Pure Appl. Chem., Vol. 78, No. 4, pp. 847–853, 2006.
doi:10.1351/pac200678040847

Synthesis and properties of phenyleneethynylene-based dendritic structures*

Jean-François Nierengarten‡

Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31077 Toulouse Cédex 4, France

Abstract: In this paper, we report on our ongoing progress on the synthesis and study of branched molecular architectures with a conjugated scaffold. Specifically, new conjugated dendrons incorporating 1,2,4-triethynyl-phenyl units have been developed and used as building blocks for the synthesis of isomeric branched conjugated systems and light-harvesting dendrimers.

Keywords: dendrimers; alkynes; cross-coupling; fullerenes; conjugation.

INTRODUCTION

The past several years have seen considerable interest in the synthesis of new linear monodisperse π-conjugated oligomers [1]. Whereas the initial driving force for the synthesis and study of well-defined oligomers was the development of structure–property relationships to rationalize the properties of the corresponding π-conjugated polymers, this research has evolved into an independent field of its own [1]. Its development has generated some spectacular molecular architectures with high potential for optoelectronic applications [1]. This has given impetus to make this research a truly interdisciplinary branch of science located at the interfaces between chemistry, physics, and materials science. It must also be added here that the bottom-up approach for the construction of electronic circuitry starting from nanometer-sized π-conjugated molecular nanowires is particularly appealing and gives rise to tremendous research efforts nowadays [2].

The rapid progress achieved in the synthesis of monodisperse π-conjugated oligomers has also stimulated the development of other fascinating families of compounds. These novel molecules include macrocyclic π-systems [3], substructures of new graphite-like two-dimensional networks [4], fullerene-like three-dimensional cages [5], and hyperbranched structures [6]. As part of this research, we have recently started to develop dendritic branches with a conjugated scaffold [7]. If one important challenge is to comprehensively investigate their optical properties [8], the characteristic features of these compounds also make them versatile photoactive components for the preparation of photochemical molecular devices [9]. In this paper, our ongoing progress in this particular field is summarized.

ISOMERIC BRANCHED π-CONJUGATED SYSTEMS

Almost all the phenylenevinylene (PV) and phenyleneethynylene (PE) dendrimers described so far have been constructed from symmetrical building blocks based on 1,3,5-trisubstituted phenyl rings [10]. As

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*Paper based on a presentation at the 11th International Symposium on Novel Aromatic Compounds (ISNA-11), St. John's, Newfoundland, Canada, 14–18 August 2005. Other presentations are published in this issue, pp. 685–888.

‡E-mail: jfnierengarten@lcc-toulouse.fr

a result of the *meta*-branching scheme, the π-conjugation of these dendritic molecules is, however, rather limited. More recently, Peng and coworkers have reported the preparation of new conjugated dendrimers based on 1,2,4-trisubstituted phenyl units in which the different branches exhibit different conjugation lengths [11]. Indeed, the unsymmetric substitution on the aromatic ring produces *para*-linked phenylacetylene (PA) units allowing an increase of the conjugation length when the dendritic generation is increased. By following a similar approach, we have described the synthesis of the isomeric branched π-conjugated systems **H1-H2** and **X1-X2** (Fig. 1) [7]. Whereas **X1** and **X2** are similar to the dendritic systems reported by Peng and coworkers, compounds **H1** and **H2** have unprecedented structural features.

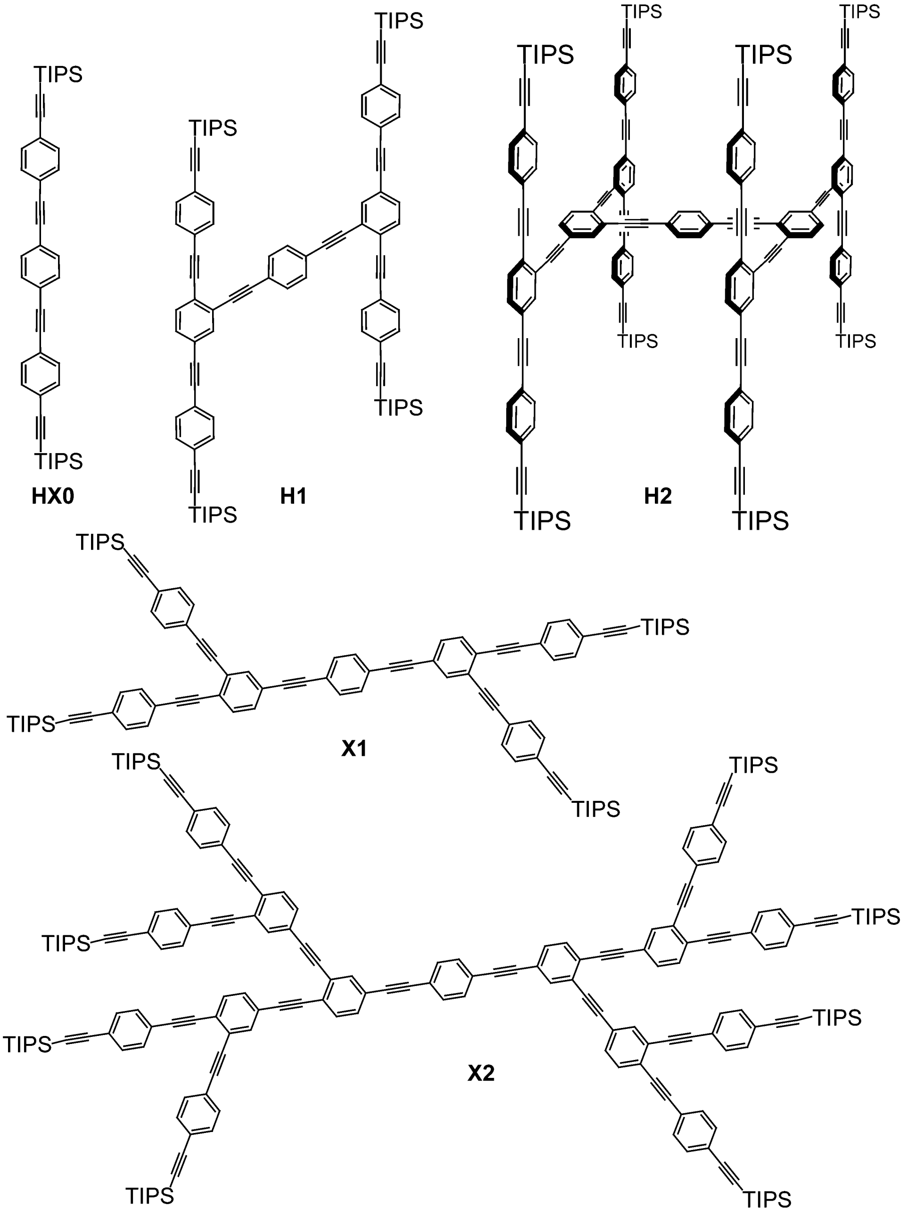


Fig. 1 Compounds **HX0**, **X1-X2**, and **H1-H2** [TIPS = Si(*i*-Pr)$_3$].

Synthesis

Starting from 4-(triisopropylsilylethynyl)phenylacetylene, the approach developed for the preparation of the branched conjugated dendritic branches relies on the following iterative reaction sequence: (i) metal-catalyzed cross-coupling reaction of the terminal alkyne with a 3,4-dibromobenzaldehyde or 2,5-dibromobenzaldehyde; (ii) Corey–Fuchs dibromoolefination and treatment with an excess of lithium diisopropylamide (LDA). The building blocks thus prepared were finally subjected to a Pd-catalyzed cross-coupling reaction with 1,4-diiodobenzene to yield the isomeric branched π-conjugated systems **X1-X2** and **H1-H2**. As a typical example, the synthesis of **X1** and **X2** is depicted in Fig. 2. Reaction of 3,4-dibromobenzaldehyde with mono-protected bisalkyne **1** under Sonogashira conditions gave the first-generation dendron **2** in 75 % yield. Dibromoolefination according to Corey–Fuchs then provided **3**, which, after treatment with an excess of LDA in tetrahydrofuran (THF) at –78 °C and quenching with NH_4Cl, afforded terminal alkyne **4**. Compound **4** was subjected to a Pd-catalyzed cross-coupling reaction with 3,4-dibromobenzaldehyde to yield the second-generation dendron **5**. Treatment with $CBr_4/PPh_3/Zn$ and subsequent reaction of the resulting intermediate **6** with an excess of LDA yielded terminal alkyne **7**. The branched π-conjugated systems **X1–X2** were finally obtained by reaction of 1,4-diiodobenzene with an excess of the appropriate terminal alkyne precursor in the presence of $PdCl_2(PPh_3)_2$, CuI, and PPh_3 in Et_3N/THF.

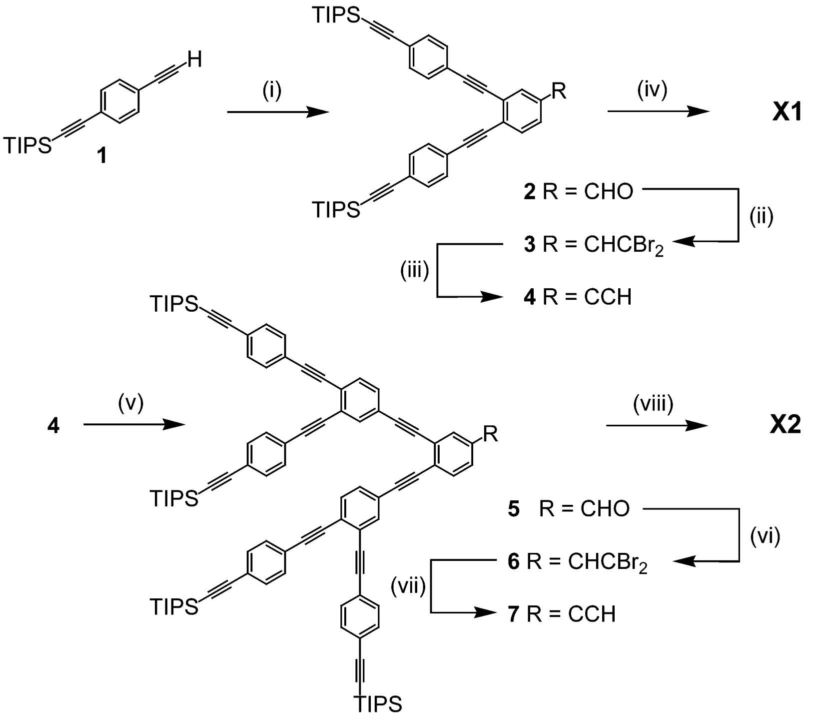


Fig. 2 Synthesis of **X1** and **X2**. *Reagents and conditions*: (i) 3,4-dibromobenzaldehyde, $PdCl_2(PPh_3)_2$, CuI, PPh_3, Et_3N, THF (75 %); (ii) CBr_4, PPh_3, Zn dust, CH_2Cl_2 (95 %); (iii) LDA, THF then NH_4Cl, H_2O (92 %); (iv) 1,4-diiodobenzene, $PdCl_2(PPh_3)_2$, CuI, PPh_3, Et_3N, THF (81 %); (v) 3,4-dibromobenzaldehyde, $PdCl_2(PPh_3)_2$, CuI, PPh_3, Et_3N, THF (78 %); (vi) CBr_4, PPh_3, Zn dust, CH_2Cl_2 (94 %); (vii) LDA, THF then NH_4Cl, H_2O (94 %); (viii) 1,4-diiodobenzene, $PdCl_2(PPh_3)_2$, CuI, PPh_3, Et_3N, THF (88 %).

The key building blocks for the synthesis of **H1** and **H2** were obtained from 2,5-dibromobenzaldehyde and alkyne **1** by following a similar synthetic approach as the one described above for the preparation of **4** and **7**. The branched π-conjugated systems **H1-H2** were then obtained by reaction of the resulting dendrons with 1,4-diiodobenzene under Sonogashira conditions.

It is worth mentioning here that the methodology based on successive Sonogashira coupling reaction of a terminal alkyne with a halobenzaldehyde, Corey–Fuchs dibromoolefination and treatment with LDA was also successfully applied to the synthesis of linear oligophenyleneethynylene derivatives [12]. It is an interesting alternative to the approaches reported by the groups of Tour [13] and Godt [14]. On the one hand, compared to the strategy based on the trimethylsilyl and the 3,3-diethyltriazene functions as complementary protecting groups for terminal alkyne and aryl iodine, respectively, it avoids the use of large amounts of rather volatile carcinogenic methyl iodide [13]. On the other hand, compared to the strategy based on the bromine-iodine selectivity of the Pd-catalyzed alkyne-aryl coupling, which is not always completely iodo-selective, it prevents the formation of undesirable symmetric byproducts [14].

Optical properties

In order to understand the influence of the conjugation pathways within these isomeric systems, the excited state properties of **H1-H2** and **X1-H2** have been investigated and compared to those of the corresponding model compound **HX0** (Fig. 1). The absorption and emission spectra of **HX0**, **H1-H2**, and **X1-X2** in cyclohexane solution are depicted in Fig. 3.

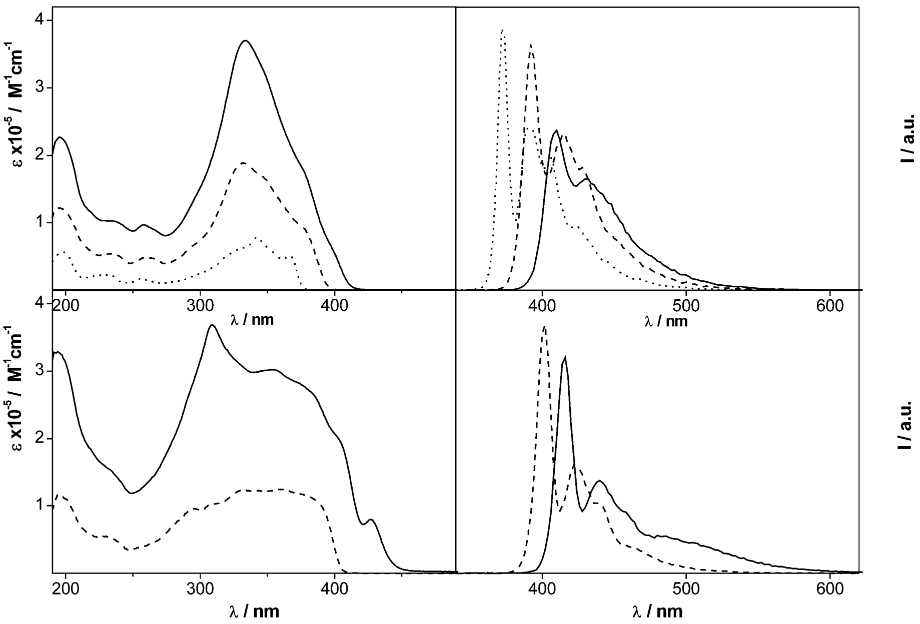


Fig. 3 Top left: Absorption spectra of **HX0** (dotted line), **H1** (dashed line), and **H2** (full line) in cyclohexane. Top right: Emission spectra of isoabsorbing solutions (A = 0.18) of **HX0** (dotted line), **H1** (dashed line), and **H2** (full line) in cyclohexane. λ_{ex} = 320 nm. Bottom left: Absorption spectra of **X1** (dashed line) and **X2** (full line) in cyclohexane. Bottom right: Emission spectra of isoabsorbing solutions (A = 0.18) of **X1** (dashed line) and **X2** (full line) in cyclohexane. λ_{ex} = 320 nm.

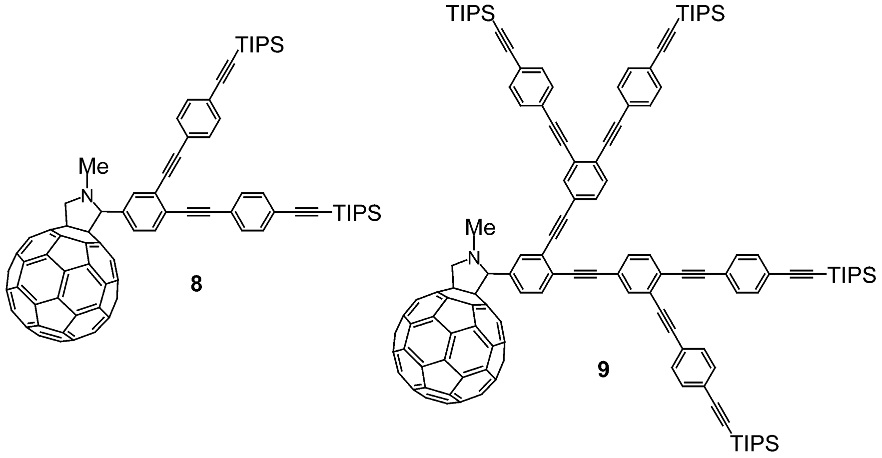
The spectrum of the reference PA **HX0** is very similar to an analogous trimer system lacking the peripheral triple bonds [15], suggesting negligible increase of π-conjugation length. By connecting two **HX0** units via an *ortho* PA bridge, little band broadening is observed with an absorption onset red-shift of only 17 nm; this indicates negligible criss-cross electronic delocalization over the all structure in **H1**. In other words, the conjugation is effective for the *p*-linked subunits but the *o*- and *m*-linked ethynylbenzene moieties do not really increase the conjugation length of the system. The fluorescence spectra of **HX0** and **H1** have practically the same shape and vibronic structure (Fig. 3, top right), but the emission maximum of **H1** is red-shifted by 20 nm, in line with the absorption trend. The singlet excited state of **HX0** deactivates only via the radiative path ($\Phi_{fl} = 1.0$), whereas for **H1** some little nonradiative deactivation occurs ($\Phi_{fl} = 0.97$), probably as a consequence of the larger structure which favors vibrational deactivation. **H2** is made of two **H1** units linked through a PA spacer, but the electronic absorption spectrum is practically identical and twice as intense relative to that of **H1** for a large part of the spectrum (190–385 nm). Notably, the spectral onset of **H2** is slightly red-shifted compared to **H1** and a weak absorption tail is observed down to 420 nm. These results suggest that, in the ground state, the two **H1**-type fragments of **H2** are substantially decoupled, but this does not prevent the occurrence of a lower-lying singlet state, as signaled by a red-shifted and longer-lived fluorescence ($\lambda_{max} = 408$ nm, $\tau = 2.4$ ns, $\Phi_{fl} = 0.89$) relative to **H1**. The excitation spectra of **HX0**, **H1** and **H2** in cyclohexane perfectly match the absorption profile at any emission wavelength and no evidence of molecular aggregation (e.g., excimer emission) is detected within the range of concentrations used for the optical measurements ($10^{-5}/10^{-7}$ M).

The electronic absorption spectra of **X1** and **X2** in cyclohexane solution (Fig. 3) are broad and poorly resolved (especially **X1**) and do not bear much resemblance to those of **4** and **7**, which may be considered the end units of **X1** and **X2**. This indicates that the electronic π-delocalization mainly occurs through the central molecular backbone made of 5 and 7 *para*-PA units for **X1** and **X2**, respectively; this pattern mainly dictates the absorption profile. The larger delocalization of the central molecular wire in **X2** leads to 36-nm red-shift of the absorption onset relative to **X1**, and a 14-nm shift of the first feature of the fluorescence spectra (Fig. 3). The fluorescence quantum yield and the singlet excited state lifetime of **X1** ($\lambda_{max} = 402$ nm, $\tau = 0.6$ ns, $\Phi_{fl} = 1.0$) are identical to that of the reference system **HX0**. The excitation spectra of **X1** and **X2** in cyclohexane match the absorption profile at any emission wavelength. It must be emphasized that **H1/X1** and **H2/X2** are isomer couples whose different electronic π-conjugation pattern is reflected in the differences of the absorption spectra (Fig. 3). The **X**-type molecules exhibit a lower-lying absorption onset and a wider spectral profile. The fluorescence yield is virtually unitary for **H1** and **X1**, whereas for **X2** ($\lambda_{max} = 416$ nm, $\tau = 0.7$ ns, $\Phi_{fl} = 0.61$) a substantially lower value is found, compared to **H2** ($\lambda_{max} = 408$ nm, $\tau = 2.4$ ns, $\Phi_{fl} = 0.89$).

LIGHT-HARVESTING DENDRIMERS

The synthesis and study of dendrimer-based light-harvesting structures have attracted increased attention in the past decade [16]. In such systems, an array of peripheral chromophores is able to transfer the collected energy to the central core of the dendrimer, thus mimicking the natural light-harvesting complex where antenna molecules collect sunlight and channel the absorbed energy to a single reaction center. The fullerene C_{60} is an attractive functional core for the preparation of light-harvesting dendrimers [17]. Effectively, its first singlet and triplet excited-states are relatively low in energy and photoinduced energy-transfer events have been evidenced in fullerene-based dyads [18]. In particular, photophysical investigations of some pyrrolidinofullerene derivatives substituted with PV-based dendritic branches revealed a very efficient singlet–singlet PV $\rightarrow C_{60}$ photoinduced energy transfer [19]. Based on these observations, the functionalization of [60]fullerene with the conjugated dendrons described in the previous section appear as potentially interesting systems with light-harvesting properties.

Fullerodendrimers **8** and **9** are depicted in Fig. 4. The synthetic approach used for the preparation of compounds **8** and **9** relies upon the 1,3-dipolar cycloaddition of the dendritic azomethine ylides generated in situ from the corresponding aldehydes and *N*-methylglycine. This methodology has proven to be a powerful procedure for the functionalization of C_{60} due to its versatility and the ready availability of the starting materials [20]. Thus, reaction of aldehydes **2** and **5** with *N*-methylglycine and C_{60} in refluxing toluene gave the corresponding pyrrolidinofullerene **8** and **9** in 37 and 44 % isolated yields, respectively [21].



8

9

Fig. 4 Fullerodendrimers **8** and **9**.

The absorption spectra of the fullerodendrimers **8** and **9** in CH_2Cl_2 present the spectral features of both component units. However, exact matching with the spectral profiles calculated by summing the absorption spectra of pyrrolidinofullerene and the pertinent dendritic PE fragment is never obtained, in line with previous reports [18]. Upon excitation at the dendritic PE band maximum, dramatic quenching of PE fluorescence is observed for both fullerodendrimers. This is attributable to a PE → C_{60} singlet–singlet energy-transfer process, as inferred by excitation spectra recorded at λ_{em} = 730 nm.

CONCLUSIONS

We have developed an iterative approach for the preparation of new branched conjugated systems with a terminal alkyne function starting from 4-(triisopropylsilylethynyl)phenylacetylene (**1**) by applying the following reaction sequence: (i) metal-catalyzed cross-coupling reaction of the terminal alkyne with a dibromobenzaldehyde derivative; (ii) Corey–Fuchs dibromoolefination and treatment with an excess of LDA. The building blocks thus prepared have been subjected to a Pd-catalyzed cross-coupling reaction with 1,4-diiodobenzene to yield the isomeric branched π-conjugated systems containing 7 (**H1** and **X1**) or 15 (**H2** and **X2**) phenyl units connected by ethynyl spacers. The different π-conjugation patterns in those isomeric derivatives have a dramatic effect on their electronic properties as attested by the differences observed in their absorption spectra. Finally, it can be added that all these extended conjugated derivatives are highly luminescent with nearly quantitative emission quantum yields. The results described in this paper provide a hint for the design of novel branched conjugated systems with tailored optical properties. The characteristic features of these compounds make them attractive photoactive components for the preparation of photochemical molecular devices as illustrated with fullerodendrimers **8** and **9** in which photoinduced energy transfer has been evidenced. The further functionalization of these fullerodendrimers with a suitable electron donor is now underway to produce a multicomponent artificial photosynthetic system in which the photoinduced energy transfer to the C_{60} core is followed by electron transfer.

ACKNOWLEDGMENTS

This work was supported by the CNRS, the French Ministry of Research, and the EU (RTN "FAMOUS", HPRN-CT-2002-00171). I would like to warmly thank all my coworkers and collaborators for their outstanding contributions; their names are cited in the references.

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