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Synthesis of Nanostructures Based on 1,4- and 1,3,5-Ethynylphenyl Subunits with π-Extended Conjugation. Carbon Dendron Units

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Nanometer-sized conjugated 1,4- and 1,3,5-ethynylphenyl oligomers were synthesized starting from 3,5-di(trimethylsilylethynyl)phenylacetylene and *p*-[3,5-di(trimethylsilylethynyl)-1-ethynylphenyl]-phenyl acetylene by cross-coupling reaction with a convenient haloaryl derivative, catalyzed by palladium(II)/copper(I), in excellent yield. The terminal acetylenes were efficiently prepared by a specific protection-deprotection methodology. All ethynylphenyl homologues obtained show fluorescence emission, with the bathochromic shift of approximately 20 nm by each ethynylphenyl unit increasing the conjugate chain. Parallel conjugated ethynylphenyl chains were prepared through the insertion of a 1,5-naphthalene subunit, and the compounds exhibit fluorescence radiation emission.

Introduction

The synthesis and characterization of nanometer-sized conjugated molecules of precise length and constitution are of widespread interest, which is due to their inherent synthetic flexibility that permits the design of molecular architectures with important properties.[1,2] Molecules showing π-extended conjugation, in general, can present electroconductive, magnetic, and optical properties.[3]

A variety of potential applications such as artificial photosynthesis,[4] photocatalysis,[5] molecular photovoltaic cells,[6] molecular informatics,[7] and optoelectronic devices[8,9] are beginning to emerge from this new field of research.

Conjugated systems integrated by 1,2-, 1,3-, 1,4-diethynyl and 1,3,5-triethynylphenyl units have been used in the preparation of aromatic monomers bearing multiple ethynyl groups with electroluminescence properties[10] poly(phenylvinylene) with fluorescence properties, as well as dendrimers[11] with the poly(yne) chain.[12] The triple bonds play the role of a wire while the polyaromatic systems behave as an energy relay subunit.

We now report the controlled synthesis of a novel family of rigid conjugated nanostructures based on 1,4-di(ethynylphenyl) and 1,3,5-tri(ethynylphenyl) units, which serve to prepare stable and geometrically well-defined nanostructures. The diethynyl or triethynyl substituted benzene show a variety of geometric possibilities by their hexagonal structure such as 1,4-linear, 1,3-trigonal and 1,2-closed angle structures (60°).

Results and Discussion

Nanostructure compounds were prepared by linking conjugated subunits with the appropriate geometry. The linear 1,2-di(*p*-iodophenyl)acetylene subunit (**2**)[13] was obtained in practically quantitative yield (98%), starting with the corresponding *E*/*Z* ethenyl mixture **1**,[14] by bromine addition followed by dehydrobromination with potassium *tert*-butoxide, at room temperature. The ethenyl derivative (**1**) was satisfactorily obtained (85%) by the Wittig reaction between *p*-(iodophenyl)carboxaldehyde and the *p*-(iodobenzyl)(triphenyl) phosphonium ylide, prepared in situ, from the corresponding phosphonium salt with potassium *tert*-butoxide in toluene. Scheme 1.

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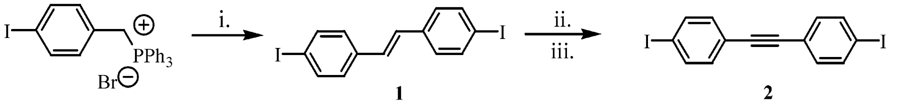
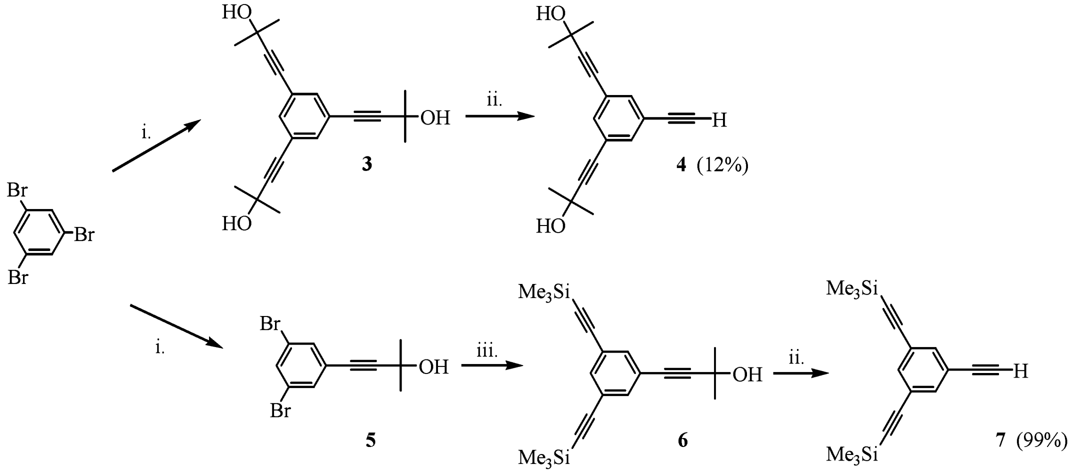
10.1021/jo034972b CCC: $25.00

SCHEME 1[a]



[a] (i) ^{t}BuOK, toluene, *p*-iodobenzaldehyde, (ii) Br_2, CCl_4, (iii) ^{t}BuOK.

SCHEME 2[a]



[a] (i) 2-Methyl-3-butyn-2-ol, $Cl_2Pd(Ph_3P)_2$, CuI, NEt_3, (ii) NaOH, toluene at reflux; (iii) trimethylsilylethyne, $Cl_2Pd(Ph_3P)_2$, CuI, NEt_3, rt.

On the other hand, the synthesis of protected molecular subunits with trigonal geometry was undertaken starting with 1,3,5-tribromobenzene, Scheme 2. Thus, 1,3,5-[tris-(3-hydroxy-3-methyl-1-butynyl)]benzene (**3**)[15] was obtained by heterocoupling of 1,3,5-tribromobenzene with 2-methyl-3-butyn-2-ol in the presence of the palladium/copper catalyst system, in good yield (80%). However, 3,5-[bis(3-hydroxy-3-methyl-1-butynyl)]-1-ethynylbenzene (**4**) was isolated pure in low yield (12%) by deprotection with powdered sodium hydroxide in dry toluene at reflux temperature,[16] Scheme 2.

Because of the low yield of the propargylic derivative **4**, other synthetic methodology was applied. An alternative synthesis of a diprotected derivative involved the heterocoupling reaction between 1,3,5-tribromobenzene and 2-methyl-3-butyn-2-ol, in the presence of the palladium catalyst, to obtain the mono heterocoupled compound **5**[17] (80%), which was doubly heterocoupled with trimethylsilylethyne in triethylamine with the palladium catalyst, at reflux temperature, to give **6** in good yield (85%). The specific deprotection of the propargylic group was carried out with powdered sodium hydroxide in dry toluene at reflux temperature, giving the doubly protected terminal acetylene **7** (colorless oil),[18] Scheme 2.

The specific method for deprotection of 2-methyl-3-butyn-2-ol in dry toluene, in the presence of the trimethylsilylethyne protecting group, requires rigorous anhydrous conditions. There are many references for trimethylsilyl deprotection with different bases such as aqueous sodium hydroxide.[19] Under the anhydrous conditions, sodium hydroxide dissociation was avoided and thus the sodium hydroxide can only behave as a basic group abstracting the acid proton of the alcohol with elimination of acetone. In contrast, in the presence of a small amount of water or MeOH the sodium hydroxide is partially dissociated and a nucleophilic attack of the OR anion to the silicon atom takes place, with formation of Me_3Si-OR and the elimination of the trimethylsilylethyne groups.

Synthesis of Terminal Acetylenes with Trigonal-Linear Geometry. Following the specific deprotection methodology, terminal acetylenes with trigonal-linear geometry were synthesized. Thus, the heterocoupling reaction of the terminal acetylene **7** with 4-(3-hydroxy-3-methyl-1-butynyl)-1-iodobenzene,[20] catalyzed by the palladium/copper system, gives **8** in good yield, which by the specific deprotection of the propargylic group affords **9**, Scheme 3. Likewise, the heterocoupling reaction between **9** and 4-(3-hydroxy-3-methyl-1-butynyl)-1-iodobenzene, in the presence of the palladium/copper system, gives **10** in good yield, which by specific deprotection of the propargylic group affords **11**.

Now, we can synthesize a new family of ethynylphenyl nanostructures with π-extended conjugation along the lineal axis, employing the terminal acetylenes **7**, **9**, and **11**, Scheme 4. Thus, *p*-diiodobenzene as the linear separator unit was doubly heterocoupled with **7** (or **9**), in the presence of the palladium/copper catalyst system, giving **12** (or **13**), Scheme 4.

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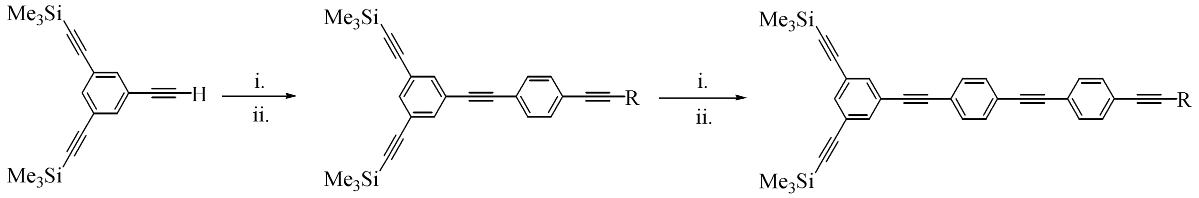
SCHEME 3[a]



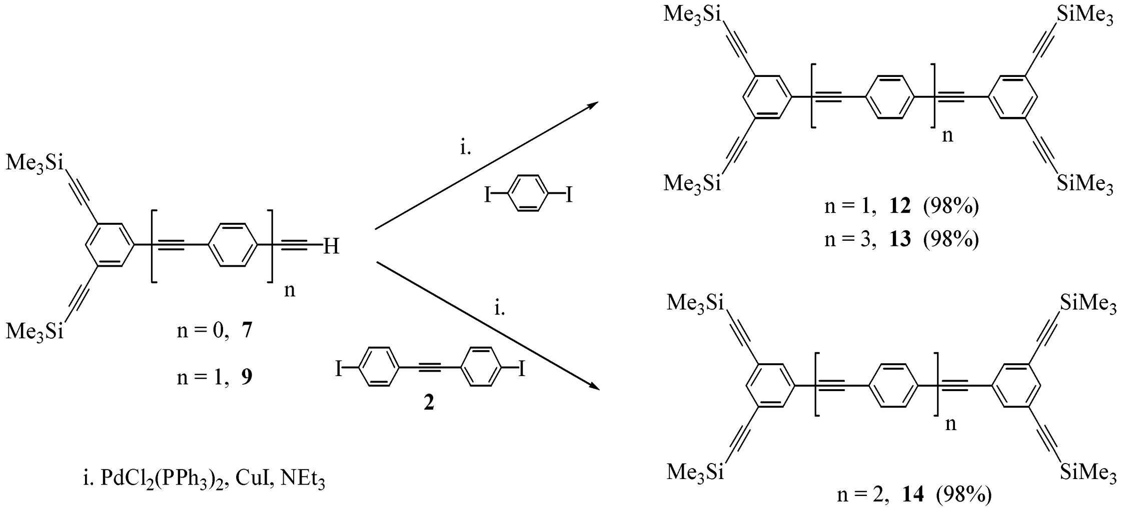
7

8, R= $C(CH_3)_2OH$ (90%)
9, R= H (99%)

10, R= $C(CH_3)_2OH$ (88%)
11, R= H (99%)

[a] (i) $PdCl_2(PPh_3)_2$, CuI, NEt_3, 4-(3-hydroxy-3-methyl-1-butyn)-1-iodobenzene, (ii) NaOH, toluene at reflux temperature.

SCHEME 4[a]



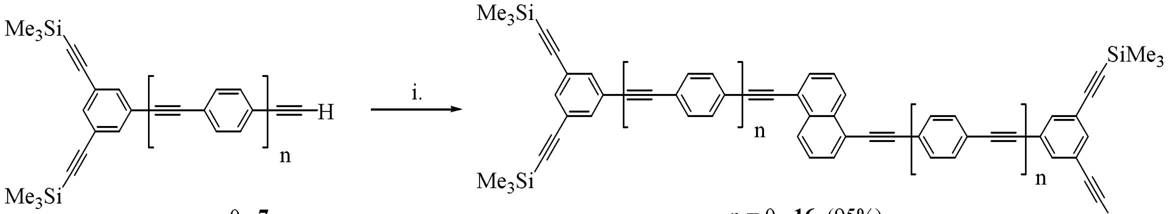
n = 0, **7**
n = 1, **9**

n = 1, **12** (98%)
n = 3, **13** (98%)

n = 2, **14** (98%)
n = 4, **15** (85%)

[a] (i) $PdCl_2(PPh_3)_2$, CuI, NEt_3.

SCHEME 5[a]



n = 0, **7**
n = 1, **9**
n = 2, **11**

n = 0, **16** (95%)
n = 1, **17** (95%)
n = 2, **18** (85%)

[a] (i) $PdCl_2(PPh_3)_2$, CuI, NEt_3, 1,5-diiodonaphthalene.

Moreover, a longer linear separator unit was used for the preparation of the ethynylphenyl homologue compound **14** (or **15**). Thus, double heterocoupling between 1,2-di(*p*-iodophenyl)ethyne (**2**) and the terminal acetylene **7** (or **9**), catalyzed by the palladium/copper system, gives **14** (or **15**) in good yield, Scheme 4.

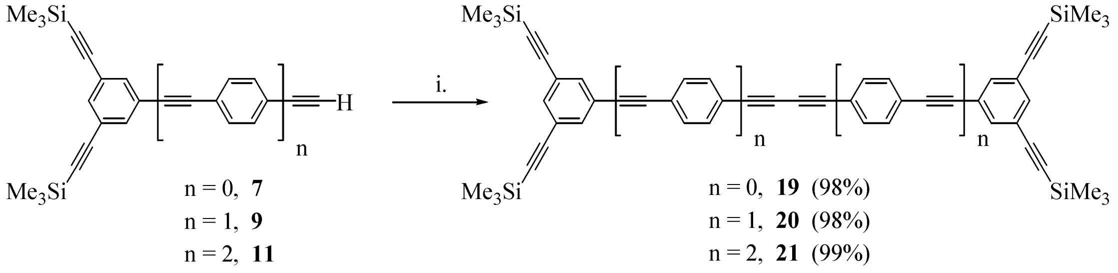
Synthesis of Conjugated Parallel Extended Trigonal-Linear Nanostructures. The intercalation of the 1,5-naphthylethynyl structural module permits extension of a parallel conjugated linear chain. The optical properties of the new nanostructure compounds were analyzed.

Our experience shows that the 1,5-disubstituted naphthylethynyl rings present π-extended conjugation.[16]

The synthesis of a parallel trigonal-linear growing chain structure was undertaken for heterocoupling reaction of the terminal acetylenes with 1,5-diiodonaphthalene. Hence, the heterocoupling reaction between the terminal acetylene **7** (or **9** or **11**) and 1,5-diiodonaphthalene, in the presence of the palladium/copper catalyst system, gives **16** (or **17** or **18**) in good to excellent yield (85−95%), Scheme 5.

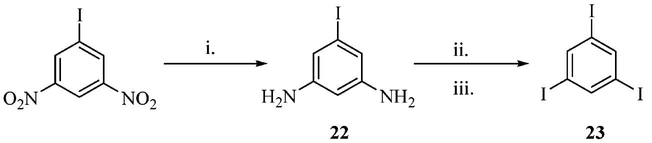
Synthesis of 1,3-Butadiyne Conjugated Nanostructures by Oxidative Dimerization. A practical method to extend the conjugation of the ethynylphenyl chains was the oxidative homocoupling of the corresponding terminal acetylene by the Eglinton-Glaser reac-

SCHEME 6[a]



[a] (i) CuCl, O_2, pyridine.

SCHEME 7[a]



[a] (i) Cl_2Sn, AcOEt, reflux, (ii) $NaNO_2$, H_2SO_4, 0 °C, (iii) KI, H_2O.

tion.[21] The oxidative dimerization of terminal acetylene **7** (or **9**, or **11**) was catalyzed by a cuprous salt (chloride or iodide) in pyridine, under oxygen atmosphere, to give the corresponding 1,3-diyne **19** (or **20**, or **21**), Scheme 6.

Synthesis of Ethynylphenyl Dendrons with a 1,3,5-Trisubstituted Benzene Core. The terminal acetylene subunits were employed for the preparation of the dendron base unit in 1,3,5-trisubstituted benzene with a planar conjugated *star* disposition. However, the heterocoupling reaction of 1,3,5-tribromobenzene with the terminal acetylenes only provided the oxidative dimerization to the corresponding 1,3-diynes, as the Eglinton–Glaser behavior of the catalyst. The more reactive 1,3,5-triiodobenzene was synthesized. The direct iodination of benzene gives a mixture of products that results in low yield and tedious purification.[22,23] A new practical synthesis of 1,3,5-triiodobenzene has been developed to prepare 1,3,5-tri(ethynylphenyl)benzene derivatives.

The synthesis of 1,3,5-triidobenzene was carried out by reduction of 1-iodo-3,5-dinitrobenzene with stannous chloride in ethyl acetate, to obtain 1-iodo-3,5-diaminobenzene (**22**)[24] in practically quantitative yield (98%). The diamino derivate **22** was transformed in 1,3,5-triiodobenzene (**23**) through the double diazonium salt with successive potassium iodide treatment.[16,25,26] Compound **23** was purely obtained as a white solid in good yield (68%), Scheme 7.

The heterocoupling reaction between the terminal acetylene **7** (or **9** or **11**) with 1,3,5-triiodobenzene gives the ethynylphenyl dendron unit **24** (or **25** or **26**), in good yield (80–93%), Scheme 8.

TABLE 1. Wavelengths for First Absorption and Fluorescence Emission Maxima for Compounds 12–15 in CH_2Cl_2 at Room Temperature

compd	UV–vis λ_{max}, nm	ϵ (M^{-1} cm^{-1})	fluorescence λ_{max}, nm	Φ_f[a]
12 ($n = 1$)	326 (348, sh)	44900 (67100)	355, 373	0.65
13 ($n = 3$)	354 (375, sh)	103600 (74600)	394, 413	0.72
14 ($n = 2$)	344 (365, sh)	76300 (61000)	376, 394	0.68
15 ($n = 4$)	360 (383, sh)	114000 (86700)	414, 435	0.77

[a] Fluorescence quantum yield was determined in CH_2Cl_2 relative to 2-aminopyridine in 0.1 N H_2SO_4.

TABLE 2. Wavelengths for First Absorption and Fluorescence Emission Maxima for Compounds 16–18 in CH_2Cl_2 at Room Temperature

compd	UV–vis λ_{max}, nm	ϵ (M^{-1} cm^{-1})	fluorescence λ_{max}, nm	Φ_f[a]
16	352 (368, sh)	33800 (27500)	377, 398	0.60
17	365 (373, sh)	65100 (57300)	397, 418	0.81
18	366 (389, sh)	97800 (73500)	418, 438	0.82

[a] Fluorescence quantum yield was determined in dichloromethane relative to 2-aminopyridine in 0.1 N H_2SO_4.

UV–vis and Fluorescence Analysis of the Conjugated Compounds 12–26 in Dichloromethane. The UV–vis absorption analysis of diluted solutions of the conjugated compounds **12–26** was carried out in dichloromethane. The maxima absorption wavelength (λ_{max}) showed a strong bathochromic shift with the increasing number *n* of repeated units, which is a characteristic for short oligomers of conjugated systems. The corresponding molar extinction coefficients ϵ_{max} also increase with *n*, Tables 1–4.

The conjugated synthesized nanostructures **12–26**, exhibit high fluorescent emission radiation in solution of dichloromethane. An analysis of the optical properties of this family of compounds was carried out. Figure 1 shows the fluorescence spectra of the linear family of the compounds **12–15**.

Compounds **12–15** exhibit two emission bands, which present a bathochromic shift of 20 nm for each ethynylphenyl unit in the chain, while the quantum yield shows a moderate increase (for an estimate error of 3%). This effect seems to be of analytically useful interest to determine the number of ethynylphenyl units in a polymer by means of the fluorescence analysis data.

Figure 2 shows the fluorescence spectra of the naphthylethynyl nanostructures **16–18**. A bathochromic shift of 20 nm between the naphthylethynyl homologues was

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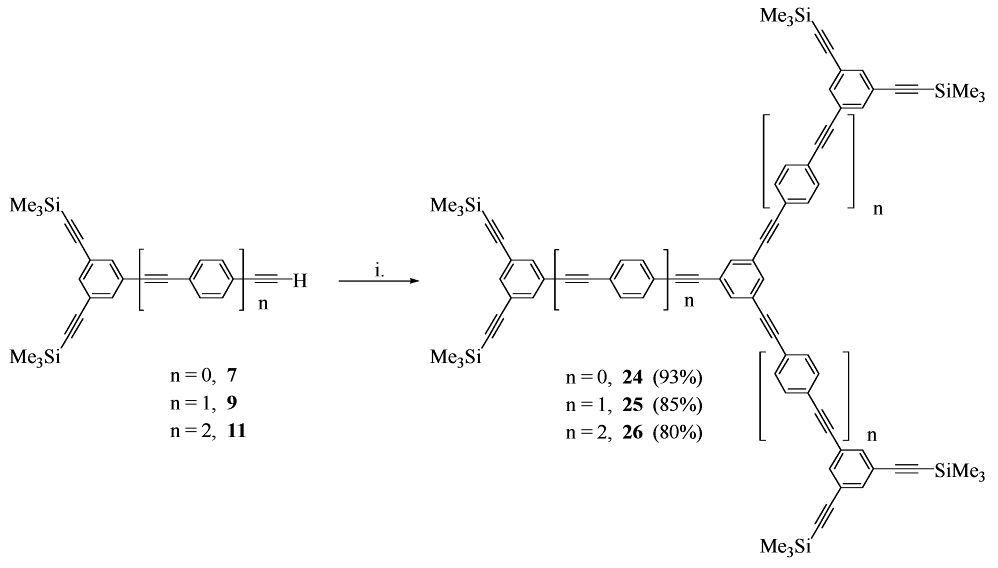
SCHEME 8[a]



n = 0, **7**
n = 1, **9**
n = 2, **11**

n = 0, **24** (93%)
n = 1, **25** (85%)
n = 2, **26** (80%)

[a] (i) 1,3,5-Triiodobenzene, $Cl_2Pd(PPh_3)_2$, CuI, NEt_3.

TABLE 3. Wavelengths for First Absorption and Fluorescence Emission Maxima for Compounds 19−21 in CH_2Cl_2 at Room Temperature

compd	UV−vis λ_{max}, nm	ϵ (M^{-1} cm^{-1})	fluorescence λ_{max}, nm	Φ_f[a]
19	314 (336, sh)	28200 (22800)	365, 388	<0.01
20	346 (375, sh)	96000 (64800)	386, 412	0.33
21	369 (387, sh)	123900 (98500)	414, 438	0.54

[a] Fluorescence quantum yield was determined in dichloromethane relative to 2-aminopyridine in 0.1 N H_2SO_4.

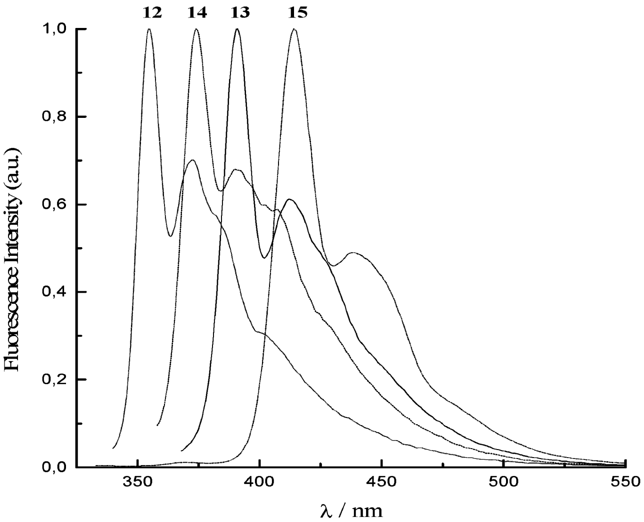


FIGURE 1. Normalized emission spectra for compounds **12**−**15** in CH_2Cl_2 at room temperature.

also observed, while high quantum yield values were measured, 81% and 82% for **17** and **18**, respectively, Table 2.

Figure 3 shows the fluorescence spectra of the 1,3-diyne family compounds **19**−**21**. A bathochromic shift was also observed, although the wavelength of the emission shows variable increasing values closely to 20 nm for each ethynylphenyl unit in the chain, Table 3.

TABLE 4. Wavelengths for First Absorption and Fluorescence Emission Maxima for Compounds 24−26 in CH_2Cl_2 at Room Temperature

compd	UV−vis λ_{max}, nm	ϵ (M^{-1} cm^{-1})	fluorescence λ_{max}, nm	Φ_f[a]
24	291 (308, sh)	89800 (87400)	353, 367	0.16
25	329 (351, sh)	181200 (143700)	356, 377	0.48
26	347 (366, sh)	187500 (156000)	377, 398	0.80

[a] Fluorescence quantum yield was determined in dichloromethane relative to 2-aminopyridine in 0.1 N H_2SO_4.

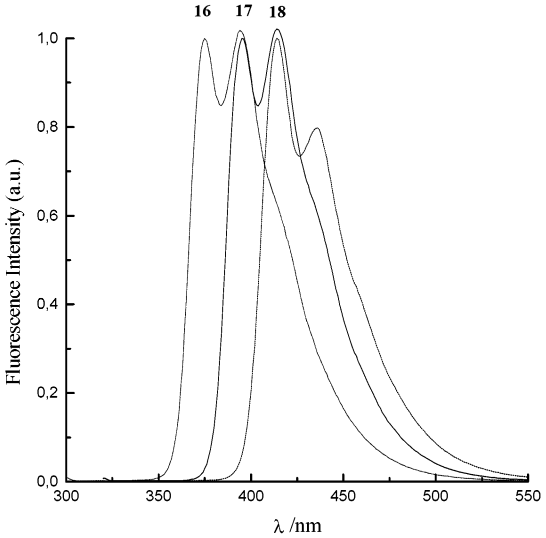


FIGURE 2. Normalized emission spectra for compounds **16**−**18** in CH_2Cl_2 at room temperature.

Finally, Figure 4 shows the fluorescence spectra for the conjugated 1,3,5-trisubstituted benzene dendron units **24**−**26**. The bathochromic wavelength shift effect, increasing by 20 nm, was only observed between compounds **25** and **26**, and this increase fails for the compounds **24** (linked to the benzene core) and **25**, in the two emission bands. However, the quantum yield shows

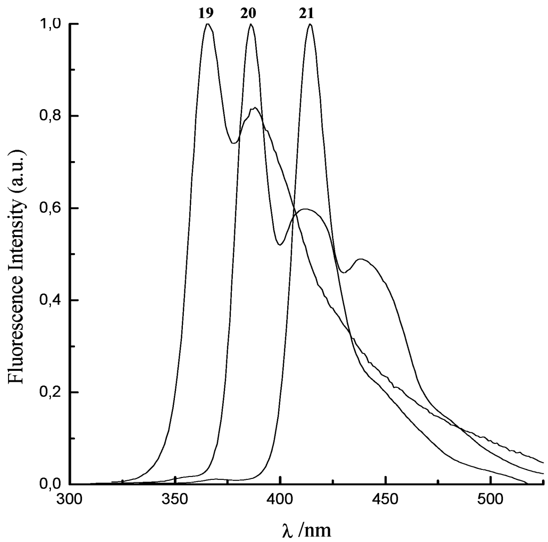


FIGURE 3. Normalized emission spectra for compounds **19**–**21** in CH_2Cl_2 at room temperature.

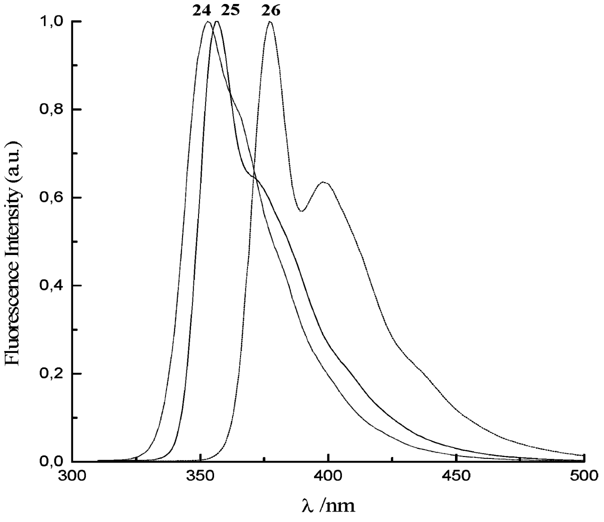


FIGURE 4. Normalized emission spectra for compounds **24**–**26** in CH_2Cl_2 at room temperature.

high increasing with the number of the ethynylphenyl units in the chain, Table 4.

Conclusions

This work describes a simple and useful synthetic route to prepare 1,4- and 1,3,5-ethynylphenyl oligomers by means of the specific deprotection of the terminal acetylene bond. The Sonogashira cross-coupling reaction between a convenient haloaryl derivative and a terminal acetylene such as 3,5-di(trimethylsilylethynyl)phenylacetylene or *p*-[3,5-di(trimethylsilylethynyl)-1-ethynylphenyl]phenylacetylene, catalyzed by the palladium/copper system, give the corresponding ethynylphenyl oligomers in excellent yield. In the UV–vis spectra, the maxima absorption wavelengths λ_{max} show a bathochromic shift with the conjugated ethynylphenyl number *n* of repeated units. The corresponding molar extinction coefficients ϵ_{max} also increase with *n*. All the ethynylphenyl homologue compounds obtained show a fluorescence emission radiation, with a bathochromic shift of 20 nm for each ethynylphenyl unit increasing the conjugated chain. In general, the homologue compounds show high quantum yields (65–82%), which increase whith the conjugation.

Experimental Section

General Procedures. Melting points were determined in open capillaries and are uncorrected. IR spectra were recorded using KBr pellets or NaCl plates, and only partial data is reported. Proton nuclear magnetic resonance (^1H NMR) spectra were recorded at 300 MHz. Chemical shifts are reported in delta (δ) units, parts per million (ppm) downfield from trimethylsilane. Coupling constants are reported in hertz (Hz). Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded at 75 MHz. Chemical shifts are reported in delta (δ) units, parts per million (ppm) relative to the center of the triplet at 77.00 ppm for deuteriochloroform. Mass spectra were obtained at an ionizing potential of 70 eV and reported as *m*/*e* (relative intensity). Accurate masses are reported for the molecular ion (M + 1) or a suitable fragment ion. Flash chromatography was performed on silica gel 60 (200–400 mesh) using the indicated solvents. The UV–vis spectra frequencies are given in nm and ϵ in L mol^{-1} cm^{-1}.

3,5-[Bis(3-hydroxy-3-methyl-1-butynyl)]-1-ethynylbenzene (4). General Procedure for Synthesis of Arylacetylenes.[27] To a solution of **3** (1 g, 3.08 mmol) in anhydrous toluene (30 mL) was added finely powdered sodium hydroxide (37 mg, 9.26 mmol) under argon atmosphere. The mixture was warmed at the reflux temperature for 3 h (monitored by TLC) and then filtered. The solvent was removed, giving **4** as a pale brown solid (98.3 mg, 12%), mp 95–97 °C. IR (KBr): cm^{-1} 3302 (≡C–H), 3270 (O–H), 2200 (C≡C), 1580 and 1413 (C=C), 1160 (C–OH), 883 (1,3,5 trisubst). ^1H NMR ($CDCl_3$): δ 7.44 (br s, 3H), 3.06 (s, 1H), 1.52 (s, 12H). ^{13}C NMR ($CDCl_3$): δ 134.2, 123.2, 122.6, 94.8, 81.8, 80.5, 78.2, 65.5, 31.07. $C_{18}H_{18}O_2$ (266.33): anal. calcd C 81.17, H 6.81; found C 81.32, H 6.51.

3,5-Bis(trimethylsilylethynyl)-1-(3-hydroxy-3-methyl-1-butynyl)benzene (6). General Procedure of the Heterocoupling Reaction. To a solution of compound **5** (1.0 g, 3.14 mmol), trimethylsilylethyne (1.11 mL, 7.85 mmol), and 2-methyl-3-butyn-2-ol (3.17 g, 38.22 mmol) in freshly distilled triethylamine (30 mL) under argon atmosphere and at room temperature, was added dichloro bis(triphenylphosphine)-palladium (551 mg, 0.785 mmol) and a small amount of cuprous iodide. The mixture was stirred at 60 °C for 15 h (monitored by TLC) and then, the amine was removed under reduced pressure. The crude residue was washed with a saturated aqueous ammonium chloride solution with a small amount of KCN and extracted with dichloromethane. The extracts were dried on anhydrous sodium sulfate, and after filtration the solvent was removed and the residue was purified by silica gel column chromatography, eluting with hexane/ethyl acetate (4:1). Compound **6** was isolated as a white solid (939 mg, 85%), mp 85–86 °C. IR (KBr): cm^{-1} 3312 (O–H), 2160 (C≡C), 1581 and 1412 (C=C), 1250 (Si–CH_3), 882 (1,3,5 trisubst.), 759 (C–Si). ^1H NMR ($CDCl_3$): δ 7.47 (t, 1H, J = 1.4 Hz), 7.43 (d, 2H, J = 1.4 Hz), 1.57 (s, 6H), 0.21 (s, 18H). ^{13}C NMR ($CDCl_3$): δ 134.7, 134.5, 123.6, 123.2, 103.1, 95.5, 94.8, 80.4, 65.4, 31.3, −0.19. $C_{21}H_{28}OSi_2$ (362.62): anal. calcd C 71.53, H 8.00; found C 71.59, H 7.93.

3,5-Bis(trimethylsilylethynyl)-1-ethynylbenzene (7). Following the general method used for the synthesis of **4**, to a solution of compound **6** (280 mg, 0.79 mmol) in anhydrous toluene (40 mL) was added finely powdered sodium hydroxide (3.16 mg, 0.079 mmol). The mixture was stirred for 4 h and then filtered. The solvent was removed, giving **7** as colorless oil[18] (229 mg, 99%). IR (NaCl): cm^{-1} 3302 (≡C–H), 2162 (C≡C), 1580 and 1413 (C=C), 1250 (Si–CH_3), 883 (1,3,5 trisubst.), 760 (C–Si). ^1H NMR ($CDCl_3$): δ 7.53 (t, 1H, J = 1.4 Hz), 7.50 (d, 2H, J = 1.4 Hz), 3.06 (s, 1H), 0.23 (s, 18H). ^{13}C NMR

(CDCl$_3$): δ 135.3, 135.0, 123.7, 122.6, 102.9, 95.5, 81.8, 78.2, −0.19. $C_{18}H_{22}Si_2$ (294.54): anal. calcd C 73.40, H 7.53; found C 73.52, H 7.46.

1-[(3,5-Bis-trimethylsilylethynylphenyl)ethynyl]-4-(3-hydroxy-3-methyl-1-butynyl)benzene (8). Following the general method used for the synthesis of **6**, a mixture of 4-(3-hydroxy-3-methyl-1-butynyl)-1-iodobenzene[20] (350 mg, 1.225 mmol), compound **7** (360 mg, 1.225 mmol), dichloro bis(triphenylphosphine)palladium (88 mg, 0.013 mmol), and triethylamine (30 mL) was stirred for 12 h. Purification was carried out by flash chromatography on a silica gel column, eluting with hexane/ethyl acetate (4:1), providing **8** as a white solid (498 mg, 90%), mp 95−97 °C. IR (KBr): cm^{-1} 3356 (O−H), 2157 (C≡C), 1576 and 1506 (C═C), 1249 (Si−CH$_3$), 1161 (C−OH), 840 (1,3,5 trisubst.), 758 (C−Si). ^{1}H NMR (CDCl$_3$): δ 7.54 (d, 2H, J = 1.6 Hz), 7.52 (t, 2H, J = 1.6 Hz), 7.43 (d, 2H, J = 8.5 Hz), 7.38 (d, 2H, J = 8.5 Hz), 1.62 (s, 6H), 0.23 (s, 18H). ^{13}C NMR (CDCl$_3$): δ 134.9, 134.5, 131.6, 131.4, 123.7, 123.4, 122.9, 122.5, 103.1, 95.76, 96.7, 89.9, 89.6, 81.7, 65.6, 31.4, −0.17. $C_{28}H_{32}OSi_2$ (452.73): anal. calcd C 76.93, H 7.12; found C 77.02, H 7.06.

1-[(3,5-Bis-trimethylsilylethynylphenyl)ethynyl]-4-ethynylbenzene (9). Following the general method used for the synthesis of **4**, a mixture of compound **8** (350 mg, 0.774 mmol), anhydrous toluene (40 mL), and finely powdered sodium hydroxide (3.2 mg, 0.0774 mmol) was stirred for 4 h and then filtered. The solvent was removed, giving **9** as an orange solid (302 mg, 99%), mp 80−83°C. IR (KBr): cm^{-1} 3302 (≡C−H), 2157 (C≡C), 1576 and 1506 (C═C), 1249 (Si−CH$_3$), 840 (1,3,5 trisubst.), 758 (C−Si). ^{1}H NMR (CDCl$_3$): δ 7.57 (d, 2H, J = 1.6 Hz), 7.54 (t, 1H, J = 1.6 Hz), 7.48 (d, 2H, J = 8.5 Hz), 7.45 (d, 2H, J = 8.5 Hz), 3.19 (s, 1H,), 0.26 (s, 18H). ^{13}C NMR (CDCl$_3$): δ 135.0, 134.5, 132.1, 131.4, 123.7, 123.4, 123.1, 122.2, 103.1, 95.76, 89.9, 89.6, 83.1, 79.1, −0.17. $C_{26}H_{26}Si_2$ (394.66): anal. calcd C 79.13, H 6.64; found C 79.19, H 6.58.

1-{[(3,5-Bis-trimethylsilylethynylphenyl)ethynylphenyl]-ethynyl}-4-(3-hydroxy-3-methyl-1-butynyl)benzene (10). Following the general method used for the synthesis of **6**, a mixture of 4-(3-hydroxy-3-methyl-1-butynyl)-1-iodobenzene[20] (181 mg, 0.642 mmol), compound **9** (250 mg, 0.642 mmol), dichloro bis(triphenylphosphine)palladium (45 mg, 0.06 mmol), and triethylamine (30 mL) was stirred for 15 h. Purification was carried out by flash chromatography on a silica gel column, eluting with hexane/ethyl acetate (4:1), providing **10** as a white solid (312 mg, 88%), mp 214−215 °C. IR (KBr): cm^{-1} 3355 (O−H), 2157 (C≡C), 1580 and 1511 (C═C), 1250 (Si−CH$_3$), 1161 (C−OH), 840 (1,3,5 trisubst), 758 (C−Si). ^{1}H NMR (CDCl$_3$): δ 7.55 (d, 2H, J = 1.6 Hz), 7.53 (t, 2H, J = 1.6 Hz), 7.48 (br s, 4H), 7.46 (d, 2H, J = 8.3 Hz), 7.39 (d, 2H, J = 8.3 Hz), 1.62 (s, 6H), 0.24 (s, 18H). ^{13}C NMR (CDCl$_3$): δ 134.9, 134.5, 131.5, 131.4, 123.8, 123.4, 123.1, 122.8, 103.12, 96.12, 95.76, 90.9, 90.7, 90.0, 89.6, 65.6, 31.4, −0.22. $C_{37}H_{36}OSi_2$ (552.85): anal. calcd C 80.38, H 6.56; found C 80.45, H 6.49.

1-{[(3,5-Bis-trimethylsilylethynylphenyl)ethynylphenyl]-ethynyl}-4-ethynylbenzene (11). Following the general method used for the synthesis of **4**, a mixture of compound **10** (270 mg, 0.48 mmol), anhydrous toluene (40 mL), and finely powdered sodium hydroxide (2 mg, 0.048 mmol) was stirred for 4 h and then filtered. The solvent was removed giving **11** as an orange solid (235 mg 99%), mp 148−150 °C. IR (KBr): cm^{-1} 3302 (≡C−H), 2157 (C≡C), 1576 and 1506 (C═C), 1249 (Si−CH$_3$), 840 (1,3,5 trisubst), 758 (C−Si). ^{1}H NMR (CDCl$_3$): δ 7.57 (d, 2H, J = 1.6 Hz), 7.55 (t, 2H, J = 1.6 Hz), 7.51 (d, 2H, J = 8.7 Hz), 7.48 (s a, 4H), 7.47 (d, 2H, J = 8.7 Hz), 3.20 (s, 1H), 0.26 (s, 18H). ^{13}C NMR (CDCl$_3$): δ 134.9, 134.5, 132.0, 131.5, 131.4, 123.8, 123.5, 123.4, 123.0, 122.8, 122.1, 103.1, 95.76, 90.9, 90.8, 89.6, 83.2, 79.08, −0.17. $C_{34}H_{30}Si_2$ (494.77): anal. calcd C 82.54, H 6.11; found C 82.58, H 6.41.

1,4-Bis[(3,5-bis-trimethylsilylethynylphenyl)ethynyl]-benzene (12). Following the general method used for the synthesis of **6**, a mixture 1,4-diiodobenzene (112 mg, 0.34 mmol), compound **7** (200 mg, 0.68 mmol), dichloro bis(triphenylphosphine)palladium (45 mg, 0.068 mmol), and triethylamine (30 mL) was stirred for 15 h. Purification was carried out by flash chromatography on a silica gel column, eluting with hexane, giving **12** as a white solid (220 mg, 98%), mp 220−221 °C. UV−vis (CH$_2$Cl$_2$), λ_{max} (nm): 348 (sh, ϵ, 44900), 326 (ϵ, 67100), 270 (ϵ, 142300). Fluorescence (CH$_2$Cl$_2$), λ_{max} (nm): 373, 355 (ϕ = 0.65). IR (KBr): cm^{-1} 2158 (C≡C), 1579 and 1508 (C═C), 1251 (Si−CH$_3$), 840 (1,3,5 trisubst), 758 (C−Si). ^{1}H NMR (CDCl$_3$): δ 7.56 (d, 4H, J = 1.6 Hz), 7.53 (t, 2H, J = 1.6 Hz), 7.46 (br s, 4H), 0.24 (s, 36H). ^{13}C NMR (CDCl$_3$): δ 134.9, 134.5, 131.6, 123.7, 123.4, 122.7, 103.1, 95.7, 89.9, 89.6, −0.17. MS m/z (relative intensity): 662.1 (M$^+$ 80), 559 (10), 316.2 (55). $C_{42}H_{46}Si_4$ (663.16): anal. calcd C 76.07, H 6.99; found C 76.15, H 6.91.

1,4-Bis{(3,5-bis-trimethylsilylethynylphenyl)ethynyl-phenyl]ethynyl}benzene (13). Following the general method used for the synthesis of **6**, a mixture of 1,4-diiodobenzene (100 mg, 0.303 mmol), compound **9** (239 mg, 0.61 mmol), dichloro bis(triphenylphosphine)palladium (42.5 mg, 0.06 mmol), and triethylamine (30 mL) was stirred for 12 h. Purification was carried out by flash chromatography on a silica gel column, eluting with hexane, providing **13** as a green solid (256 mg, 98%), mp 270−273 °C. UV−vis (CH$_2$Cl$_2$), λ_{max} (nm): 375 (sh, ϵ, 74600), 354 (ϵ, 103600), 269 (ϵ, 86700), 255 (ϵ, 82000), 240 (ϵ, 84800). Fluorescence (CH$_2$Cl$_2$), λ_{max} (nm): 413, 394 (ϕ = 0.72). IR (KBr): cm^{-1} 2157 (C≡C), 1578 and 1518 (C═C), 1249 (Si−CH$_3$), 842 (1,3,5 trisubst), 758 (C−Si). ^{1}H NMR (CDCl$_3$): δ 7.56 (d, 4H, J = 1.6 Hz), 7.53 (t, 2H, J = 1.6 Hz), 7.51−7.49 (m, 12H), 0.24 (s, 36H). ^{13}C NMR (CDCl$_3$): δ 134.9, 134.5, 131.6, 123.7, 123.4, 123.1, 123.0, 122.7, 103.0, 95.7, 91.0, 91.1, 90.0, 89.6, −0.17. MS m/z (relative intensity): 862.1 (M$^+$ 100), 416.2 (66). $C_{58}H_{54}Si_4$ (863.39): anal. calcd C 80.68, H 6.30; found C 80.79, H 6.21.

Di{4-[(3,5-bis-trimethylsilylethynylphenyl)ethynyl-phenyl]ethynyl}ethyne (14). Following the general method used for the synthesis of **6**, a mixture of compound **2** (50 mg, 0.12 mmol), compound **7** (68.41 mg, 0.24 mmol), dichloro bis(triphenylphosphine)palladium (16,3 mg, 0.024 mmol), and triethylamine (30 mL) was stirred for 15 h. Purification was carried out by flash chromatography on a silica gel column, eluting with hexane providing **14** as a green solid (89.7 mg, 98%), mp 220−223 °C. UV−vis (CH$_2$Cl$_2$), λ_{max} (nm): 365 (sh, ϵ, 61000), 344 (ϵ, 76300), 266 (ϵ, 68200), 254 (ϵ, 75800), 240 (ϵ, 75500). Fluorescence (CH$_2$Cl$_2$), λ_{max} (nm): 394, 376 (ϕ = 0.68). IR (KBr): cm^{-1} 2160 (C≡C), 1578 and 1466 (C═C), 1250 (Si−CH$_3$), 878 (1,3,5 trisubst), 759 (C−Si). ^{1}H NMR (CDCl$_3$): δ 7.56 (d, 4H, J = 1.6 Hz), 7.53 (t, 2H, J = 1.6 Hz), 7.51 (d, 4H, J = 8.9 Hz), 7.47 (d, 4H, J = 8.9 Hz), 0.24 (s, 36H). ^{13}C NMR (CDCl$_3$): δ 134.9, 134.5, 131.6, 123.7, 123.4, 123.1, 122.7, 103.0, 95.7, 91.0, 90.0, 89.6, −0.19. MS m/z (relative intensity): 762.2 (M$^+$ 100), 690.2 (5), 366.3 (55). $C_{50}H_{50}Si_4$ (763.27): anal. calcd C 78.68, H 6.60; found C 78.75, H 6.53.

Di{4-[((3,5-bis-trimethylsilylethynylphenyl)ethynyl-phenyl)ethynylphenyl]ethynyl}ethyne (15). Following the general method used for the synthesis of **6**, a mixture of compound **2** (109 mg, 0.254 mmol), compound **9** (200 mg, 0.507 mmol), dichloro bis(triphenylphosphine)palladium (19 mg, 0.02 mmol), and triethylamine (30 mL) was stirred for 15 h. Purification was carried out by flash chromatography on a silica gel column, eluting with hexane, providing **15** as a green solid (208 mg, 85%), mp 273−275 °C. UV−vis (CH$_2$Cl$_2$), λ_{max} (nm): 383 (sh, ϵ, 86700), 360 (ϵ, 114000), 267 (ϵ, 78500), 240 (ϵ, 96000). Fluorescence (CH$_2$Cl$_2$), λ_{max} (nm): 435, 414 (ϕ = 0.77). IR (KBr): cm^{-1} 2160 (C≡C), 1578 and 1466 (C═C), 1250 (Si−CH$_3$), 878 (1,3,5 trisubst), 759 (C−Si). ^{1}H NMR (CDCl$_3$): δ 7.56 (d, 4H, J = 1.6 Hz), 7.52−7.49 (m, 18H), 0.24 (s, 36H). ^{13}C NMR (CDCl$_3$): δ 134.9, 134.5, 131.6, 123.8, 123.5, 123.1, 123.0, 122.8, 103.1, 95.8, 91.0, 91.1, 90.0, 89.6, −0.17. MS m/z (relative intensity): 962.2 (M$^+$ 100), 663.2 (51). $C_{66}H_{58}Si_4$ (963.51): anal. calcd C 82.27, H 6.07; found C 82.32, H 6.01.

1,5-Bis[(3,5-bis-trimethylsilylethynylphenyl)ethynyl]-naphthalene (16). Following the general method used for the synthesis of **6**, a mixture of 1,5-diiodonaphthalene[16] (100 mg, 0.26 mmol), compound **7** (154.8 mg, 0.52 mmol), dichloro bis(triphenylphosphine)palladium (36.9 mg, 0.052 mmol) and triethylamine (30 mL) was stirred for 12 h. Purification was carried out by flash chromatography on a silica gel column, eluting with hexane, providing **16** as a white solid (176.1 mg, 95%), mp 228−230 °C: UV−vis (CH$_2$Cl$_2$), λ_{max} (nm): 368 (sh, ϵ, 27500), 352 (ϵ, 33800), 268 (ϵ, 80700), 254 (ϵ, 80200), 243 (ϵ, 95400). Fluorescence (CH$_2$Cl$_2$), λ_{max} (nm): 398, 377 ($\phi = 0.60$). IR (KBr): cm^{-1} 2152 (C≡C), 1583 and 1410 (C=C), 1250 (Si−CH$_3$), 843 (1,3,5 trisubst), 759 (C−Si). ^{1}H NMR (CDCl$_3$): δ 8.41 (d, 2H, J = 8.61 Hz), 7.79 (d, 2H, J = 6.5 Hz), 7.68 (d, 4H, J = 1.6 Hz), 7.55−7.6 (m, 4H), 0.26 (s, 36H). ^{13}C NMR (CDCl$_3$): δ 135.0, 134.5, 133.0, 131.2, 127.3, 126.3, 123.8, 123.7, 120.9, 103.1, 95.8, 93.0, 88.3, −0.14. MS m/z (relative intensity): 712.3 (M$^+$ 100), 609.2 (8), 341.3 (50). $C_{46}H_{48}Si_4$ (713.22): anal. calcd C 77.46, H 6.78; found C 77.52, H 6.71.

1,5-Bis{[(3,5-bis-trimethylsilylethynylphenyl)ethynylphenyl]ethynyl}naphthalene (17). Following the general method used for the synthesis of **6**, a mixture of 1,5-diiodonaphthalene[16] (100 mg, 0.26 mmol), compound **9** (204.8 mg, 0.52 mmol), dichloro bis(triphenylphosphine) palladium (36.9 mg, 0.052 mmol), and triethylamine (30 mL) was stirred for 12 h. Purification was carried out by flash chromatography on a silica gel column, eluting with hexane, providing **17** as a yellow solid (255.6 mg, 95%), mp 271−273 °C. UV−vis (CH$_2$Cl$_2$), λ_{max} (nm): 373 (sh, ϵ, 57300), 365 (ϵ, 65100), 270 (ϵ, 106600), 247 (ϵ, 110500). Fluorescence (CH$_2$Cl$_2$), λ_{max} (nm): 418, 397 ($\phi = 0.81$). IR (KBr): cm^{-1} 2158 (C≡C), 1579 and 1411 (C=C), 1250 (Si−CH$_3$), 843 (1,3,5 trisubst), 757 (C−Si). ^{1}H NMR (CDCl$_3$): δ 8.45 (d, 2H, J = 8.5 Hz), 7.83 (d, 2H, J = 6.5 Hz), 7.51−7.64 (m, 16H), 0.25 (s, 36H). ^{13}C NMR (CDCl$_3$): δ 134.9, 134.5, 133.0, 131.69, 131.63, 131.113, 127.2, 126.2, 123.8, 123.8, 123.5, 123.3, 122.8, 121.1, 103.1, 95.8, 94.3, 90.0, 89.6, 89.3, −0.19. MS m/z (relative intensity): 912.5 (M$^+$ 100), 441.4 (43), 207.0 (17). $C_{62}H_{56}Si_4$ (913.45): anal. calcd C 81.52, H 6.18; found C 81.60, H 6.10.

1,5-Bis{[((3,5-bis-trimethylsilylethynylphenyl)ethynylphenyl)ethynylphenyl]ethynyl}naphthalene (18). Following the general method used for the synthesis of **6**, a mixture of 1,5-diiodonaphthalene[16] (38.44 mg, 0.103 mmol), compound **11** (100 mg, 0.205 mmol), dichloro bis(triphenylphosphine) palladium (10 mg, 0.02 mmol), and triethylamine (30 mL) was stirred for 12 h. Purification was carried out by flash chromatography on a silica gel column, eluting with hexane, providing **18** as a yellow solid (97.5 mg, 85%), mp 298−300 °C. UV−vis (CH$_2$Cl$_2$), λ_{max} (nm): 389 (sh, ϵ, 73500), 366 (ϵ, 97800), 268 (ϵ, 58900), 241 (ϵ, 88100). Fluorescence (CH$_2$Cl$_2$), λ_{max} (nm): 438, 418 ($\phi = 0.82$). IR (KBr): cm^{-1} 2159 (C≡C), 1578 and 1411 (C=C), 1253 (Si−CH$_3$), 843 (1,3,5 trisubst), 757 (C−Si). ^{1}H NMR (CDCl$_3$): δ 8.45 (d, 2H, J = 8.5 Hz), 7.83 (d, 2H, J = 6.5 Hz), 7.47−7.66 (m, 24H), 0.25 (s, 36H). ^{13}C NMR (CDCl$_3$): δ 135.0, 134.6, 133.1, 131.66, 131.16, 127.2, 126.2, 123.5, 123.3, 123.2, 123.1, 122.8, 121.1, 103.1, 95.8, 94.4, 91.1, 91.0, 90.0, 89.7, 89.3, −0.14. MS m/z (relative intensity) FAB+: 1112.5 (M$^+$ 100). $C_{78}H_{64}Si_4$ (1113.68): anal. calcd C 84.12, H 5.79; found C 84.17, H 5.74.

1,4-Di(3,5-bis-trimethylsilylethynylphenyl)butadiyne (19) by Homocoupling Reaction of Arylacetylene. General Procedure. To a solution of cuprous chloride (74 mg, 0.33 mmol) in dry pyridine (25 mL), under oxygen atmosphere at 40°C, was added a solution of the arylacetylene **7** (400 mg, 1.35 mmol) in dry pyridine (10 mL), and the mixture was stirred for 40 min. The solvent was removed, giving a residual solid that was washed with ammonium hydroxide until the blue color disappeared and then extracted with dichloromethane. The organic layer was dried on anhydrous magnesium sulfate, and after filtration and solvent evaporation a brown solid was obtained, which was purified by silica gel column chromatography, eluting with hexane/dichloromethane (4:1), giving **19** as a white solid (390 mg 98%), mp 198−201 °C. UV−vis (CH$_2$Cl$_2$), λ_{max} (nm): 336 (sh, ϵ, 22800), 314 (ϵ, 28200), 269 (ϵ, 90000), 256 (ϵ, 77100). Fluorescence (CH$_2$Cl$_2$), λ_{max} (nm): 388, 365 ($\phi < 0.01$). IR (KBr): cm^{-1} 2158 (C≡C), 1577 and 1503 (C=C), 1249 (Si−CH$_3$), 842 (1,3,5 trisubst), 758 (C−Si). ^{1}H NMR (CDCl$_3$): δ 7.55 (t, 2H, J = 1.6 Hz), 7.52 (d, 4H, J = 1.6 Hz), 0.24 (s, 36H). ^{13}C NMR (CDCl$_3$): δ 135.8, 135.2, 123.8, 122.1, 102.7, 96.2, 80.1, 74.5, −0.22. MS m/z (relative intensity): 586.1 (M$^+$ 100), 483.1 (35), 278.2 (39), 73 (84). $C_{36}H_{42}Si_4$ (587.06): anal. calcd C 73.65, H 7.21; found C 73.70, H 7.17.

1,4-Di[4-(3,5-bis-trimethylsilylethynylphenyl)ethynylphenyl]butadiyne (20). Following the general method used for the preparation of **19**, a mixture of cuprous chloride (37.9 mg, 0.19 mmol) in dry pyridine (25 mL) and compound **9** (301.9 mg, 0.76 mmol) in dry pyridine (20 mL) was stirred for 1 h. Purification was carried out by flash chromatography on a silica gel column, eluting with hexane/dichloromethane (4:1), providing **20** as a green solid (293.2 mg, 98%), mp 249−252 °C. UV−vis (CH$_2$Cl$_2$), λ_{max} (nm): 375 (sh, ϵ, 64800), 346 (ϵ, 96000), 270 (ϵ, 122100). Fluorescence (CH$_2$Cl$_2$), λ_{max} (nm): 412, 386 ($\phi = 0.33$). IR (KBr): cm^{-1} 2158 (C≡C), 1577 and 1503 (C=C), 1249 (Si−CH$_3$), 842 (1,3,5 trisubst), 758 (C−Si). ^{1}H NMR (CDCl$_3$): δ 7.56 (d, 4H, J = 1.6 Hz), 7.53 (t, 2H, J = 1.6 Hz), 7.51 (d, 4H, J = 8.5 Hz), 7.45 (d, 4H, J = 8.5 Hz), 0.24 (s, 36H). ^{13}C NMR (CDCl$_3$): δ 135.0, 134.5, 132.4, 131.6, 123.8, 123.3, 121.7, 103.1, 95.8, 90.3; 89.8, 82.1, 75.7, −0.19. MS m/z (relative intensity): 786.1 (M$^+$ 100), 378.2 (48), 73 (54). $C_{52}H_{50}Si_4$ (787.30): anal. calcd C 79.33, H 6.40; found C 79.38, H 6.37.

1,4-Di{4-[(3,5-bis-trimethylsilylethynylphenyl)ethynylphenyl]ethynylphenyl}butadiyne (21). Following the general method used for the preparation of **19**, a mixture of cuprous chloride (22 mg, 0.11 mmol) in dry pyridine (25 mL) and compound **11** (220 mg, 0.445 mmol) in dry pyridine (20 mL) was stirred for 1 h. Purification was carried out by flash chromatography on a silica gel column, eluting with hexane/dichloromethane (4:1), providing **21** as a green solid (217.5 mg, 99%), mp 253−255 °C. UV−vis (CH$_2$Cl$_2$), λ_{max} (nm): 387 (sh, ϵ, 98500), 369 (ϵ, 123900), 269 (ϵ, 73300), 253 (ϵ, 78100), 240 (ϵ, 88400). Fluorescence (CH$_2$Cl$_2$), λ_{max} (nm): 438, 414 ($\phi = 0.54$). IR (KBr): cm^{-1} 2160 (C≡C), 1578 and 1502 (C=C), 1250 (Si−CH$_3$), 841 (1,3,5 trisubst), 758 (C−Si). ^{1}H NMR (CDCl$_3$): δ 7.56 (d, 4H, J = 1.6 Hz), 7.53 (t, 2H, J = 1.6 Hz), 7.52 (d, 4H, J = 8.5 Hz), 7.51 (d, 4H, J = 8.9 Hz), 7.47 (d, 4H, J = 8.5 Hz), 7.45 (d, 4H, J = 8.9 Hz), 0.24 (s, 36H). ^{13}C NMR (CDCl$_3$): δ 135.0, 134.5, 132.4, 131.6, 123.9, 123.8, 123.5, 123.0, 122.9, 121.6, 103.1, 95.8, 91.8, 90.9, 90.0, 89.7, 82.1, 75.7, −0.17. MS m/z (relative intensity): 986.1 (M$^+$ 100), 478.2 (38), 73 (57). $C_{68}H_{58}Si_4$ (987.53): anal. calcd C 87.70, H 5.92; found C 87.76, H 5.88.

1,3,5-Tris[(3,5-bis-trimethylsilylethynylphenyl)ethynyl]benzene (24). Following the general method used for the synthesis of **6**, a mixture of 1,3,5-triiodobenzene (100 mg, 0.22 mmol), compound **7** (206 mg, 0.7 mmol), dichloro bis(triphenylphosphine)palladium (49 mg, 0.07 mmol), and triethylamine (30 mL) was stirred for 12 h. Purification was carried out by flash chromatography on a silica gel column, eluting with hexane, providing **24** as a white solid (195 mg, 93%), mp 118−120 °C. UV−vis (CH$_2$Cl$_2$), λ_{max} (nm): 308 (sh, ϵ, 87400), 291 (ϵ, 89800), 267 (ϵ, 134500), 254 (ϵ, 119800). Fluorescence (CH$_2$Cl$_2$), λ_{max} (nm): 367, 353 ($\phi = 0.16$). IR (KBr): cm^{-1} 2156 (C≡C), 1587 and 1411 (C=C), 1250 (Si−CH$_3$), 848 (1,3,5 trisubst), 758 (C−Si). ^{1}H NMR (CDCl$_3$): δ 7.58 (s, 3H), 7.56 (d, 6H, J = 1.6 Hz), 7.54 (t, 3H, J = 1.6 Hz), 0.25 (s, 54H). ^{13}C NMR (CDCl$_3$): δ 135.1, 134.6, 134.3, 123.8, 123.7, 123.1, 103.0, 95.9, 89.0, 88.5, −0.19. MS m/z (relative intensity): 954.0 (M$^+$ 57), 73 (100). $C_{60}H_{66}Si_6$ (955.68): anal. calcd C 75.41, H 6.96; found C 75.46, H 6.89.

1,3,5-Tris{[(3,5-bis-trimethylsilylethynylphenyl)ethynylphenyl]ethynyl}benzene (25). Following the general method used for the synthesis of **6**, a mixture of 1,3,5-triiodobenzene (100 mg, 0.22 mmol), compound **9** (270 mg, 0.7 mmol), dichloro bis(triphenylphosphine)palladium (49 mg, 0.07 mmol), and triethylamine (30 mL) was stirred for 12 h. Purification was carried out by flash chromatography on a silica gel column, eluting with hexane, providing **25** as a green solid (234.5 mg, 85%), mp 145−146 °C. UV−vis (CH_2Cl_2), λ_{max} (nm): 351 (sh, ϵ, 143700), 329 (ϵ, 181200), 270 (ϵ, 106600), 255 (ϵ, 102000). Fluorescence (CH_2Cl_2), λ_{max} (nm): 377, 356 ($\phi = 0.48$). IR (KBr): cm^{-1} 2156 (C≡C), 1580 and 1411 (C=C), 1249 (Si−CH_3), 843 (1,3,5 trisubst), 759 (C−Si). ^{1}H NMR ($CDCl_3$): δ 7.67 (s, 3H), 7.57 (d, 6H, J = 1.6 Hz), 7.54 (t, 3H, J = 1.6 Hz), 7.52 (d, 6H, J = 8.9 Hz), 7.48 (d, 6H, J = 8.9 Hz), 0.25 (s, 54H). ^{13}C NMR ($CDCl_3$): δ 135.0, 134.5, 134.2, 131.6, 123.9, 123.8, 123.5, 123.0, 122.8, 103.1, 95.8, 90.3, 89.9; 89.7, 89.6, −0.17. MS m/z (relative intensity) FAB+: 1255.1 (M$^+$ 100). $C_{84}H_{78}Si_6$ (1254.47): anal. calcd C 80.32, H 6.26; found C 80.39, H 6.20.

1,3,5-Tris{[((3,5-bis-trimethylsilylethynylphenyl)ethynylphenyl)ethynylphenylethynyl}benzene (26). Following the general method used for the synthesis of **6**, a mixture of 1,3,5-triiodobenzene (40 mg, 0.089 mmol), compound **11** (130 mg, 0.2 mmol), dichloro bis(triphenylphosphine)palladium (14 mg, 0.02 mmol), and triethylamine (30 mL) was stirred for 12 h. Purification was carried out by flash chromatography on a silica gel column, eluting with hexane, providing **25** as a yellow solid (109.4 mg, 80%), mp 201−203 °C. UV−vis (CH_2Cl_2), λ_{max} (nm): 366 (sh, ϵ, 156000), 347 (ϵ, 187500), 268 (ϵ, 105000), 254 (ϵ, 123000). Fluorescence (CH_2Cl_2), λ_{max} (nm): 398, 377 ($\phi = 0.80$). IR (KBr): cm^{-1} 2159 (C≡C), 1580 and 1411 (C=C), 1250 (Si−CH_3), 845 (1,3,5 trisubst), 759 (C−Si). ^{1}H NMR ($CDCl_3$): δ 7.67 (s, 3H), 7.56 (d, 6H, J = 1.6 Hz), 7.55−7.53 (m, 15H), 7.50 (d, 6H, J = 8.6 Hz), 7.49 (d, 6H, J = 8.6 Hz), 0.25 (s, 54H). ^{13}C NMR ($CDCl_3$): δ 135.0, 134.5, 134.2, 131.6, 123.9, 123.8, 123.5, 123.2, 123.1, 122.8, 122.7, 103.1, 95.8, 91.1, 91.0, 90.3, 90.0, 89.6, −0.17. MS m/z (relative intensity) FAB+: 1555.6 (M$^+$ 80). $C_{108}H_{90}Si_6$ (1536.38): anal. calcd C 83.34, H 5.83; found C 83.39, H 5.78.

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