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# Synthesis of nanostructures based on 1,4- and 1,3,5-phenylethynyl units with π-extended conjugation. Carbon networks dendrimer base units

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**Abstract**—A convenient and efficient synthesis of 3,5-di(silylethynyl)phenylacetylene and *p*-[3,5-di(silylethynyl)phenylethynyl]-phenylacetylene has been carried out. These compounds serve to prepare nanometer-sized conjugated 1,4- and 1,3,5-phenylethynyl oligomers, by means of cross-coupling with a convenient haloaryl derivative, catalysed by palladium(II), in excellent yields. The phenylethynyl homologues show fluorescence emission, the wavelength of which is displaced by approximately 20 nm by each phenylethynyl unit increasing the conjugate chain. © 2003 Elsevier Science Ltd. All rights reserved.

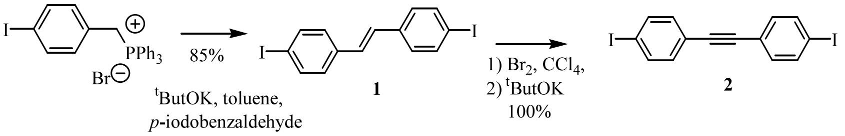
The synthesis and characterisation of nanometer-sized conjugated molecules of precise length and constitution are of wide-spread interest, due to their inherent synthetic flexibility which permits the design of molecular architectures with important properties.[1,2] Molecules showing π-extended conjugation, in general exhibit high thermal stability and 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 containing 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(phenylenevinylene) with fluorescence properties as well as dendrimers[11] with 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 are molecular modules to prepare stable and geometrically well defined nanostructures.

The construction of controlled 1,4-di(ethynylphenyl) and 1,3,5-tri(ethynylphenyl) conjugated nanostructures, has been undertaken. The diethynyl or triethynyl substituted benzenes show a variety of geometric possibilities, due to their hexagonal structure; 1,4-linear, 1,3-trigonal, and 1,2-angular structures (60°).

*p*-Di(iodophenyl)acetylene (**2**) was obtained in practically quantitative yield, from the correponding *E*/*Z* ethenyl mixture **1**, by bromine addition followed by dehydrobromination with potassium *tert*-butoxide, at room temperature (Scheme 1). The ethenyl derivative (**1**) was satisfactorily obtained by a Wittig reaction between *p*-(iodophenyl) carboxaldehyde and the *p*-(iodobenzyl)(triphenyl)phosphonium ylide, prepared in



**Scheme 1.**

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*Keywords*: trigonal geometry; 1,3,5-tri(phenylethynyl) nanostructures; π-extended conjugation; Sonogashira reaction; dendrimer base units.

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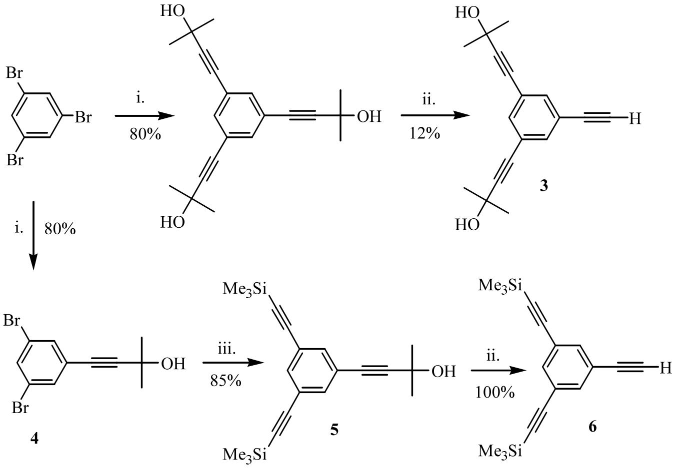
situ from the appropriate phosphonium salt with potassium *tert*-butoxide in toluene.

The synthesis of molecular units of trigonal geometry was undertaken starting from 1,3,5-tribromobenzene. Thus, 3,5-[di(2-methyl-2-hydroxybutynyl)phenyl]ethyne was obtained by heterocoupling of 1,3,5-tribromobenzene and 2-methyl-3-butyn-2-ol in the presence of palladium(II). 1,3,5 - Tris(2-methyl - 2 - hydroxy - 3 - butynyl)-benzene, was obtained in 80% of yield. However, 3,5-[di(2-methyl-2-hydroxybutynyl)phenyl]ethyne (**3**) (mp 95–97°C) was isolated pure in low yield (12%) by deprotection with powdered sodium hydroxide in dry toluene at reflux (Scheme 2).[13] Moreover, due to the low solubility of these propargylic derivatives, another synthetic methodology was undertaken.

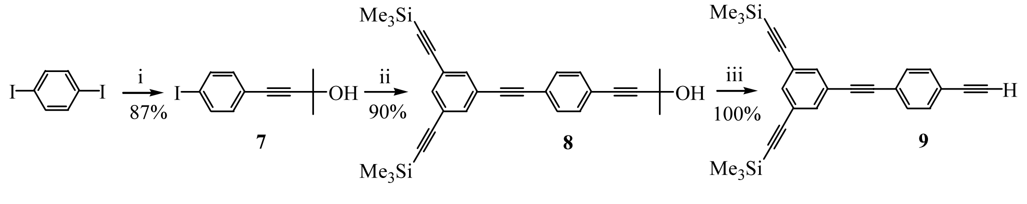
An alternative was the synthesis of the doubly protected molecular units **6** and **9**, which were employed to obtain nanostructures with a trigonal geometry. The heterocoupling between 1,3,5-tribromobenzene and 2-methyl-3-butyn-2-ol, in the presence of palladium(II), affords **4** (mp 52–54°C, 80%), which was coupled with trimethylsilylacetylene, in triethylamine at reflux in the presence of palladium(II), to give **5** (mp 85–86°C) in good yield. The selective deprotection of the propargylic group was carried out with powdered sodium hydroxide in dry toluene at reflux, giving the terminal acetylene **6** (transparent oil), in practically quantitative yield (Scheme 2). Heterocoupling between 1,4-diiodobenzene and 2-methyl-3-butyn-2-ol, catalysed by a palladium(II), gives **7** (mp 89–90°C) (Scheme 3). Compound **6** was heterocoupled with **7**, to give **8** (mp 95–97°C). The selective deprotection of the propargylic group affords **9** in practically quantitative yield. Treatment of **5** with sodium hydroxide in toluene with small amounts of water or in THF–methanol (4:1) produces a mixture of all the possible terminal acetylene compounds. Thus, under dry conditions, solid sodium hydroxide enables only proton abstraction and acetone elimination of the propargylic group, while in the presence of water or methanol a nucleophile attack of the $^{-}$OR anion to the silicon atom (R = H or $CH_3$) occurs with $C_{sp}$-$SiMe_3$ cleavage.[13]



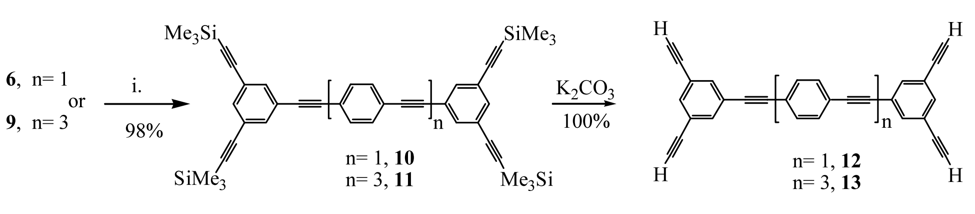
**Scheme 2.** *Reagents and conditions*: (i) 2-Methyl-3-butyn-2-ol, $Cl_2Pd(Ph_3P)_2$, $Cu_2I_2$, $NEt_3$; (ii) NaOH, toluene at reflux; (iii) trimethylsilylethyne, $Cl_2Pd(Ph_3P)_2$, $Cu_2I_2$, $NEt_3$, rt.

Thus, the double heterocoupling reaction between *p*-diiodobenzene and **6** (or **9**), in presence of palladium(II), gives **10** (mp 219–220°C) (or **11**, mp 270–273°C) in practically quantitative yield. Both compounds were deprotected by treatment with potassium carbonate in THF/MeOH (4:1) to give quantitatively the terminal tetraacetylene **12** (or **13**) (Scheme 4).

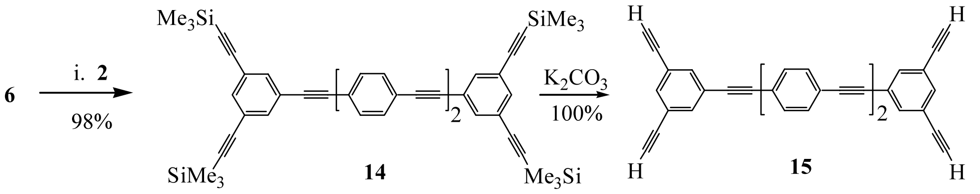
Moreover, the phenylethynyl homologous compound **14** was prepared by double heterocoupling between 1,2-di(*p*-iodophenyl)ethyne (**2**) and the terminal acetylenes **6**, catalysed by palladium(II), in practically quantitative yield (Scheme 5). Compound **14** (mp 220–223°C) was completely deprotected to the terminal tetraacetylene **15** by treatment with potassium carbonate in THF–MeOH (4:1).



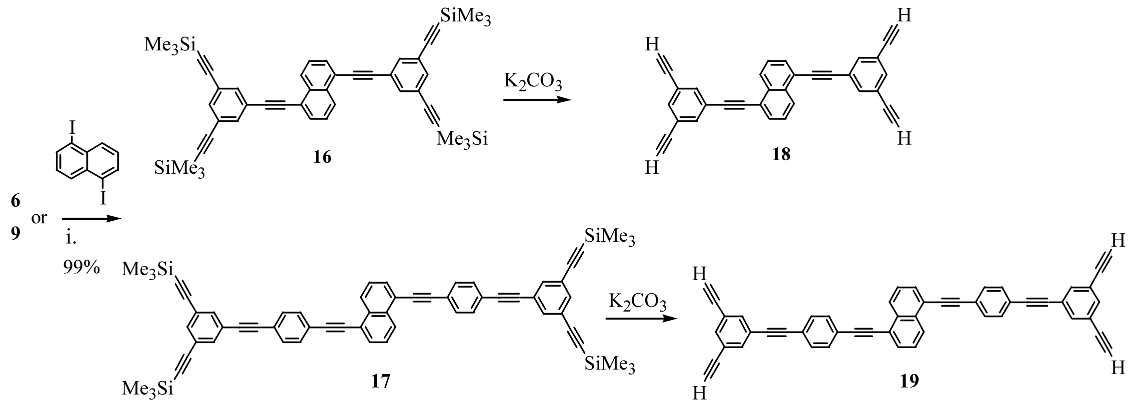
**Scheme 3.** *Reagents and conditions*: (i) 2-Methyl-3-butyn-2-ol, $Cl_2Pd(PPh_3)_2$, $Cu_2I_2$, $NEt_3$, rt; (ii) **6** and **7**, $Cl_2Pd(PPh_3)_2$, $Cu_2I_2$, $NEt_3$, rt; (iii) NaOH, toluene, at reflux.



**Scheme 4.** *Reagents and conditions*: (i) *p*-Diiodobenzene, $Cl_2Pd(PPh_3)_2$, $Cu_2I_2$, $NEt_3$.



**Scheme 5.** *Reagents and conditions*: (i) $Cl_2Pd(PPh_3)_2$, $Cu_2I_2$, $NEt_3$.



**Scheme 6.** *Reagents and conditions*: (i) $Cl_2Pd(PPh_3)_2$, $Cu_2Cl_2$, $NEt_3$.

**Table 1.** UV–vis and fluorescence spectra data of conjugated compounds **10**, **11**, **14**, **16** and **17**

| Compd | UV–vis[a] ($CH_2Cl_2$) $\lambda_{max}$ (nm) | $\varepsilon$ ($M^{-1}$ $cm^{-1}$) | $F^b$ ($CH_2Cl_2$) $\lambda_{max}$ (nm) | $\Phi_f{}^c$ |
|---|---|---|---|---|
| **10** | 348 | 44900 | 355, 373 | 0.65 |
| **11** | 354 | 103600 | 394, 413 | 0.72 |
| **14** | 344 | 76300 | 376, 394 | 0.68 |
| **16** | 352 | 33800 | 377, 398 | 0.60 |
| **17** | 365 | 65100 | 397, 418 | 0.81 |

[a] All spectra were recorded at room temperature.

[b] All fluorescence spectra were recorded at room temperature at $c \cong 10^{-8}$ M.

[c] The fluorescence quantum yield was determined in dichloromethane relative to 2-aminopyridine in 0.1N $H_2SO_4$.

On the other side, the synthesis of a parallel trigonal-linear growing structure chain was undertaken for heterocoupling of **6** (or **9**) with 1,5-diiodonaphthalene.

Hence, the reaction in the presence of palladium(II), gives **16** (mp 228–230°C) (or **17**, mp 271–273°C) in quantitative yield (Scheme 6).

Compounds **16** and **17** were completely deprotected to the terminal tetraacetylene compounds **18** and **19** by treatment with potassium carbonate in THF/MeOH (4:1).

Compounds **10**, **11**, **14**, **16** and **17** show a strong fluorescence emission radiation with a wavelength increasing by a fixed value close to 20 nm for each phenylethynyl unit. All the compounds show excellent quantum yield fluorescence, which increase with the conjugation[14] (Table 1).

## Acknowledgements

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14. All the new compounds give satisfactory elemental analyses. Selected spectral data of the new terminal acetylene compounds ($^{1}$H and $^{13}$C NMR were recorded in CDCl$_3$ at 300 and 75 MHz, respectively, in $\delta$ ppm) are given. Compound **6**: $^{1}$H NMR: 7.53 (t, 1H, $J$=1.42 Hz), 7.50 (d, 2H, $J$=1.42 Hz), 3.06 (s, 1H), 0.23 (s, 18H); $^{13}$C NMR: 135.3, 135.0, 123.7, 122.6, 102.9, 95.5, 81.8, 78.2, −0.19. Compound **9**: $^{1}$H NMR: 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: 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. Compound **12**: $^{1}$H NMR: 7.61 (d, 4H, $J$=1.6 Hz), 7.56 (t, 2H, $J$=1.6 Hz), 7.50 (br s, 4H); 3.12 (s, 4H); $^{13}$C NMR: 135.2, 135.1, 131.6, 123.7, 122.9, 122.8, 90.0, 89.4, 81.7, 78.6. Compound **13**: $^{1}$H NMR: 7.49–7.62 (m, 17H); 3.12 (s, 4H); $^{13}$C NMR: 134.9, 134.5, 131.6, 123.7, 123.4, 123.1, 123.0, 122.7, 91.0, 91.1, 90.0, 89.6, 81.7, 78.6. Compound **15**: $^{1}$H NMR: 7.6 (d, 4H, $J$=1.6 Hz), 7.54 (t, 2H, $J$=1.6 Hz), 7.51 (d, 4H, $J$=8.89), 7.47 (d, 4H, $J$=8.89,), 3.12 (s, 4H); $^{13}$C NMR: 135.2, 135.1, 131.6, 123.7, 123.2, 122.9, 122.6, 91.0, 90.0, 89.2, 81.7, 78.6. Compound **18**: $^{1}$H NMR: 8.41 (d, 2H, $J$=8.61 Hz), 7.78 (d, 2H, $J$=6.45 Hz), 7.7 (d, 4H, $J$=1.6), 7.56–7.61 (m, 4H), 3.14 (s, 4H); $^{13}$C NMR: 135.2, 135.1, 133.0, 131.3, 127.3, 126.3, 123.8, 123.7, 120.7, 93.0, 88.0, 81.7, 78.7. Compound **19**: $^{1}$H NMR: 8.45 (d, 2H, $J$=8.49 Hz), 7.83 (d, 2H, $J$=6.47 Hz), 7.51–7.64 (m, 16H), 3.14 (s, 4H); $^{13}$C NMR: 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, 94.3, 90.0, 89.6, 89.3, 81.7, 78.7.