7.01 (s, 1H), 6.99 (s, 1H), 4.03 (t, J = 6.5 Hz, 4H), 2.23 (s, 1H), 1.87 (m, 4H), 1.64 (s, 6H), 1.57 (m, 4H), 1.38 (m, 8H), 0.93 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 153.8, 153.7, 143.2, 140.01, 139.96, 137.7, 134.5, 132.13, 132.06, 127.3, 126.8, 126.7, 124.7, 122.7, 122.0, 120.5, 116.9, 116.8, 114.4, 113.5, 95.0, 94.7, 94.1, 88.3, 87.0, 81.9, 69.7, 69.6, 65.7, 31.61, 31.58, 31.49, 29.33, 29.30, 25.76, 25.74, 22.65, 22.63, 14.03; MALDI-TOF MS *m*/*z* 1297.7 (M^+). Anal. Calcd for $C_{91}H_{92}O_7$: C, 84.22; H, 7.15. Found: C, 84.26; H, 7.03.

Compound 22. By analogy to the synthesis of **20**, compound **21** (0.45 g, 0.35 mmol), toluene (40 mL), and NaOH (0.2 g) were refluxed for 5 h to yield **22** as orange crystals (0.38 g, 92%, mp 166.8−168.2 °C) after column chromatography (silica gel, chloroform−petroleum ether bp 40−60 °C, 4:1 v/v) and recrystallization from chloroform−ethanol: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.63 (d, J = 7.5 Hz, 1H), 7.59 (m, 8H), 7.48 (d, J = 7.8 Hz, 1H), 7.02 (s, 1H), 7.01 (s, 1H), 4.04 (t, J = 6.3 Hz, 4H), 3.15 (s, 1H), 1.87 (m, 4H), 1.57 (m, 4H), 1.38 (m, 8H), 0.93 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.1, 153.69, 153.59, 143.1, 140.56, 139.8, 137.7, 134.4, 132.6, 132.1, 127.2, 126.84, 126.79, 124.6, 122.8, 121.3, 120.5, 116.8, 116.7, 114.3, 113.4, 94.9, 94.1, 88.2, 87.0, 83.4, 78.1, 69.6, 69.5, 31.61, 31.58, 29.30, 29.27, 25.74, 22.7, 22.6, 14.1; MALDI-TOF MS *m*/*z* 1180.7 (M^+). Anal. Calcd for $C_{85}H_{80}O_5$: C, 86.40; H, 6.82. Found: C, 86.36; H, 6.78.

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Supporting Information Available: X-ray crystallographic file for **21** in CIF format and a discussion of the optical data presented in Table 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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