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Tetrahedron
Tetrahedron 63 (2007) 7120–7132

An effective, orthogonal deprotection strategy for differentially functionalized, linear and Y-shaped oligo phenylene ethynylenes

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Received 17 January 2007; revised 24 April 2007; accepted 1 May 2007
Available online 6 May 2007

Abstract—Several methodologies for the selective deprotection acetylenes have been reported previously. However, as is shown here, they are often not reliable or convenient. Here, an approach is reported that is efficient and general. Use of this approach to synthesize several two- and three-armed oligo(phenylene ethynylene) molecules with differentiated end groups is reported. In addition, preliminary characterization of the fluorescent properties of some of these molecules and their ability to form self-assembled monolayers (SAMs) is reported.

1. Introduction

Oligo- and polymeric phenylene ethynylene molecules (OPEs) have been widely used as molecular wires to study charge transport in molecular electronics testbeds,[1] as rigid scaffolds in the construction of nanometric architectures,[2–4] as dendrimers,[5,6] as foldamers,[7,8] and as sensors.[9–12] Thus, as we considered new methodologies for nanometric construction, we were attracted to the body of work describing their preparation. However, as we sought to adapt this methodology, we encountered several questions and issues. In particular, we required a methodology for differential deprotection of acetylene groups on each end (or ends) of an OPE molecular structure. Although, as will be described below, there are several published methodologies that nominally could serve these requirements, these were frequently not acceptable for the synthesis of the molecules described here.

In this paper, we compare methodologies for orthogonal deprotection of OPE structures and illustrate a route to differentially protected OPE precursors that is most efficient. This methodology is then used to synthesize series of bi-functional and tri-functional OPEs. Furthermore, it is shown that this approach tolerates the installation of thioacetate and isonitrile groups at the ends of the OPEs. Thioacetate and isonitrile are the functional groups that offer the best chance to selectively bind to gold and platinum-based nanostructures, respectively, as shown originally by Wrighton and Whitesides[13,14] and more recently by us.[15] Selective binding is a requirement for the construction of differentiated, nanometer-scale architectures composed of particles and is the long-term goal of our work.

2. Results and discussion

2.1. Linear OPE structures

2.1.1. Differentially functionalized, three-ringed OPE. Our first goal was to prepare a differentially functionalized, three-ringed OPE containing thioacetate and isonitrile end groups. The synthesis of this molecule (**10**) is shown in Scheme 1. Compound **2** was prepared as described in the literature with a yield similar to those previously reported.[9,10,16] Palladium catalyzed coupling afforded the previously unreported compound **3**.

Differential deprotection of two ends of an OPE-type structure has received substantial attention.[17–20] Compound **4** has been reported previously several times in the literature, usually by differentially deprotecting a trimethylsilyl acetylene in the presence of the TIPS-acetylene,[2–4,21–25] although other methods have been employed.[26,27] In our hands, however, purification of the intermediates produced by this route was difficult whereas the purification of compound **3** was much more straightforward. The ynol portion of this molecule can be selectively deprotected in the presence of the TIPS-acetylene.[28] The resulting, mono-deprotected molecule **4** could then be reacted with the known *N*-(4-iodophenyl)-formamide (**5**)[29,30] to give **6**. Use of tetrabutyl ammonium fluoride followed by palladium/copper catalyzed coupling with known *p*-thioacetyl phenyl iodide (**8**) provided molecule **9**. This molecule could then be dehydrated to

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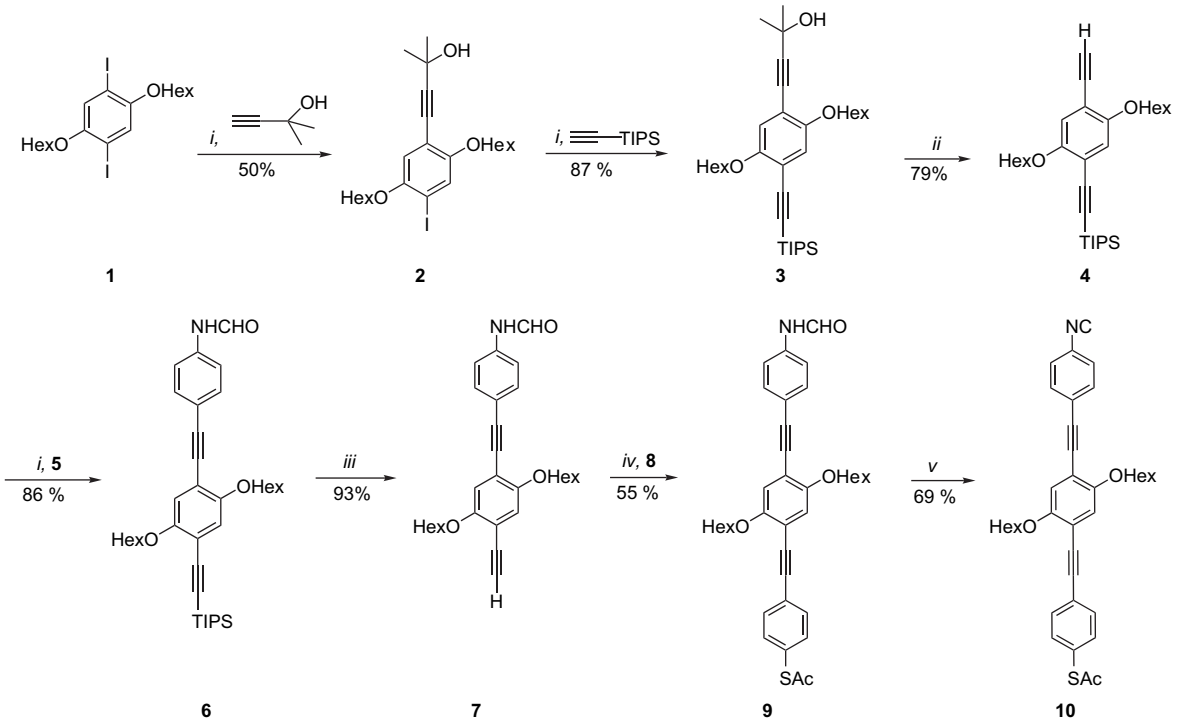
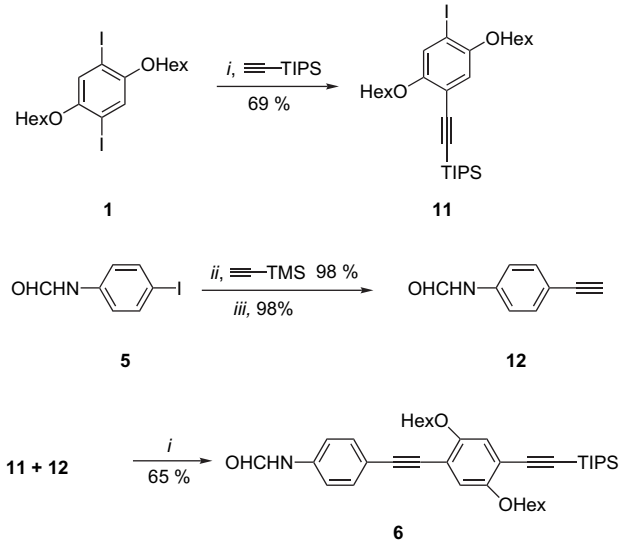
doi:10.1016/j.tet.2007.05.006



Scheme 1. Synthesis of **10**. OHex=O$(CH_2)_5CH_3$; conditions: (i) $Pd_2(dba)_3 \cdot CHCl_3$, PPh_3, CuI, Et_3N, 75 °C; (ii) NaOH, toluene, reflux; (iii) TBAF, THF, rt; (iv) same as (i) except rt; (v) triphosgene, benzyl triethylammonium chloride, Et_3N, CH_2Cl_2.

provide the three-ringed compound with thioacetate and isonitrile groups (**10**).

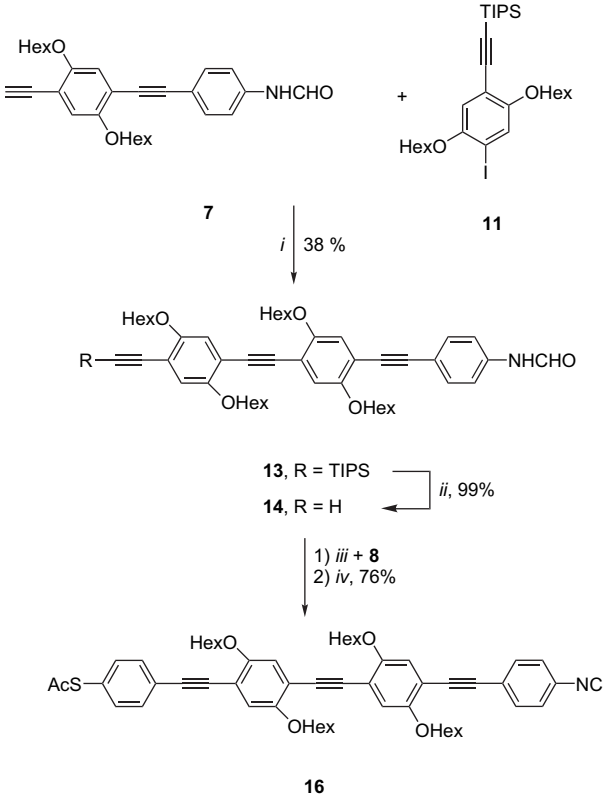
An alternate route to intermediate **6** is shown in Scheme 2. It employs molecule **12**, which we obtained in similar yield to that previously reported.[30] This molecule was then coupled to **11**. Both routes require four steps. However, this alternate route provides **6** in an overall yield of 43% while the route shown in Scheme 1 provides **6** in an overall yield of 20%.



Scheme 2. Alternate route to **6**. Conditions: (i) $Pd_2(dba)_3 \cdot CHCl_3$, PPh_3, CuI, Et_3N, 65–70 °C; (ii) $Pd_2(dba)_3 \cdot CHCl_3$, PPh_3, CuI, $(i\text{-Pr})_2EtN$, THF (4:3), rt; (iii) K_2CO_3, CH_3OH/CH_2Cl_2 (1:1), rt.

2.1.2. Differentially functionalized, four-ringed OPE.

The analogous oligomer containing four rings was synthesized as shown in Scheme 3. Reaction of aryl iodide **11** with terminal acetylene **7** yielded compound **13** albeit in poor yield. Deprotection, palladium catalyzed coupling,



Scheme 3. Synthesis of **16**. Conditions: (i) $Pd_2(dba)_3 \cdot CHCl_3$, PPh_3, CuI, Et_3N, 65–70 °C; (ii) TBAF, THF, rt; (iii) $Pd_2(dba)_3 \cdot CHCl_3$, PPh_3, CuI, $(i\text{-Pr})_2EtN$, THF (4:3), rt; (iv) triphosgene, benzyl triethylammonium chloride, Et_3N, CH_2Cl_2.

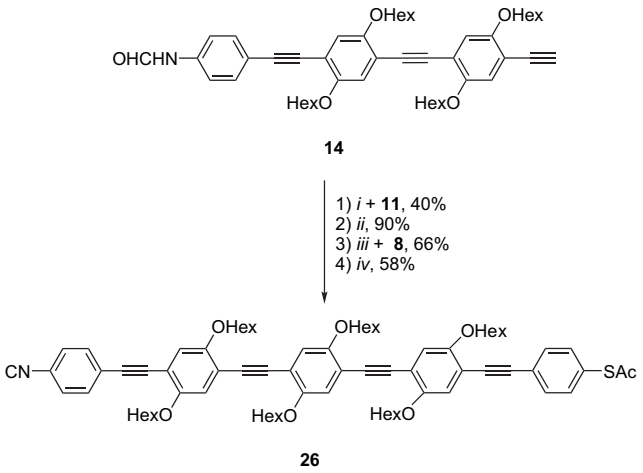
and dehydration of the formamide group provided the four-ringed oligomer with thioacetate and isonitrile groups (**16**).

2.1.3. Differentially functionalized, five-ringed OPE. The synthesis of five-ringed oligomers are shown in Schemes 4 and 5. For the preparation of molecule **23** (Scheme 4), the key intermediate, molecule **18** was synthesized in excellent yield and facilitated differential deprotection of each end and facile purification. The formamide end group was introduced first, followed by extension using intermediate **11**, introduction of the aryl thioacetate group, and finally, dehydration to form **23**.

For the synthesis of **26** in which all three of the central rings were substituted with bis-hexyloxy groups, a simple, stepwise extension sequence was employed. As TIPS deprotection was most efficient, sequential TIPS deprotections followed by reaction with **11** or **8** provided the desired compound in seven steps from molecule **7** (Schemes 2, 3 and 5).

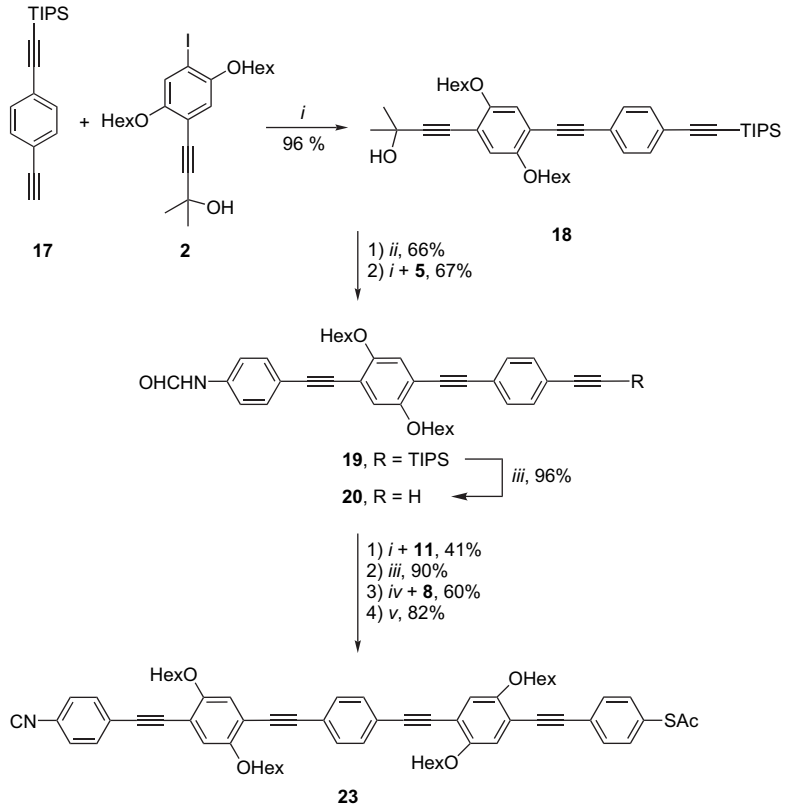
2.2. Homofunctionalized, three-armed oligo phenylene ethynylenes

Prior to implementing a scheme for the orthogonal synthesis of three-armed oligo phenylene ethynylenes with differentiated end groups, we re-investigated the synthesis of the tris-thioacetyl functionalized molecule (Scheme 6, compound **29**). This molecule[31–33] and molecules similar to this in structure[34] have been prepared previously. However, the route shown in Scheme 6 requires fewer synthetic steps and provides an overall higher yield.

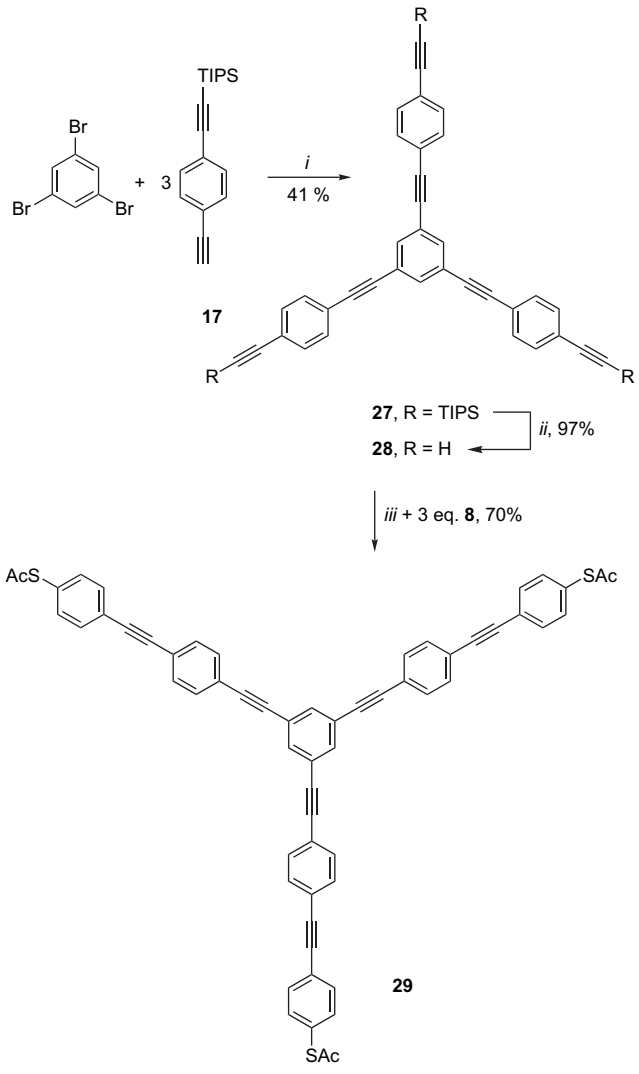


Scheme 5. Synthesis of **26**. Conditions: (i) $Pd_2(dba)_3 \cdot CHCl_3$, PPh_3, CuI, Et_3N, 75 °C; (ii) TBAF, THF; (iii) same as (i) except Et_3N/THF (2:1) as solvent and rt; (iv) triphosgene, benzyl triethylammonium chloride, Et_3N, CH_2Cl_2.

The yield of the tris-coupling of **17** to 1,3,5-tribromobenzene was modest. This yield undoubtedly could be improved through the use of 1,3,5-triiodobenzene in this sequence. However, we chose not to pursue this route as 1,3,5-triiodobenzene is significantly more expensive when purchased commercially and, if one assesses the added effort to prepare the compound, the overall yield for the sequence is likely to be little improved. Another notable feature of this sequence is the illustration that compound **28** (the intermediate as the result of step ii in the sequence) could be smoothly converted



Scheme 4. Synthesis of **23**. Conditions: (i) $Pd_2(dba)_3 \cdot CHCl_3$, PPh_3, CuI, Et_3N, 75 °C; (ii) NaOH, toluene, reflux; (iii) TBAF, THF; (iv) same as (i) except Et_3N/THF (2:1) as solvent and rt; (v) triphosgene, benzyl triethylammonium chloride, Et_3N, CH_2Cl_2.



Scheme 6. Synthesis of **29**. Conditions: (i) $Pd_2(dba)_3 \cdot CHCl_3$, PPh_3, CuI, Et_3N, 65–70 °C; (ii) TBAF, THF; (iii) same as (i) except rt.

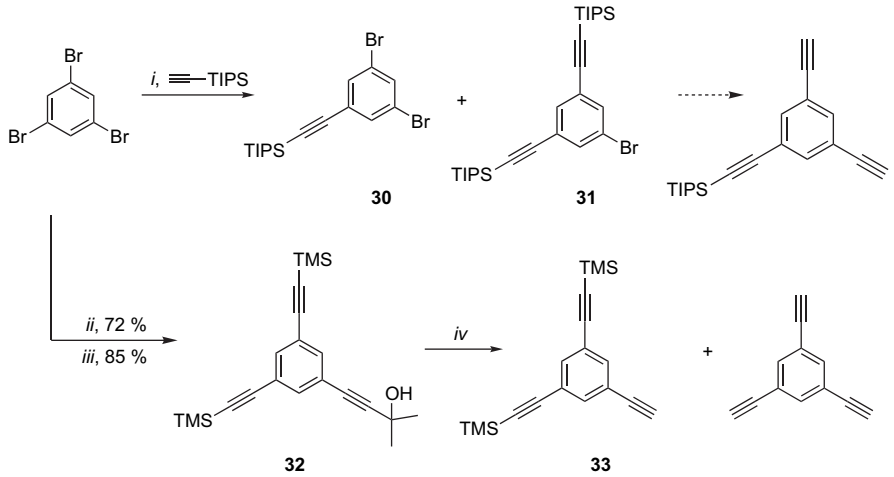
to **29** in good yield. Although concerns have been expressed previously in the literature[35] that oxidative coupling or polymerization of monofunctionalized acetylenes could limit their use, we did not observe any problem of this type using this route.

2.3. Heterofunctionalized, three-armed oligo phenylene ethynylenes

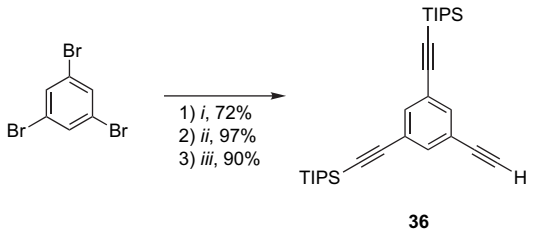
We then sought to prepare three-armed oligo phenylene ethynylenes such as molecule **29** but with differentiated end groups. Such molecules are, to our knowledge, unreported in the literature. The idea of differentiating phenyl acetylenes around a 1,3,5-trihalobenzene core, however, does have some precedent in the literature. Indeed, our first attempt at this chemistry involved the selective deprotection of TMS-acetylene groups in the presence of a TIPS-acetylene. The synthesis and selective deprotection of TMS-acetylene groups in the presence of TIPS-acetylene had been reported previously by Onitsuka et al.[36] Following this protocol (Scheme 7), we attempted to prepare the mono-TIPS-protected triethynyl benzene via molecule **30**.[37] However, in our hands, we could not purify molecule **30** away from **31** that was statistically formed. The problem of separation of aromatic halides and their corresponding TMS-[38] or TIPS-protected[39] ethynylated compounds has been mentioned previously by others.[38] This purification problem became exacerbated in subsequent steps, and ultimately this method was abandoned. Given this problem, we turned to reports by Rodriguez et al.[35] and Wang et al.[19] in which formal removal of acetone as a protecting group was accomplished in the presence of TMS-protected acetylenes (e.g., conversion of **32** to **33**). This route also was problematic in our hands, resulting in substantial amounts of 1,3,5-triethynyl benzene as a side product, presumably due to removal of the TMS groups competitively with the acetone.

We devised a modified approach to circumvent these problems (Scheme 8). Employing TIPS-protected acetylenes rather than TMS-protected acetylenes allowed the selective removal of acetone from the intermediate to give **36**. The route to molecule **36** provided high yields and no difficulties in purification.

The intermediate molecule **36** could then be used to prepare AAB-type three-armed phenyl ethynylenes. The example

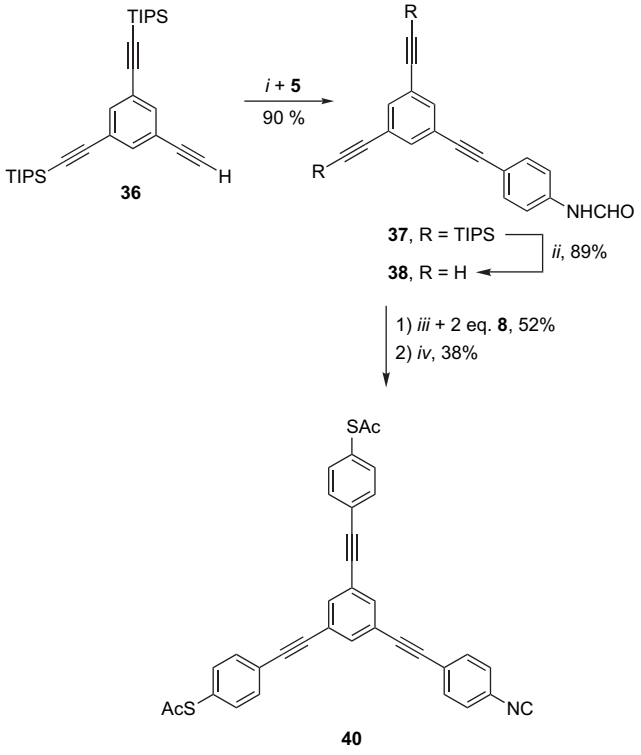


Scheme 7. Ineffective methods for orthogonal deprotection to form **33**. Conditions: (i) $Pd_2(dba)_3 \cdot CHCl_3$, PPh_3, CuI, Et_3N, 65–70 °C; (ii) $HC{\equiv}CC(CH_3)_2OH$, $Pd_2(dba)_3 \cdot CHCl_3$, PPh_3, CuI, pyridine, Et_3N, 100 °C; (iii) 2 equiv $HC{\equiv}CTMS$, $Pd(PPh_3)_2Cl_2$, Et_3N, 60 °C; (iv) NaOH, toluene, reflux.



Scheme 8. Synthesis of **36**. Conditions: (i) $Pd_2(dba)_3 \cdot CHCl_3$, PPh_3, CuI, Et_3N, pyridine, $HC{\equiv}CC(OH)(CH_3)_2$, 100 °C; (ii) same as (i) except with 2 equiv TIPS-acetylene and no pyridine; (iii) NaOH, toluene, reflux.

presented (Scheme 9) illustrates the method used to arrive at the three-armed phenyl ethynylene in which two arms terminate with thioacetate group and the third arm terminates with an isonitrile group (**40**). Although the palladium coupling chemistry proceeded in only modest yield, there were no problems with purification and isolation of the desired compounds.



Scheme 9. Synthesis of **40**. Conditions (i) $Pd_2(dba)_3 \cdot CHCl_3$, PPh_3, CuI, Et_3N, 65–70 °C; (ii) TBAF, THF; (iii) same as (i) except rt; (iv) triphosgene, benzyl triethylammonium chloride, Et_3N, CH_2Cl_2.

In preparation for the synthesis of larger, three-armed molecules, molecule **43** was prepared as shown in Scheme 10. This molecule can serve as a starting material for similar subsequent chemistry. Specifically, the orthogonal deprotection of the dimethyl-ynol and TIPS-acetylene groups should afford molecules with differentiated end groups as shown above.

2.4. Fluorescence properties

Table 1 contains the absorbance maximum, fluorescence maximum, and quantum yield (relative to quinine bisulfate) for several of the differentially functionalized, linear compounds. The UV absorption and emission maxima increase with molecular length. The quantum yield doubles between the three-ring compound **10** and the four-ring compound **16** but then is similar to the five-ring compounds **23** and **26**.

2.5. Self-assembled monolayers

Self-assembled monolayers (SAMs) composed of compounds **10** and **23** were prepared on both gold and platinum surfaces. Film thickness as measured by ellipsometry (Table 2) agreed well with calculated molecular lengths indicating reasonably high coverage SAMs were formed. X-ray photoelectron spectroscopy also indicated the presence of these molecules on both surfaces. Although it was hoped that differences in the S2p and N1s binding energies would indicate a preference for nitrile versus thiol binding when SAMs on gold and platinum were compared, little difference was observed. Indeed, in prior work, little difference in the binding energy between free and bound sulfur or nitrogen in SAMs was observed by XPS. Moreover, S2p binding energies reported in the literature for thiol-bound SAMs vary several electron volts for different molecules. Rather, the dipole moment of the molecule and, more specifically, the charge distribution across it appear to be more significant to the XPS binding energy.[40] Further work to determine the relative affinity of the thiol versus the isonitrile on gold compared to platinum is in progress and will be reported separately.

3. Conclusions

It has been determined that the selective deprotection of a dimethyl-ynol in the presence of TIPS-acetylene groups is the most efficient route to prepare two- and three-armed, oligo(phenylene ethynylene) molecules with differentiated end groups. This strategy could be employed for the relatively efficient synthesis of several new compounds.

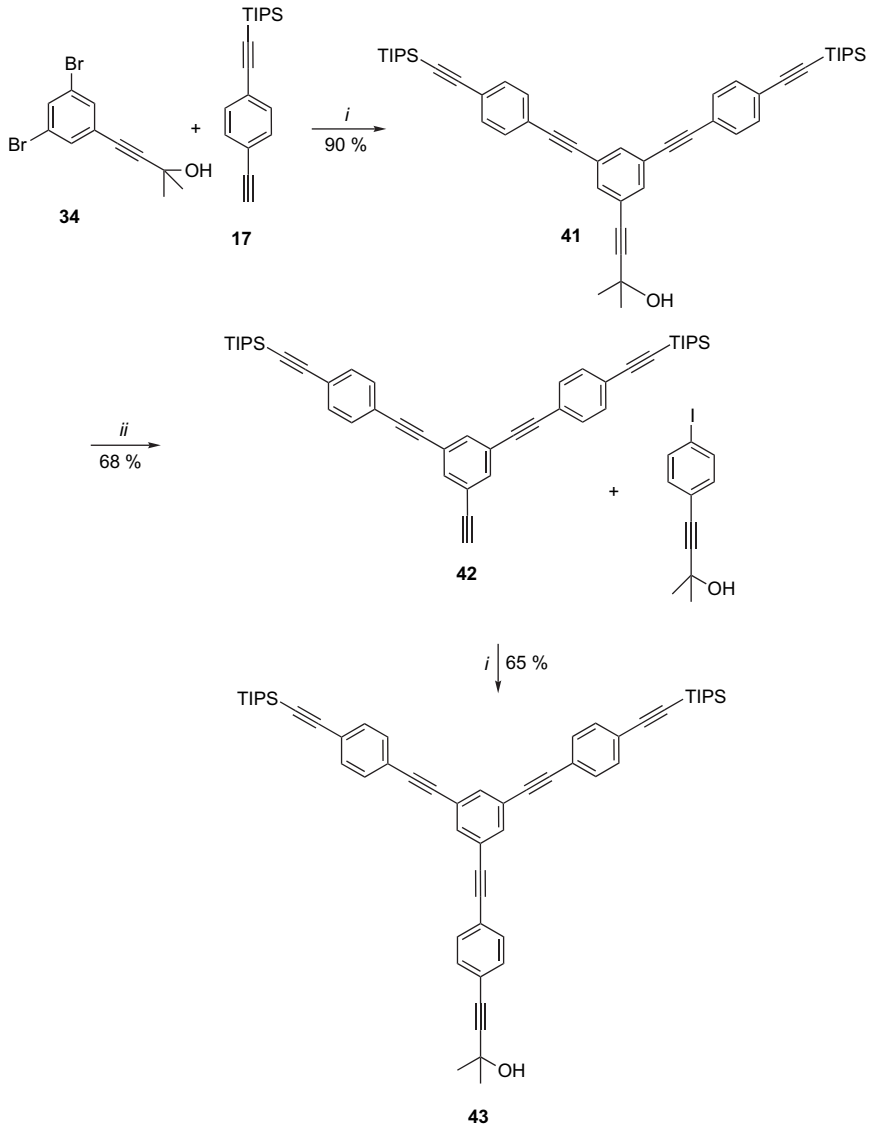
4. Experimental

4.1. General

Molecules **1**,[41] **5**,[30] **8**,[42,43] **11**,[23] **12**,[30] **32**[35] and **33**[35] were prepared as described previously and determined to have ^1H NMR and ^{13}C NMR spectra consistent with those reported.

4.2. Absorption and fluorescence measurements

Absorption spectra were recorded on a Hewlett Packard Diode array UV–vis–NIR Spectrometer. Quantum-corrected emission spectra were measured with an LS 50B luminescence spectrometer (Perkin–Elmer). Solutions for fluorescence measurements were prepared inside an anerobic glovebox at specific concentrations in THF distilled over Na. The solutions were introduced into a quartz cuvette equipped with a Teflon cap to minimize contact with air. The emission spectra were obtained under the excitation of 354 nm with a slit width of 2.5 nm. Four-sided quartz cells with a length of 1 cm were used, and the detector



Scheme 10. Synthesis of **43**. Conditions: (i) $Pd_2(dba)_3 \cdot CHCl_3$, PPh_3, CuI, Et_3N, 70 °C; (ii) NaOH, toluene, reflux.

Table 1. Fluorescence quantum yields (Φ) of compounds **10**, **16**, **23**, and **26** in anhydrous THF with maximum wavelengths of UV absorption and emission[a]

Compound		**10**	**16**	**23**	**26**
λ_{max} (nm)	Absorption	380	398	398	406
	Emission	438	443	438	453
Φ		0.38	0.73	0.75	0.76

[a] All solutions were prepared and transferred into the fluorescence cuvette in the dry box.

Table 2. Film thicknesses and XPS data for SAMs of compounds **10** and **23** on Au and Pt surfaces

SAM	Molecular length[a]	Thickness[b] (Å)	Binding energy[c] (eV)			
			C1s	O1s	S2p	N1s
10 on Au	21.0	19.5	284.6	532.3	164.2	398.4
23 on Au	34.7	31.6	284.5	532.1	164.4	400.1
10 on Pt	22.9	22.1	284.5	532.1	163.7	398.9
23 on Pt	36.2	34.4	284.1	531.7	164.2	399.5

[a] Calculated from AM1 geometry optimized molecular structures.
[b] Measured by ellipsometry.
[c] Measured by X-ray photoelectron spectroscopy.

was arranged perpendicular to the incident beam. Photoluminescence quantum yields were calculated against quinine sulfate in 1 N sulfuric acid as a standard.

4.3. Preparation of self-assembled monolayers

Polycrystalline gold films were purchased from EMF. Pt films were deposited onto glass substrates by first deposition of 5 nm Cr and a followed deposition of 100 nm of Pt. The gold substrates were cleaned with 'piranha' solution (7:3 H_2SO_4/H_2O_2), washed with water and ethanol and followed by the sonication in ethanol for 10 min and rinse with ethanol. *Caution!* 'piranha' solution should be handled carefully because of its violent reactivity with organic molecules. The Pt substrates were cleaned by soaking in sulfuric acid for 20 min followed by the sonication in ethanol for 10 min, which were then rinsed with water and ethanol and dried over nitrogen. SAMs of **10**, **16**, **23**, and **26** were formed on Pt in 0.5 mM THF solutions for 2 days. SAMs on Au were prepared using the same procedure except that the thioacetyl group was cleaved by the addition of 10 μL NH_4OH to the sample solutions, which was incubated for 20 min.

4.4. Ellipsometry measurements

The ellipsometric measurements were recorded using a variable angle spectroscopic ellipsometer (J. A. Woollam, Inc., Lincoln, NE). He–Ne laser light was incident at 70° on the sample. The experimental polarization angles were used to determine film thickness. All the thickness were calculated based on isotropic film models in which the complex refractive index is described as a scalar, $n=n+ik$. The absorption index (k) was set to zero, while n was estimated to be 1.55 and 1.3 for SAMs on Au and Pt, respectively.

4.5. XPS measurements

XPS spectra were recorded on a Kratos Axis Ultra X-ray Photoemission Spectrometer using an Al kα source monochromatized at 1486.6 eV. The radiation was generated at 10 mA under 15 kV. Pass energy of 160 and 20 eV was used for survey and regional spectrum, respectively. The core level binding energies were corrected by a rigid shift to bring the Au $4f_{7/2}$ and Pt $4f_{7/2}$ peaks to 84 and 71.3 eV, respectively.

4.6. 4-(2,5-Bis-hexyloxy-4-iodo-phenyl)-2-methyl-but-3-yn-2-ol (2)

Inside a N_2-filled dry box, **1** (2.5 g, 4.7 mmol), tris(dibenzylideneacetone)bispalladium (146 mg, 0.141 mmol), triphenylphosphine (123 mg, 0.47 mmol), and copper iodide (90 mg, 0.47 mmol) were weighed in an oven dried Schlenk flask. Triethylamine (12 mL) and pyridine (4 mL) were added to the reaction mixture and stirred for 10 min followed by the addition of 2-methyl-3-butyn-2-ol (477 μL, 4.7 mmol). The reaction mixture was stirred for 48 h at 75 °C. The reaction mixture was cooled to room temperature and filtered through a small silica gel plug and washed with dichloromethane. The filtrate was evaporated and the residue was purified by flash column chromatography using a mixture of ethyl acetate/hexanes (20:80) to yield 1.1 g (50%) of **2**. Mp 42 °C; IR (thin film): 3403, 2930, 2863, 1618, 1465, 1024 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): 7.24 (s, 1H), 6.78 (s, 1H), 3.91 (t, J=6.3 Hz, 4H), 2.27 (s, 1H, –OH), 1.76 (m, 4H), 1.61 (s, 6H), 1.48 (m, 4H), 1.34 (m, 8H), 0.89 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): 154.5, 151.9, 123.9, 116.3, 113.2, 98.8, 87.6, 78.4, 70.3, 69.9, 65.9, 31.8, 31.7, 31.6, 29.5, 29.3, 25.9, 25.9, 22.8, 22.8, 14.4. Mass calculated for (M^+) $C_{23}H_{35}IO_3$ 486.1631, found (HRMS-FAB) 486.1617.

4.7. General procedure for Sonogashira coupling

Inside a N_2-filled dry box, aryl iodide (1 mmol), tris(dibenzylideneacetone)bispalladium (31 mg, 0.03 mmol), triphenylphosphine (26 mg, 0.10 mmol), copper iodide (19 mg, 0.01 mmol), and terminal acetylene (1 mmol) were weighed in an oven dried Schlenk flask. Triethylamine (10 mL) was added to the reaction mixture. The reaction mixture was stirred for 48 h at 75 °C. The reaction mixture was cooled to room temperature and filtered through a small silica gel plug and washed with dichloromethane. The filtrate was evaporated and the residue was purified by flash column chromatography.

4.7.1. 4-{2,5-Bis-hexyloxy-4-[(triisopropylsilanyl)-ethynyl]-phenyl}-2-methyl-but-3-yn-2-ol (3). The general procedure for Sonogashira coupling was followed using TIPS-acetylene (1.05 equiv) and a reaction time of 48 h at 70 °C. The crude compound was purified by flash column chromatography in ethyl acetate/hexanes (80:20) to yield pure compound **3**. Yield 87% (640 mg); mp 43 °C; IR (thin film): 3405, 2893, 2864, 1498, 1382, 1216 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): 6.88 (s, 1H), 6.83 (s, 1H), 3.94 (m, 4H), 2.04 (s, 1H, –OH), 1.77 (m, 4H), 1.62 (s, 6H), 1.47 (m, 4H), 1.31 (m, 8H), 1.13 (s, 21H), 0.89 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): 154.4, 153.5, 117.7, 116.7, 114.1, 113.5, 103.0, 99.1, 96.5, 78.8, 69.7, 69.4, 66.0, 31.9, 31.8, 31.6, 29.6, 29.5, 26.1, 25.9, 22.8, 18.9, 14.3, 11.6. Mass calculated for (M^+) $C_{34}H_{56}O_3Si$ 540.3999, found (HRMS-FAB) 540.3965.

4.8. General procedure for base-promoted deprotection of trialkyl-silyl acetylenes

Trialkyl-silyl acetylene (2.2 mmol) was taken in dry toluene (20 mL) under nitrogen atmosphere. Powdered sodium hydroxide (140 mg, 3.3 mmol) was added to the reaction mixture. The reaction mixture was refluxed for 24 h under nitrogen. The reaction mixture was cooled to room temperature and filtered off the solid residue. The filtrate was evaporated and residue purified over flash column chromatography.

4.8.1. (4-Ethynyl-2,5-bis-hexyloxy-phenylethynyl)-triisopropyl-silane (4). This compound has been reported previously,[44] but its synthesis and characterization have not. The general procedure for base-promoted deprotection of trialkyl-silyl acetylenes was followed using molecule **3**. The compound was purified by flash chromatography using ethyl acetate/hexanes (15:85) to yield pure compound **4**. Yield 79% (780 mg); mp 38 °C; IR (thin film): 2936, 2863, 2144, 1594, 1496, 1219 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): 6.95 (s, 2H), 3.95 (m, 4H), 3.21 (s, 1H), 1.78 (m, 4H), 1.47 (m, 4H), 1.31 (m, 8H), 1.13 (s, 21H), 0.89 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): 154.3, 154.1, 117.8, 117.3, 114.8, 112.8, 102.9, 96.8, 82.3, 80.2, 69.9, 69.4, 31.8, 31.7, 29.6, 29.3, 26.0, 25.8, 22.8, 22.8, 18.9, 14.3, 14.2, 11.5. Anal. Calcd for $C_{31}H_{50}O_2Si$: C, 77.12; H, 10.44; Si, 5.82; O, 6.63. Found: C, 76.75; H, 10.15. Mass calculated for (M^+) $C_{31}H_{50}O_2Si$ 482.3580, found (HRMS-FAB) 482.3571.

4.9. *N*-(4-{2,5-Bis-hexyloxy-4-[(triisopropylsilanyl)-ethynyl]-phenylethynyl}-phenyl)-formamide (6)

The general procedure for Sonogashira coupling was followed using molecules **4** and **5**. Alternatively, it was prepared by the coupling of molecules **11** and **12** using the same general procedure of Sonogashira coupling in 65% yield after purification. The crude compound was purified by flash column chromatography by using ethyl acetate/hexanes (60:40) to yield the pure compound **6**. Yield 86% (483 mg); mp 76 °C; IR (thin film): 2893, 2864, 1691, 1519, 1408, 1215 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): 8.69 (d, J=11.7 Hz, 0.36H), 8.34 (s, J=11.7 Hz, 0.68H), 8.31 (d, J=1.5 Hz, 0.22H), 7.49–7.40 (m, 4H), 7.20 (s, 0.15H), 7.01 (d, J=8.7 Hz, 0.89H), 6.87 (s, 2H), 3.96–3.87 (m, 4H), 1.76–1.67 (m, 4H), 1.47–1.42 (m, 4H), 1.28–1.22 (m, 8H), 1.08 (s, 21H), 0.84 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): 162.4, 159.1, 154.5, 153.5, 137.0, 136.7, 133.2,

132.6, 120.5, 119.9, 119.7, 118.3, 117.9, 116.4, 114.3, 114.1, 113.9, 103.1, 96.9, 96.7, 94.4, 93.9, 86.7, 86.2, 69.9, 69.5, 31.9, 31.8, 29.6, 29.5, 26.0, 25.9, 22.8, 18.9, 14.3, 14.2, 11.5. Mass calculated for (M^+) $C_{38}H_{55}NO_3Si$ 601.3951, found (HRMS-FAB) 601.3961.

4.10. General procedure for fluoride-promoted deprotection of trialkyl-silyl acetylenes

Trialkyl-silyl acetylene (1 mmol) was taken in dry THF (6 mL) under nitrogen atmosphere and added a 1.0 M solution of tetrabutyl ammonium fluoride (1.4 mL, 1.4 mmol). The reaction mixture was stirred overnight, extracted with ethyl acetate, and washed with brine. The organic layer was dried over sodium sulfate before drying it under vacuum. The crude compound was purified over flash column chromatography.

4.10.1. *N*-[4-(4-Ethynyl-2,5-bis-hexyloxy-phenylethynyl)-phenyl]-formamide (7). The general procedure for fluoride-promoted deprotection of trialkyl-silyl acetylenes was followed using molecule **6** (1.2 g). Yield 93% (830 mg); mp 74 °C; IR (thin film): 3285, 2930, 1689, 1520, 1407, 1275 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): 8.69 (d, J=9.6 Hz, 0.38H), 8.32 (s, 0.68H), 8.24 (br, 0.20H), 7.50–7.41 (m, 4H), 7.20 (s, 0.25H), 7.01 (d, J=6.9 Hz, 0.87H), 6.91 (s, 2H), 3.93 (m, 4H), 3.28 (s, 1H), 1.75 (m, 4H), 1.44 (m, 4H), 1.27 (m, 8H), 0.83 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): 162.3, 159.0, 154.3, 153.6, 137.1, 133.3, 132.6, 120.4, 119.7, 118.3, 117.9, 117.0, 114.8, 114.5, 112.9, 112.7, 94.7, 94.1, 86.4, 85.8, 82.6, 82.5, 80.2, 69.8, 31.7, 31.7, 29.4, 29.3, 25.9, 25.8, 22.8, 22.8, 14.2. Anal. Calcd for $C_{29}H_{35}NO_3$: C, 78.17; H, 7.92; N, 3.14; O, 10.77. Found: C, 78.44; H, 7.97; N, 3.27.

4.11. Thioacetic acid *S*-{4-[4-(4-formylamino-phenylethynyl)-2,5-bis-hexyloxy-phenylethynyl]-phenyl} ester (9)

The general procedure for Sonogashira coupling was followed using molecules **7** and **8**, but at room temperature for 24 h. Yield 55% (184 mg); mp 92 °C; IR (thin film): 2929, 1693, 1592, 1519, 1414 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): 8.75 (d, J=11.4 Hz, 0.5H), 8.37 (d, J=1.8 Hz, 0.7H), 8.04 (d, J=11.1 Hz, 0.5H), 7.56–7.47 (m, 6H), 7.40–7.37 (m, 2H), 7.06 (d, J=8.7 Hz, 0.6H), 6.99 (m, 2H), 4.02 (m, 4H), 2.43 (s, 3H), 1.84 (m, 4H), 1.54 (m, 4H), 1.35 (m, 8H), 0.89 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): 194.1, 162.5, 159.4, 153.9, 153.7, 153.7, 137.3, 136.9, 134.4, 133.2, 132.6, 132.3, 128.1, 125.1, 119.8, 119.6, 118.3, 117.1, 116.9, 114.5, 113.6, 94.9, 94.2, 88.1, 86.0, 69.8, 31.8, 30.5, 29.5, 25.9, 22.8, 14.3. Mass calculated for (M^+) $C_{37}H_{41}NO_4S$ 595.2756, found (HRMS-FAB) 595.2751.

4.12. General procedure for phosgene-mediated dehydration of formamide to isonitrile

Formamide (0.26 mmol) and triphosgene (38 mg, 0.13 mmol) were weighed in an oven dried Schlenk flask. The flask was evacuated and back filled with nitrogen (two times). To this was added dry dichloromethane (5 mL), cooled to 0 °C, and added triethylamine (2 mL). A solution of benzyltriethyl ammonium chloride (6.0 mg, 0.026 mmol) in 2 mL of dry dichloromethane was added dropwise. The reaction mixture was stirred for 7 h and allowed to warm gradually to room temperature. The reaction mixture was taken in water and extracted with dichloromethane. The organic layer was washed with water and brine, respectively. The organic layer was dried over sodium sulfate before drying it under vacuum. The crude compound was purified over column chromatography.

4.12.1. Thioacetic acid *S*-{4-[2,5-bis-hexyloxy-4-(4-isocyano-phenylethynyl)-phenylethynyl]-phenyl} ester (10). General procedure for phosgene-mediated dehydration of formamide to isonitrile was followed using molecule **9** (150 mg). The crude compound was purified by flash column chromatography using ethyl acetate/hexanes (20:80) to yield pure compound **10**. Yield 69% (100 mg); mp 80 °C; IR (thin film): 2930, 2862, 2120, 1709, 1508, 1216 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): 7.48 (dd, J=8.1, 6.0 Hz, 4H), 7.31 (dd, J=13.5, 8.4 Hz, 4H), 6.95 (s, 1H), 6.94 (s, 1H), 3.96 (m, 4H), 2.37 (s, 3H), 1.78 (m, 4H), 1.47 (m, 4H), 1.29 (m, 8H), 0.83 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): 193.6, 165.9, 154.0, 153.9, 134.4, 132.6, 132.3, 128.3, 126.6, 125.1, 124.8, 117.0, 114.5, 113.5, 94.6, 93.4, 89.1, 87.7, 69.8, 69.7, 31.8, 30.5, 29.5, 25.9, 22.8, 14.2. Mass calculated for (M^+) $C_{37}H_{39}NO_3S$ 577.2651, found (HRMS-FAB) 577.2665.

4.13. *N*-[4-(4-{2,5-Bis-hexyloxy-4-[(triisopropylsilanyl)-ethynyl]-phenylethynyl}-2,5-bis-hexyloxy-phenylethynyl)-phenyl]-formamide (13)

The general procedure for Sonogashira coupling was followed using molecules **7** and **11**. The crude compound was purified by flash column chromatography using ethyl acetate/hexanes (60:40) to yield pure compound **13**. Yield 38% (170 mg); mp 54 °C; IR (thin film): 2930, 2863, 1692, 1594, 1213 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): 8.75 (d, J=10.8 Hz, 0.5H), 8.36 (s, 0.6H), 8.24 (d, J=11.1 Hz, 0.4H), 7.51 (m, 4H), 7.40–7.32 (m, 2H), 7.07 (d, J=7.8 Hz, 0.8H), 6.99 (s, 2H), 6.95 (s, 2H), 3.92–4.03 (m, 8H), 1.84 (m, 8H), 1.51 (m, 8H), 1.33 (m, 16H), 1.14 (s, 21H), 0.89 (m, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz): 162.1, 159.0, 154.5, 153.8, 153.7, 153.4, 137.0, 136.6, 133.2, 132.6, 120.6, 119.9, 119.7, 118.4, 118.1, 117.2, 117.1, 116.9, 116.7, 114.6, 114.5, 114.4, 114.2, 114.2, 114.1, 113.8, 103.2, 96.8, 96.7, 94.6, 94.1, 91.9, 91.8, 91.5, 91.4, 86.7, 86.2, 70.0, 69.9, 69.7, 69.4, 31.9, 31.8, 31.8, 29.6, 29.5, 29.4, 26.0, 25.9, 25.8, 22.8, 18.9, 14.2, 14.2, 11.6. Mass calculated for (M^+) $C_{58}H_{83}NO_5Si$ 901.6041, found (HRMS-FAB) 901.6060.

4.14. *N*-{4-[4-(4-Ethynyl-2,5-bis-hexyloxy-phenylethynyl)-2,5-bis-hexyloxy-phenylethynyl]-phenyl}-formamide (14)

The general procedure for fluoride-promoted deprotection was employed on molecule **13**. The crude compound was purified by flash chromatography using ethyl acetate/hexanes (60:40) to yield pure compound **14**. Yield 99% (140 mg); mp 98 °C; IR (thin film): 3284, 2930, 2863, 1691, 1599, 1419, 1275, 1022 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): 8.75 (d, J=11.4 Hz, 0.5H), 8.39 (d, J=1.8 Hz, 0.7H), 7.88 (d, J=11.4 Hz, 0.5H), 7.52 (m, 3H), 7.27 (m,

1H), 7.06 (d, J=8.9 Hz, 0.5H), 6.99 (m, 4H), 4.01 (m, 8H), 3.34 (s, 1H), 1.84 (m, 8H), 1.51 (m, 8H), 1.34 (m, 16H), 0.89 (m, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz): 162.2, 159.1, 154.3, 153.7, 153.7, 153.5, 137.0, 136.7, 133.2, 132.6, 120.5, 119.8, 119.7, 118.4, 118.1, 117.2, 117.2, 115.1, 114.3, 114.0, 112.7, 94.7, 94.2, 91.7, 91.4, 86.7, 86.1, 82.6, 80.2, 69.9, 69.8, 31.6, 31.7, 29.5, 29.4, 29.3, 25.9, 25.8, 25.8, 22.8, 22.8, 14.2. Anal. Calcd for $C_{49}H_{63}NO_5$: C, 78.89; H, 8.51; N, 1.88; O, 10.72. Found: C, 78.52; H, 8.51; N, 1.85.

4.15. Thioacetic acid *S*-(4-{4-[2,5-bis-hexyloxy-4-(4-isocyano-phenylethynyl)-phenylethynyl]-2,5-bis-hexyloxy-phenylethynyl}-phenyl) ester (16)

The general procedure for Sonogashira coupling was followed using **14** and **8** (1.0 equiv) and a reaction time of 48 h at 70 °C. The crude compound was purified by flash column chromatography using ethyl acetate/hexanes (60:40) to yield pure **15**. Yield 48% (42 mg); ^{1}H NMR ($CDCl_3$, 300 MHz): 8.75 (d, J=11.4 Hz, 0.5H), 8.38 (d, J=1.8 Hz, 0.7H), 7.88 (d, J=11.4 Hz, 0.5H), 7.57–7.48 (m, 6H), 7.40–7.32 (m, 2H), 7.06 (d, J=8.9 Hz, 0.6H), 7.01 (m, 4H), 4.04 (m, 8H), 2.44 (s, 3H), 1.85 (m, 8H), 1.54 (m, 8H), 1.35 (m, 16H), 0.89 (m, 12H). This molecule was then taken and subjected to the general procedure for phosgene-mediated dehydration of formamide to isonitrile was followed using the molecule **15**. The crude compound was purified by flash column chromatography using ethyl acetate/hexanes (20:80) to yield pure **16**. Yield 76% (32 mg); mp 84 °C; IR (thin film): 2928, 2361, 1710, 1511, 1276, 1217 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): 7.56–7.52 (m, 4H), 7.41–7.35 (m, 4H), 7.01 (m, 4H), 4.02 (m, 8H), 2.44 (s, 3H), 1.85 (m, 8H), 1.53 (m, 8H), 1.35 (m, 16H), 0.89 (m, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz): 193.7, 165.8, 154.0, 153.9, 153.7, 153.6, 134.4, 132.6, 132.3, 128.2, 126.6, 125.2, 124.9, 117.2, 115.2, 114.6, 113.9, 113.1, 94.3, 93.2, 92.0, 91.6, 89.2, 87.9, 69.9, 69.9, 69.7, 69.6, 31.8, 31.8, 30.5, 29.4, 25.9, 25.8, 22.8, 14.2. Mass calculated for (M^+) $C_{37}H_{67}NO_5S$ 877.4740, found (HRMS-FAB) 877.4752.

4.16. (2-(4-Ethynylphenyl)ethynyl)triisopropylsilane (17)

This compound has been reported previously and prepared according to a previously reported procedure.[45] Yield 91%; ^{1}H NMR ($CDCl_3$, 300 MHz): 7.42 (s, 4H), 3.16 (s, 1H), 1.13 (s, 21H); ^{13}C NMR ($CDCl_3$, 75 MHz): 132.1, 124.2, 122.1, 106.5, 93.2, 83.4, 79.0, 18.8, 11.5.

4.17. 4-(2,5-Bis-hexyloxy-4-{4-[(triisopropylsilanyl)-ethynyl]-phenylethynyl}-phenyl)-but-3-yn-2-ol (18)

The general procedure for Sonogashira coupling was followed using **2** and **17** (1.0 equiv) and a reaction time of 48 h at 75 °C. The crude compound was purified by flash column chromatography in ethyl acetate/hexanes (80:20) to yield pure compound **18**. Yield 96% (615 mg); IR (thin film): 3410, 2933, 2863, 2152, 1505, 1216 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): 7.39 (s, 4H), 6.89 (s, 1H), 6.83 (s, 1H), 3.90 (m, 4H), 1.74 (m, 4H), 1.57 (s, 6H), 1.45 (m, 4H), 1.28 (m, 8H), 1.08 (s, 21H), 0.84 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): 153.8, 153.7, 132.1, 131.5, 123.5, 123.5, 117.1, 116.9, 113.8, 113.8, 106.9, 99.6, 94.6, 92.9, 88.0, 78.6, 69.7, 69.6, 65.8, 31.8, 31.6, 29.5, 25.9, 25.9, 22.8, 18.8, 14.2, 14.2, 11.5. Anal. Calcd for $C_{42}H_{60}O_3Si$: C, 78.70; H, 9.43; Si, 4.38; O, 7.49. Found: C, 78.14; H, 9.25.

4.18. *N*-[4-(2,5-Bis-hexyloxy-4-{4-[(triisopropylsilanyl)-ethynyl]-phenylethynyl}-phenylethynyl)-phenyl]-formamide (19)

Compound **18** (615 mg) was subjected to the general procedure for base-promoted deprotection of trialkyl-silyl acetylenes. The compound was purified by flash column chromatography using ethyl acetate/hexanes (20:80) to yield the intermediate for the next step. Yield 66% (370 mg); IR (thin film): 3307, 2931, 2863, 2361, 2149, 1502, 1217 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): 7.39 (s, 4H), 6.93 (s, 1H), 6.91 (s, 1H), 3.94 (m, 4H), 3.29 (s, 1H), 1.77 (m, 4H), 1.45 (m, 4H), 1.29 (m, 8H), 1.08 (s, 21H), 0.85 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): 154.3, 153.7, 132.1, 131.5, 123.5, 123.4, 117.9, 117.0, 114.5, 113.0, 106.9, 94.8, 93.0, 87.8, 82.6, 80.1, 69.8, 69.8, 31.8, 31.7, 29.4, 29.3, 25.9, 25.8, 22.8, 22.8, 18.8, 14.2, 11.5. This intermediate compound was taken and subjected to Sonogashira coupling using **5** (1.0 equiv) following the general procedure. The crude compound was purified by flash column chromatography using ethyl acetate/hexanes (50:50) to yield the pure compound **19**. Yield 67% (300 mg); IR (thin film): 3281, 2938, 2864, 2211, 2153, 1691, 1519, 1216 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): 8.68 (d, J=11.4 Hz, 0.18H), 8.34 (br s, 0.4H), 7.50–7.42 (m, 4H), 7.39 (s, 3H), 7.19 (s, 1H), 6.99 (d, J=8.7 Hz, 1H), 6.94 (s, 2H), 3.96 (t, J=6.3 Hz, 4H), 1.78 (m, 4H), 1.50 (m, 4H), 1.29 (m, 8H), 1.07 (s, 21H), 0.84 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): 161.8, 158.8, 153.8, 153.8, 136.9, 133.3, 132.7, 132.1, 131.5, 123.5, 120.6, 119.9, 119.7, 118.4, 116.9, 114.3, 114.0, 113.8, 106.9, 94.8, 94.7, 94.1, 93.0, 87.9, 86.7, 86.1, 69.8, 31.8, 29.5, 25.9, 22.8, 18.8, 14.2, 11.5. Mass calculated for (M^+) $C_{46}H_{59}NO_3Si$ 701.4264, found (HRMS-FAB) 701.4274.

4.19. *N*-{4-[4-(4-Ethynyl-phenylethynyl)-2,5-bis-hexyl-oxy-phenylethynyl]-phenyl}-formamide (20)

The compound **19** was deprotected by following the general procedure of fluoride-promoted deprotection of trialkyl-silyl acetylenes. The crude compound was purified by flash column chromatography using ethyl acetate/hexanes (50:50) to yield pure **20**. Yield 96% (215 mg); IR (thin film): 3288, 2930, 2864, 2205, 2108, 1691, 1598, 1214 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): 8.68 (d, J=11.4 Hz, 0.38H), 8.34 (br s, 0.53H), 7.50–7.42 (m, 4H), 7.41 (s, 3H), 7.19 (s, 1H), 6.99 (d, J=8.7 Hz, 1H), 6.94 (s, 2H), 3.96 (t, J=6.3 Hz, 4H), 3.12 (s, 1H), 1.78 (m, 4H), 1.46 (m, 4H), 1.29 (m, 8H), 0.83 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): 162.0, 158.9, 153.9, 153.7, 133.3, 132.6, 132.2, 131.6, 119.7, 118.3, 116.9, 113.7, 83.5, 79.1, 69.8, 31.8, 29.5, 25.9, 22.8, 14.2. Anal. Calcd for $C_{37}H_{39}NO_3$: C, 81.43; H, 7.20; N, 2.57; O, 8.80. Found: C, 81.30; H, 7.20; N, 2.55.

4.20. *N*-{4-[4-(4-{2,5-Bis-hexyloxy-4-[(triisopropylsilanyl)-ethynyl]-phenylethynyl}-phenylethynyl)-2,5-bis-hexyloxy-phenylethynyl]-phenyl}-formamide (21)

The general procedure for Sonogashira coupling was followed using **20** and **11** (1.0 equiv) at 70 °C. The crude

compound was purified by flash column chromatography using ethyl acetate/hexanes (60:40) to yield pure **21**. Yield 41% (150 mg); IR (thin film): 2928, 2863, 1594, 1215 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): 8.75 (d, J=11.4 Hz, 0.4H), 8.38 (d, J=1.8 Hz, 0.5H), 7.53–7.49 (m, 8H), 7.06 (d, J=8.9 Hz, 0.6H), 7.01 (s, 2H), 6.94 (s, 2H), 4.05–3.97 (m, 8H), 1.83 (m, 8H), 1.54 (m, 8H), 1.36 (m, 16H), 1.15 (s, 21H), 0.91 (m, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz): 162.1, 159.2, 154.5, 153.9, 153.7, 153.6, 137.2, 136.7, 133.2, 132.6, 132.2, 131.6, 123.4, 120.5, 119.8, 118.4, 117.8, 116.9, 116.5, 114.4, 114.0, 113.9, 113.8, 123.4, 120.5, 119.8, 118.4, 117.8, 116.9, 116.5, 114.4, 114.0, 113.9, 113.8, 103.1, 96.9, 94.8, 94.6, 94.2, 88.3, 88.2, 86.0, 69.9, 69.8, 69.5, 31.9, 31.8, 31.8, 29.6, 29.5, 26.0, 25.9, 25.9, 22.8, 18.9, 14.3, 14.2, 11.5. Anal. Calcd for $C_{66}H_{87}NO_5Si$: C, 79.07; H, 8.75; N, 1.40; Si, 2.80; O, 7.98. Found: C, 78.82; H, 8.73; N, 1.48.

4.21. Thioacetic acid *S*-[4-(4-{4-[2,5-bis-hexyloxy-4-(4-isocyano-phenylethynyl)-phenylethynyl]-phenylethynyl}-2,5-bis-hexyloxy-phenylethynyl)-phenyl] ester (23)

Compound **21** (150 mg) was taken and subjected to the general procedure for fluoride-promoted deprotection. The crude compound was purified by flash column chromatography using ethyl acetate/hexanes (60:40) to give pure compound, which was used in the next step. Yield 90% (110 mg); IR (thin film): 3286, 2928, 2863, 1690, 1410, 1215 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): 8.75 (d, J=11.4 Hz, 0.5H), 8.38 (d, J=1.8 Hz, 0.7H), 7.88 (d, J=11.4 Hz, 0.5H), 7.56–7.47 (m, 8H), 7.06 (d, J=8.9 Hz, 0.6H), 6.99 (m, 4H), 4.03 (m, 8H), 3.35 (s, 1H), 1.84 (m, 8H), 1.54 (m, 8H), 1.35 (m, 16H), 0.89 (m, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz): 162.1, 159.0, 154.3, 153.9, 153.8, 153.7, 137.1, 133.2, 132.6, 132.2, 131.6, 123.5, 123.3, 120.5, 119.7, 118.4, 117.9, 117.0, 114.5, 114.4, 114.1, 113.8, 113.0, 94.8, 87.9, 86.1, 82.6, 80.2, 69.8, 31.8, 31.7, 29.9, 29.5, 29.3, 25.9, 25.8, 22.8, 22.8, 14.2. The resulting intermediate was taken and subjected to the general procedure Sonogashira coupling with 4-iodo-phenyl thioacetate (**8**) but at room temperature. The crude compound was purified by flash column chromatography using ethyl acetate/hexanes (60:40) to yield pure **22**. Yield 60% (78 mg); ^1H NMR ($CDCl_3$, 300 MHz): 8.60 (d, J=11.1 Hz, 0.4H), 8.21 (s, 0.5H), 7.93 (d, J=11.4 Hz, 0.4H), 7.44–7.36 (m, 10H), 7.28–7.23 (m, 2H), 6.91 (d, J=8.1 Hz, 0.5H), 6.86 (s, 4H), 3.88 (t, J=6.6 Hz, 8H), 2.29 (s, 3H), 1.69 (m, 8H), 1.39 (m, 8H), 1.21 (m, 16H), 0.75 (m, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz): 193.8, 162.1, 159.0, 153.9, 153.9, 153.8, 153.8, 137.0, 134.4, 133.2, 132.6, 132.3, 131.6, 128.2, 124.9, 123.4, 119.8, 119.7, 118.4, 117.0, 114.4, 114.2, 114.0, 95.0, 94.8, 94.3, 88.1, 87.9, 86.1, 69.8, 31.8, 31.8, 30.5, 29.5, 25.9, 25.9, 22.8, 14.2. The general procedure for phosgene-mediated dehydration of formamide to isonitrile was followed using molecule **22**. The crude compound was purified by flash column chromatography using ethyl acetate/hexanes (20:80) to yield pure **23**. Yield 82% (62 mg); mp 118 °C; IR (thin film): 2929, 2852, 2360, 2119, 1709, 1512, 1215, 1018 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): 7.51–7.45 (m, 8H), 7.35–7.28 (m, 4H), 6.95 (s, 2H), 6.94 (s, 2H), 3.97 (t, J=6.3 Hz, 8H), 2.37 (s, 3H), 1.79 (m, 8H), 1.50 (m, 8H), 1.29 (m, 16H), 0.85 (m, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz): 193.7, 165.9, 154.0, 153.9, 153.8, 134.4, 132.6, 132.3, 131.7, 128.2, 126.6, 125.1, 124.9, 123.5, 123.3, 117.0, 116.9, 114.7, 114.2, 114.0, 113.3, 95.2, 94.9, 94.4, 93.3, 89.1, 88.2, 88.0, 87.9, 69.8, 69.7, 31.8, 30.5, 29.5, 29.4, 25.9, 25.9, 22.8, 14.2. Mass calculated for (M^+) $C_{65}H_{71}NO_5S$ 977.5053, found (HRMS-FAB) 977.5060.

4.22. *N*-{4-[4-(4-{2,5-Bis-hexyloxy-4-[(triisopropylsilanyl)-ethynyl]-phenylethynyl}-2,5-bis-hexyloxy-phenylethynyl)-2,5-bis-hexyloxy-phenylethynyl]-phenyl}-formamide (24)

The general procedure for Sonogashira coupling was followed using **14** and **11** (1.0 equiv) at 75 °C. The crude compound was purified by flash column chromatography using ethyl acetate/hexanes (60:40) to give pure **24**. Yield 40% (52 mg); mp 86 °C; IR (thin film): 3286, 2933, 2857, 1690, 1424, 1212, 1023 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): 8.68 (d, J=11.4 Hz, 0.33H), 8.31 (d, J=0.9 Hz, 0.49H), 7.86 (d, J=11.4 Hz, 0.28H), 7.50–7.19 (m, 4H), 7.30–6.85 (m, 6H), 3.99–3.87 (m, 12H), 1.78 (m, 12H), 1.45 (m, 12H), 1.28 (m, 24H), 1.08 (s, 21H), 0.82 (m, 18H); ^{13}C NMR ($CDCl_3$, 75 MHz): 162.0, 159.0, 154.5, 153.8, 153.7, 153.4, 137.0, 133.2, 132.6, 119.7, 118.4, 118.1, 117.4, 117.2, 116.7, 114.5, 114.2, 114.1, 103.2, 96.7, 94.6, 91.8, 91.5, 86.2, 70.0, 69.8, 69.4, 31.9, 31.8, 29.6, 29.5, 26.0, 25.9, 25.8, 22.8, 18.9, 14.2, 11.6. Mass calculated for (M^+) $C_{78}H_{111}NO_7Si$ 1201.8130, found (HRMS-FAB) 1201.8119.

4.23. Thioacetic acid *S*-[4-(4-{4-[2,5-bis-hexyloxy-4-(4-isocyano-phenylethynyl)-phenylethynyl]-2,5-bis-hexyloxy-phenylethynyl}-2,5-bis-hexyloxy-phenylethynyl)-phenyl] ester (26)

Compound **24** was taken and deprotected using the general procedure for fluoride-promoted deprotection. The compound was purified by flash column chromatography using ethyl acetate/hexanes (60:40) to give pure compound, which was used in the next step. Yield 90% (45 mg); ^1H NMR ($CDCl_3$, 300 MHz): 8.68 (d, J=11.1 Hz, 0.3H), 8.32 (d, J=1.2 Hz, 0.5H), 7.84 (d, J=11.1 Hz, 0.25H), 7.50–7.41 (m, 4H), 7.31 (s, 0.6H), 7.19 (s, 0.57H), 7.01–6.91 (m, 6H), 3.95 (m, 12H), 3.28 (s, 1H), 1.77 (m, 12H), 1.45 (m, 12H), 1.28 (m, 24H), 0.84–0.79 (m, 18H). This intermediate was then taken and subjected to the general procedure for Sonogashira coupling using 4-iodo phenyl thioacetate (**8**) but at room temperature. The crude compound was purified by flash column chromatography using ethyl acetate/hexanes (60:40) to give pure **25**. Yield 66% (30 mg); ^1H NMR ($CDCl_3$, 300 MHz): 8.68 (d, J=11.7 Hz, 0.82H), 8.32 (d, J= 1.2 Hz, 0.89H), 7.70 (d, J=11.7 Hz, 0.25H), 7.50–7.42 (m, 4H), 7.33–7.24 (m, 4H), 7.19 (s, 0.57H), 6.95 (m, 6H), 3.95 (m, 12H), 2.38 (s, 3H), 1.79 (m, 12H), 1.45 (m 12H), 1.28 (m, 24H), 0.82 (m, 18H). The general procedure for phosgene-mediated dehydration of formamide to isonitrile was followed using molecule **25**. The crude compound was purified by flash column chromatography using ethyl acetate/hexanes (20:80) to yield pure **26**. Yield 58% (17 mg); mp 120 °C; IR (thin film): 2925, 2852, 2124, 1713, 1427, 1215 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): 7.47 (m, 4H), 7.35–7.28 (m, 4H), 6.95 (s, 3H), 6.94 (s, 3H), 3.96 (m, 12H), 2.37 (s, 3H), 1.79 (m, 12H), 1.47 (m, 12H), 1.29 (m, 24), 0.83 (m, 18H). Mass calculated for (M^+) $C_{77}H_{95}NO_7S$ 1178.6829, found (HRMS-FAB) 1178.6797.

4.24. 1,3,5-Tris-(4-ethynyl-phenylethynyl)-benzene (28)

Inside a N_2-filled dry box, 1,3,5-tribromobenzene (157 mg, 0.5 mmol), 4-ethynyl-phenylethynyltriisopropyl silane (425 mg, 1.5 mmol), tris(dibenzylideneacetone)bispalladium (15.5 mg, 0.015 mmol), triphenylphosphine (13.1 mg, 0.05 mmol), and copper iodide (9.5 mg, 0.05 mmol) were weighed in an oven dried Schlenk flask. Triethylamine (5 mL) was added to the reaction mixture. The reaction mixture was stirred for 48 h at 75 °C. The reaction mixture was cooled to room temperature and filtered through a small silica gel plug and washed with dichloromethane. The filtrate was evaporated and the residue was purified by flash column chromatography using ethyl acetate/hexanes (2:98) to yield 190 mg (41%) of **27**. IR (thin film): 2942, 2864, 2154, 1462 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): 7.57 (s, 3H), 7.41 (s, 12H), 1.09 (s, 63H); ^{13}C NMR ($CDCl_3$, 75 MHz): 134.2, 133.3, 132.2, 131.7, 125.3, 124.1, 122.5, 122.2, 106.7, 93.4, 91.2, 89.0, 18.9, 11.5. This intermediate was then subjected to the general procedure for fluoride-promoted deprotection of trialkyl-silyl acetylenes was followed using compound **27** but using 3.5 equiv of TBAF. The residue was purified by column chromatography using ethyl acetate/hexanes (2:98) to give 90 mg (97%) of pure compound **28**. Spectral data matched those reported previously.[46] ^1H NMR ($CDCl_3$, 300 MHz): 7.57 (s, 3H), 7.41 (s, 12H), 3.14 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): 134.3, 133.3, 132.3, 131.8, 125.2, 123.1, 122.7, 122.2, 90.9, 89.1, 83.3, 79.5.

4.25. Thioacetic acid 4-(4-{3,5-bis-[4-(4-acetylsulfanyl-phenylethynyl)-phenylethynyl]-phenylethynyl}-phenyl-ethynyl)-phenyl ester (29)

The general procedure for Sonogashira coupling was followed using molecule **28** and *p*-iodo-phenyl thioacetate (3 equiv) at room temperature. The crude material was purified by column chromatography using ethyl acetate/hexanes (10:90) to yield 130 mg (70%) of **29**. Spectral data matched those reported previously.[32] Mp 174 °C; IR (thin film): 1709, 1553, 1108 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): 7.57–7.48 (m, 9H), 7.45 (s, 11H), 7.37–7.28 (m, 7H), 2.38 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz): 193.5, 134.4, 134.3, 132.4, 131.9, 128.6, 125.3, 124.3, 123.5, 122.7, 122.3, 91.2, 91.0, 90.8, 89.2, 30.5.

4.26. 4-(3,5-Dibromo-phenyl)-2-methyl-but-3-yn-2-ol (34)

This compound was prepared using a modification of the procedure reported previously.[47] Inside a N_2-filled dry box, 1,3,5-tribromobenzene (6 g, 19 mmol), tris-(dibenzylideneacetone)bispalladium (30 mg, 0.028 mmol), triphenylphosphine (75 mg, 0.28 mmol), and copper iodide (54 mg, 0.28 mmol) were weighed in an oven dried Schlenk flask. Triethylamine (30 mL) and pyridine (20 mL) were added to the reaction mixture. The reaction mixture was stirred for 5 min and then added 2-methyl-3-butyn-2-ol (1.9 mL, 19 mmol) to it. The reaction mixture was stirred overnight at 100 °C. The reaction mixture was cooled to room temperature and filtered through a small silica gel plug and washed with dichloromethane. The filtrate was evaporated and taken in dichloromethane, washed with 5% HCl, water and brine, respectively. The organic layer was dried over anhydrous sodium sulfate before drying in vacuum. The crude product was purified by column chromatography using ethyl acetate/hexanes (20:80) to yield 4.6 g (72%) of pure compound. Spectral data matched that reported previously.[47] Mp 48 °C; IR (thin film): 3333, 2981, 1581, 1163 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): 7.52 (s, 1H), 7.40 (d, J=2.1 Hz, 2H), 2.38 (br, 1H, –OH), 1.53 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): 134.1, 133.2, 126.3, 122.7, 96.6, 79.5, 65.7, 31.5.

4.27. 4-{3,5-Bis-[(triisopropylsilanyl)-ethynyl]-phenyl}-2-methyl-but-3-yn-2-ol (35)

Inside a N_2-filled dry box, **34** (500 mg, 1.48 mmol), tris-(dibenzylideneacetone)bispalladium (80 mg, 0.07 mmol), triphenylphosphine (100 mg, 0.38 mmol), and copper iodide (30 mg, 0.148 mmol) were weighed in an oven dried Schlenk flask. Tetrahydrofuran (5 mL) and Hunig's base (20 mL) were added to the reaction mixture. The reaction mixture was stirred for 5 min and then triisopropylsilyl acetylene (840 μL, 3.71 mmol) was added. The reaction mixture was stirred for 48 h at 60 °C. The reaction mixture was cooled to room temperature and filtered through a small silica gel plug and washed with dichloromethane. The filtrate was evaporated and the residue was purified by flash column chromatography using ethyl acetate/hexanes (20:80) to yield 658 mg (97%) of compound **35**. Mp 40 °C; IR (thin film): 3322, 2942, 2864, 2154, 1579, 1462, 1162 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): 7.46 (m, 1H), 7.45 (m, 2H), 1.60 (s, 6H), 1.12 (s, 42H); ^{13}C NMR ($CDCl_3$, 75 MHz): 134.9, 134.8, 124.2, 123.3, 105.3, 95.0, 92.3, 80.8, 65.7, 31.5, 18.8, 11.4. Anal. Calcd for $C_{33}H_{52}O_2Si_2$: C, 76.08; H, 10.06; Si, 10.78; O, 3.07. Found: C, 76.32; H, 10.05.

4.28. 1-Ethynyl-3,5-bis-[(triisopropylsilanyl)-ethynyl]-benzene (36)

This compound has been reported previously,[37] but a different approach was employed here for its synthesis. The general procedure for base-promoted deprotection of trialkyl-silyl acetylenes was followed using molecule **35**. The residue was purified by column chromatography using ethyl acetate/hexanes (10:90) to yield 388 mg (90%) of pure compound as a colorless liquid. Spectral data matched those reported previously.[37] IR (thin film): 3305, 2943, 2158, 1462 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): 7.46 (s, 3H), 3.02 (s, 1H), 1.06 (s, 42H); ^{13}C NMR ($CDCl_3$, 75 MHz): 135.3, 124.3, 122.3, 105.2, 92.5, 82.2, 78.4, 18.9, 11.5.

4.29. *N*-(4-{3,5-Bis-[(triisopropylsilanyl)-ethynyl]-phenylethynyl}-phenyl)-formamide (37)

Inside a N_2-filled dry box, **36** (320 mg, 0.665 mmol), tris-(dibenzylideneacetone)bispalladium (20 mg, 0.02 mmol), triphenylphosphine (35 mg, 0.13 mmol), copper iodide (30 mg, 0.06 mmol), and *p*-iodo-phenyl formamide **5** were weighed in an oven dried Schlenk flask. Triethylamine (5 mL) was added to the reaction mixture. The reaction mixture was stirred for 48 h at 70 °C. The reaction mixture was cooled to room temperature and filtered through a small silica gel plug and washed with dichloromethane. The filtrate was evaporated and the residue was purified by flash column chromatography using ethyl acetate/hexanes (60:40) to yield 330 mg (83%) of compound **37**. Mp 184 °C; IR (thin film):

2942, 2864, 2155, 1690, 1579, 1292 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): 8.70 (d, J=11.4 Hz, 0.5H), 8.42 (d, J=1.8 Hz, 0.5H), 8.33 (s, 0.5H), 7.51–7.45 (m, 7H), 7.02 (d, J=8.4 Hz, 0.1H), 1.07 (s, 42H); ^{13}C NMR ($CDCl_3$, 75 MHz): 162.4, 159.1, 136.3, 137.1, 134.8, 133.4, 132.8, 124.3, 124.3, 123.8, 123.7, 119.8, 119.2, 118.3, 105.4, 105.3, 92.4, 92.3, 90.2, 88.4, 87.9, 18.8, 11.4; Anal. Calcd for $C_{37}H_{51}NOSi_2$: C, 76.36; H, 8.83; Si, 9.65; N, 2.41; O, 2.75. Found: C, 76.19; H, 8.89; N, 2.39.

4.30. *N*-[4-(3,5-Diethynyl-phenylethynyl)-phenyl]-formamide (38)

Compound **37** (330 mg, 0.55 mmol) was taken in dry THF (4 mL) under nitrogen atmosphere and added a 1.0 M solution of tetrabutyl ammonium fluoride (1.4 mL, 1.4 mmol). The reaction mixture was stirred overnight and extracted from ethyl acetate and washed with brine. The organic layer was dried over sodium sulfate before drying under vacuum. The crude compound was purified by flash column chromatography using ethyl acetate/hexanes (60:40) to yield 140 mg (89%) of pure **38**. Mp 158 °C; IR (thin film): 3290, 2351, 1688, 1293 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): 8.76 (d, J=11.1 Hz, 0.4H), 8.40 (d, J=1.8 Hz, 0.6H), 8.25 (d, J=10.8 Hz, 0.2H), 7.51 (m, 7H), 7.07 (d, J=8.7 Hz, 0.8H), 3.12 (s, 1H), 3.11 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): 162.1, 159.0, 135.2, 133.4, 132.8, 123.1, 119.8, 118.3, 82.0, 78.8, 78.7; FAB(M^+): 269.08. Mass calculated for (M^+) $C_{19}H_{11}NO$ 269.0841, found (HRMS-FAB) 269.0828.

4.31. Thioacetic acid 4-[3-(4-acetylsulfanyl-phenylethynyl)-5-(4-formylaminophenyl ethynyl)-phenylethynyl]-phenyl ester (39)

Inside a N_2-filled dry box, **38** (100 mg, 0.35 mmol), tris-(dibenzylideneacetone)bispalladium (11 mg, 0.010 mmol), triphenylphosphine (9 mg, 0.035 mmol), copper iodide (6.6 mg, 0.035 mmol), and *p*-iodo-phenyl thioacetate **8** (194 mg, 0.7 mmol) were weighed in an oven dried Schlenk flask. Tetrahydrofuran (1 mL) and triethylamine (2 mL) were added to the reaction mixture. The reaction mixture was stirred for 48 h at room temperature and filtered through a small silica gel plug and washed with dichloromethane. The filtrate was evaporated and the residue was purified by flash column chromatography using ethyl acetate/hexanes (60:40) to yield 106 mg (52%) of **39**. Mp 62 °C; IR (thin film): 3317, 2194, 1699, 1519, 1117 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): 8.68 (d, J=11.4 Hz, 0.3H), 8.27 (s, 0.5H), 8.18 (d, J=10.8 Hz, 0.3H), 7.67–7.31 (m, 15H), 6.98 (d, J=8.4 Hz, 0.8H), 2.38 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): 193.9, 193.8, 162.1, 159.2, 137.5, 134.5, 134.2, 133.4, 132.8, 132.4, 128.7, 128.6, 124.3, 124.2, 124.1, 123.9, 123.8, 119.8, 118.9, 118.3, 90.0, 89.9, 89.6, 30.5. Mass calculated for (M^+) $C_{35}H_{23}NO_3S_2$ 570.1198, found (HRMS-FAB) 570.1206.

4.32. Thioacetic acid 4-[3-(4-acetylsulfanyl-phenylethynyl)-5-(4-isocyano-phenylethynyl)-phenylethynyl]-phenyl ester (40)

Compound **39** (110 mg, 0.18 mmol) and triphosgene (28 mg, 0.09) were weighed in an oven dried Schlenk flask. The Schlenk flask was evacuated and back filled with nitrogen (two times). To this was added dry dichloromethane and cooled to 0 °C, and added triethylamine. A solution of benzyltriethyl ammonium chloride (4.2 mg, 0.018 mmol) in 2 mL of dry dichloromethane was added dropwise. The reaction mixture was stirred for 7 h and allowed to warm gradually to room temperature. The reaction mixture was taken in water and extracted with dichloromethane. The organic layer was washed with water and brine, respectively. The organic layer was dried over sodium sulfate before drying it under vacuum. The crude compound was purified by flash column chromatography using ethyl acetate/hexanes (20:80) to yield 40 mg (38%) of pure compound. IR (thin film): 2942, 2864, 1690, 1292 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): 7.67 (m, 3H), 7.55 (m, 6H), 7.43–7.35 (m, 6H), 2.45 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): 193.5, 166.1, 135.3, 134.8, 134.5, 132.9, 132.6, 132.4, 131.4, 131.3, 128.8, 126.7, 124.4, 124.1, 124.0, 123.6, 90.5, 90.2, 89.3, 89.1, 30.5. Mass calculated for (M^+) $C_{35}H_{21}NO_2S_2$ 552.1092, found (HRMS-FAB) 552.1068.

4.33. 4-(3,5-Bis-{4-[(triisopropylsilanyl)-ethynyl]-phenylethynyl}-phenyl)-2-methyl-but-3-yn-2-ol (41)

The general procedure for Sonogashira coupling was followed using molecule **34** (0.5 mmol) and molecule **17** (1.0 mmol). The crude product was purified by flash column chromatography using ethyl acetate/hexanes (20:80). Yield 90% (335 mg); mp 92 °C; IR (thin film): 3333, 2942, 2864, 2153, 1582 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): 7.56 (s, 1H), 7.47 (s, 2H), 7.39 (s, 8H), 1.93 (s, 1H, –OH), 1.56 (s, 6H), 1.07 (s, 42H); ^{13}C NMR ($CDCl_3$, 75 MHz): 134.4, 134.2, 132.2, 131.6, 123.9, 123.7, 122.7, 106.7, 95.2, 93.3, 90.4, 89.6, 80.7, 65.8, 31.6, 18.8, 11.5. Mass calculated for (M^+) $C_{49}H_{61}OSi_2$ 721.4261, found (HRMS-FAB) 721.4286.

4.34. 1-Ethynyl-3,5-bis-{4-[(triisopropylsilanyl)-ethynyl]-phenylethynyl}-benzene (42)

The general procedure for base-promoted deprotection of trialkyl-silyl acetylenes was followed using molecule **41**. The crude compound was purified by flash column chromatography using ethyl acetate/hexanes (10:90) to yield pure **42**. Yield 68% (120 mg); IR (thin film): 3301, 2942, 2864, 2361, 2153, 1579 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): 7.61 (d, J=1.5 Hz, 1H), 7.54 (t, J=1.2 Hz, 2H), 7.41 (d, J=1.2 Hz, 8H), 3.06 (s, 1H), 1.08 (s, 42H); ^{13}C NMR ($CDCl_3$, 75 MHz): 134.8, 132.2, 131.6, 124.1, 124.1, 123.2, 122.7, 106.7, 93.3, 90.6, 89.5, 82.1, 78.7, 18.9, 11.5. Mass calculated for (M^+) $C_{46}H_{54}Si_2$ 663.3842, found (HRMS-FAB) 663.3886.

4.35. 4-[4-(3,5-Bis-{4-[(triisopropylsilanyl)-ethynyl]-phenylethynyl}-phenylethynyl)-phenyl]-2-methyl-but-3-yn-2-ol (43)

The general procedure for Sonogashira coupling was followed using molecule **42** and 4-(4-iodo-phenyl)-2-methyl-but-3-yn-2-ol (1.0 equiv). The crude compound was purified by column chromatography using ethyl acetate/hexanes (25:75) to yield pure **43**. Yield 65% (96 mg); mp 70 °C; IR (thin film): 2940, 2863, 2149, 1578 cm^{-1}; ^1H NMR

($CDCl_3$, 300 MHz): 7.58 (s, 3H), 7.39 (m, 12H), 2.09 (br s, 1H, –OH), 1.57 (s, 6H), 1.08 (s, 42H); ^{13}C NMR ($CDCl_3$, 75 MHz): 134.3, 132.2, 131.8, 131.7, 131.6, 124.1, 124.0, 123.2, 122.7, 106.7, 96.0, 93.3, 90.5, 89.6, 81.9, 65.8, 31.6, 18.8, 11.5. Anal. Calcd for $C_{57}H_{64}OSi_2$: C, 83.36; H, 7.85; Si, 6.84; O, 1.95. Found: C, 83.11; H, 7.76.

Acknowledgements

We thank the National Science Foundation (DMR-0303746) for the support of this work and Jennifer Ayres for a critical reading of this manuscript. Mass spectra were obtained at the Mass Spectrometry Laboratory for Biotechnology. Partial funding for the Facility was obtained from the North Carolina Biotechnology Center, North Carolina State University Department of Chemistry, and the National Science Foundation.

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