CHEMISTRY
A EUROPEAN JOURNAL

FULL PAPER

DOI: 10.1002/chem.201201555

First Perphenylated *carbo*-oligoacetylenes: An Extension of the Polytriacetylene Family

Arnaud Rives,[a, b] **Valérie Maraval,***[a, b] **Nathalie Saffon-Merceron,**[c] **and Remi Chauvin***[a, b]

Abstract: The first examples of a novel family of sp-carbon-rich n-π-conjugated oligomers/polymers, namely *carbo*-mers of polyacetylene, also referred to as "1,4-PTA" isomers of the classical polytriacetylenes (1,2-PTAs), are described in the perphenylated series. The two first representatives proved to be stable in solution, and exhibit a zigzag arrangement in the crystal state. The third member of the family, isolated in $SnCl_2$ matrix, proved to be stable in the solid state and was characterized by MALDI-TOF MS, ^1H NMR, CPMAS ^{13}C NMR, and absorption spectroscopy. An explanation for its reactivity in solution is proposed. The chromophoric properties in the visible region are shown to vary significantly and consistently along the series.

Keywords: alkynes • chromophores • conjugation • polymers • solid-state structures

Introduction

With the aim of tuning the electronic or optical properties of organic materials, the design and synthesis of conjugated oligomers and polymers are currently based on the decoration of standard hydrocarbon backbones, such as oligophenylenes (OPs), oligophenylenevinylenes (OPVs), oligophenyleneethynylenes (OPEs), and others, providing a tradeoff between stability and π-conjugation efficiency.[1] In most of these materials, however, the stabilizing aromatic phenylene units tend to act as π-insulating motifs. Nonaromatic backbones have thus also been considered by reference to polyacetylene (PA).[2] Beside the poly(diacetylene)s (PDAs),[3] the family of nonaromatic conjugated oligomers has been extended to the even more carbon-rich poly(triacetylene)s (PTAs), first exemplified in 1994 (Figure 1).[4] Since then, many examples of PTA oligomers have been considered for their physicochemical properties, at both the experimental and theoretical levels.[5] The PTAs, here termed as "1,2-PTAs", however, possess regioisomers, termed 1,4-PTA, that, in contrast, have not been exemplified, nor even considered yet to the best of our knowledge (an explanation for the 1,2- vs. 1,4-locants is illustrated in Figure 1). It should be noted that alternative denominations would also be consistent with respect to the OPE series (OMEs, "oligomethinethynylenes"), or to more classical methods for generating names ("oligopropargylidenyls"). The backbone of 1,4-PTAs is actually the *carbo*-mer of the reference PA backbone,[6] and these "*carbo*-oligoacetylenes" naturally deserve attention, for their conducting properties in particular. The chemistry of *carbo*-mers hitherto focused on cyclic molecules, and more precisely on pericyclynes[7] (*carbo*-mers of cycloalkanes)[8] and *carbo*-benzenes.[9] The extent of π-conjugation of the latter make them suitable for endowment of chromophoric properties, whereas their intrinsic associated sensitivity (to protonation, oxidation, reduction, polymerization, or π-rearrangements) was assumed to be moderated by their aromatic character.[10] A few early and recent publications, however, show that related acyclic sp-carbon-rich di- and tetra-alkynylbutatrienes are actually quite stable when they are capped with aromatic or bulky silyl substituents.[11] These reports encouraged us to undertake the synthesis of oligomeric versions of 1,4-PTAs. The results are disclosed herein.

Results and Discussion

Although, to the best of our knowledge, phenylated 1,2-PTAs are not known, the first 1,4-PTA oligomers were targeted in the perphenylated series; the synthesis of related hexaoxy[6]pericyclynes and *carbo*-benzenes is indeed easier in their aryl-substituted versions.[8b,d,9] On the other hand, in

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[a] Dr. A. Rives, Dr. V. Maraval, Prof. R. Chauvin
CNRS
LCC (Laboratoire de Chimie de Coordination)
205, route de Narbonne
31077 Toulouse (France)
Fax: (+33) 5-61-55-30-03
E-mail: vmaraval@lcc-toulouse.fr
chauvin@lcc-toulouse.fr

[b] Dr. A. Rives, Dr. V. Maraval, Prof. R. Chauvin
Université de Toulouse, UPS, INPT, LCC
31077 Toulouse (France)

[c] Dr. N. Saffon-Merceron
Université de Toulouse
UPS, Institut de Chimie de Toulouse, ICT-FR 2599
118, route de Narbonne, 31062 Toulouse (France)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201201555. It includes synthetic procedures and characterization data for all new compounds, as well as details of the crystal-structure determination of **6**.

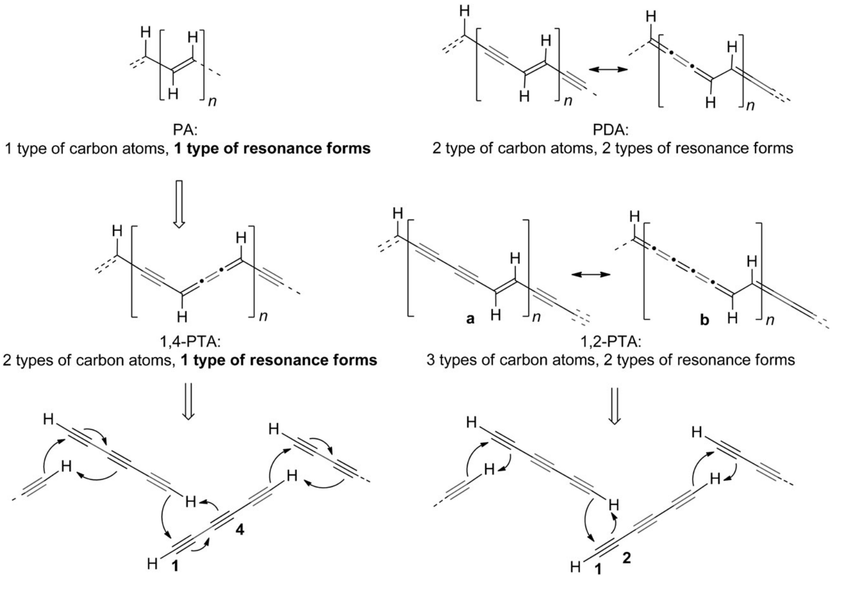
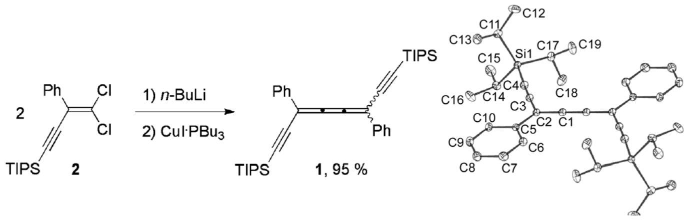
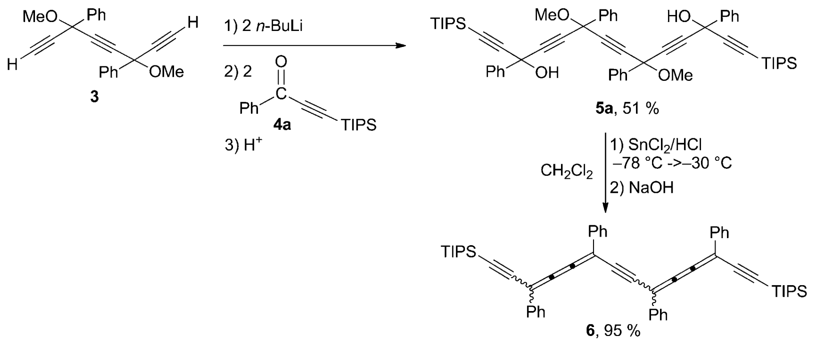


Figure 1. Examples of conjugated polymers with all-carbon nonaromatic backbones and almost homogeneous constitutions. A specificity of the 1,4-PTA backbone is that it possesses a single type of apolar resonance form, just as the reference polyacetylene does. Because the lateral substituents (or H atoms) at the sp^2-C atoms are not in vicinal positions, the formal polymerization of triacetylene relies on a sequential 1,4-CH-addition process rather than the 1,2-CH-addition process for the classical PTAs, here termed 1,2-PTAs (the direct triacetylene polymerization scheme without C−H bond cleavage also generates 1,2-PTAs through the less representative resonance form **b** involving [5]cumulenic motifs).

the challenging 1,4-PTA chain, the butatriene motifs are intrinsically more sensitive than the butyne motifs. Although terminal substitution of the external butatriene motifs by aryl groups should be more stabilizing (and possibly interesting for other purposes), the longest linearly conjugated fragments targeted here are terminated with alkynyl ends. Because alkynylbutatrienes have been shown to be stabilized by bulky aryl or trialkylsilyl substituents, tri(isopropyl)silyl (TIPS) end caps were retained. The smallest representative is the known diphenyl-bis-[tri(isopropyl)silylethynyl]-butatriene (**1**), which was prepared by reductive coupling of the *gem*-dihaloenyne **2** (Scheme 1).[11d] The 1,4-PTA monomer **1** proved to be stable both in solution and in the solid state, and was found to crystallize in its *trans* configuration.



Scheme 1. Preparation and molecular view of the X-ray crystal structure of the known diphenylated 1,4-PTA monomer **1**.[11d]



Scheme 2. Synthesis of tetraphenylated 1,4-PTA dimer **6**.

The second 1,4-PTA representative was then targeted from two known precursors, namely diether **3** (as a *meso*/*dl* mixture)[8d] and TIPS-protected ynone **4a**.[11d] Addition of the dilithium salt of triyne **3** to two equivalents of **4a** gave pentayne **5a** in 51 % yield after chromatography (Scheme 2). It must be stressed that **5a** and all related phenylcarbinoxy-skipped oligoynes described below were obtained as mixtures of stereoisomers, which were not resolved before further treatment. The diol mixture **5a** was thus submitted to acidic reductive treatment with $SnCl_2$/HCl in dichloromethane (CH_2Cl_2) at low temperature. The resulting pink-red solution was then treated with aqueous NaOH to give the conjugated bis-butatriene **6**, which was isolated in 95 % yield after chromatography.

^{1}H NMR spectroscopy in $CDCl_3$ solution showed that **6** occurs as a mixture of its three diastereoisomers (*cis-cis*, *cis-trans*, and *trans-trans*). Whereas the kinetic barrier of the binary *cis*/*trans* stereoconversion of **1** could be determined by ^{1}H NMR spectroscopy ($\Delta G^{\neq}$ (298 K) = 22 kcal mol^{-1}),[11d] similar attempts for the ternary *cis-cis*/*cis-trans*/*trans-trans* stereoconversion of **6** were not conclusive due to the overlap of the aromatic ^{1}H signals of the eight nonequivalent phenyl groups (instead of two for **1**. See Figure S1 in the Supporting Information). This 1,4-PTA dimer proved, however, to be stable, both in solution and in the solid state. Green-iridescent black crystals deposited from a $CHCl_3$/CH_3CN solution were analyzed by X-ray diffraction, and were found to correspond to the all-*trans* configuration of **6** (Figure 2).[12] The measured bond lengths and

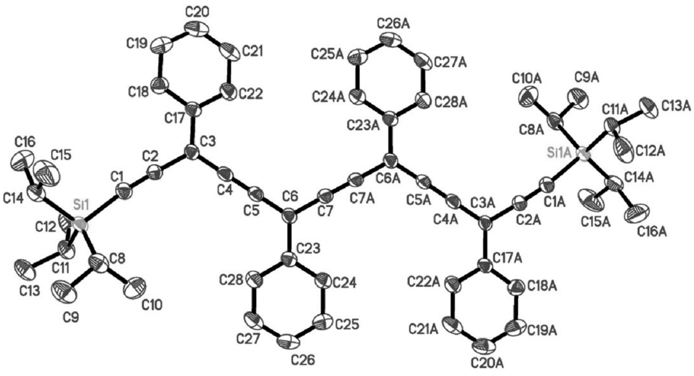
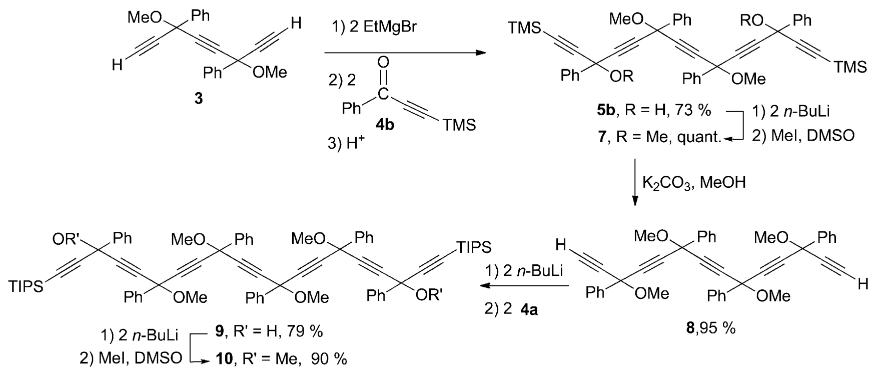


Figure 2. Molecular view of the all-*trans* isomer of the 1,4-PTA dimer **6**.[12]

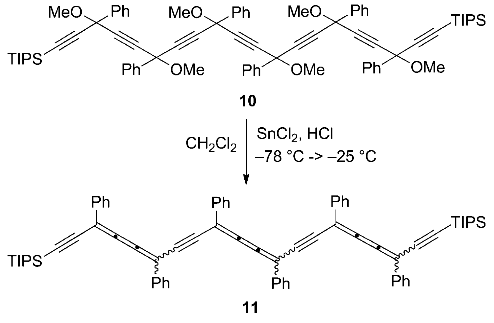
angles are similar to those measured in the previously reported monomer **1** (see Table S1 in the Supporting Information). The relative extension of the linear n-π-conjugation upon going from **1** (7 bonds) to **6** (13 bonds) thus has negligible effects on both the stability and the geometry.

The third member of the perphenylated-silyl-capped 1,4-PTA series was envisaged through the same strategy, from triyne **3** and TMS-protected ynone **4b** (Scheme 3). TMS-capped pentayne **5b** was thus obtained in 73 % yield, then methylated to the tetraether **7**, and finally desilylated to generate bis-terminal pentayne **8** in 95 % overall yield. Addition of the dilithium salt of **8** to two equivalents of ynone **4a** afforded the TIPS-capped heptayne **9** in 79 % yield (Scheme 3). Diol **9** was finally converted into diether **10** in 90 % yield by the same procedure previously used for the dimethylation of **5b** to **7** (deprotonation followed by reaction with iodomethane in the presence of DMSO).



Scheme 3. Synthesis of TIPS-capped heptayndiol **9** from triyne-diether **3**.

Since first attempts at reductive elimination from diol **9** with the $SnCl_2/HCl$ system did not give clear evidence of the formation of the 1,4-PTA target **11**, efforts focused on the diether substrate **10**. It was observed that treatment of **10** with $SnCl_2/HCl$ in CH_2Cl_2 solution at −78 °C induced the appearance of a blue color of the solution containing a dark-blue solid suspension when the temperature reached −30 °C (Scheme 4). Upon warming to room temperature, however, the medium became brown and the expected tris-butatriene **11** could be neither isolated nor even detected by ^1H NMR spectroscopy. Assuming that the blue product was the 1,4-PTA trimer **11**, the reaction mixture was carefully filtered at low temperature (−25 °C) to give the dark-blue solid, which turned out to be stable in the "dry" state at room temperature, but readily decomposed upon partial redissolution. MALDI-TOF MS analysis of the solid showed a molecular peak at m/z 1016.52, corresponding to that of the trimeric 1,4-PTA structure **11**.



Scheme 4. Preparation of hexaphenylated 1,4-PTA trimer **11**.

Further characterization of **11** was hampered by its poor solubility and stability in classical organic solvents. Indeed, light-colored blue solutions could be obtained in tetrahydrofuran (THF), CH_2Cl_2 or $CHCl_3$, but rapidly turned green, then brown. The ^1H NMR spectrum of a saturated, but low concentration, solution of **11** in $CDCl_3$ was, however, recorded at −30 °C, and it confirmed the absence of the OCH_3 signals of the precursor **10**. Revealing the presence of several stereoisomers (at least three among six possible), multiplets were observed around $\delta = 8.0$ ppm for the *ortho*-^1H nuclei of the phenyl substituents, and around $\delta = 7.5$ ppm for their *meta* and *para* congeners; the TIPS signals merged into a broad singlet at $\delta = 1.21$ ppm. Due to insufficient concentration, attempts at recording $^{13}C\{^1H\}$ spectra in $CDCl_3$ solution failed to bring out the quaternary ^{13}C signals of **11**. Nevertheless, recording the CP-MAS $^{13}C\{^1H\}$ spectrum of the dry solid allowed complete assignment of all the ^{13}C nuclei of **11**, which unambiguously confirmed the 1,4-PTA-type structure (Figure 3).

^{119}Sn NMR spectroscopy of the blue solid, however, revealed the presence of $^1H/^{13}C$ NMR-silent $SnCl_2$ in the sample (the obtained chemical shift was identical to that of a pure $SnCl_2$ sample, and no other ^{119}Sn signal was observed, showing that no significant interaction occurs between **11** and surrounding $SnCl_2$ molecules: see Figure S2 in the Supporting Information). The blue powder was thus submitted

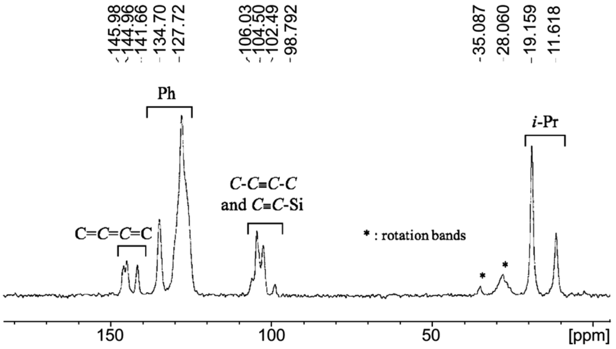


Figure 3. CP-MAS $^{13}C\{^1H\}$ NMR spectrum of **11** in the solid state.

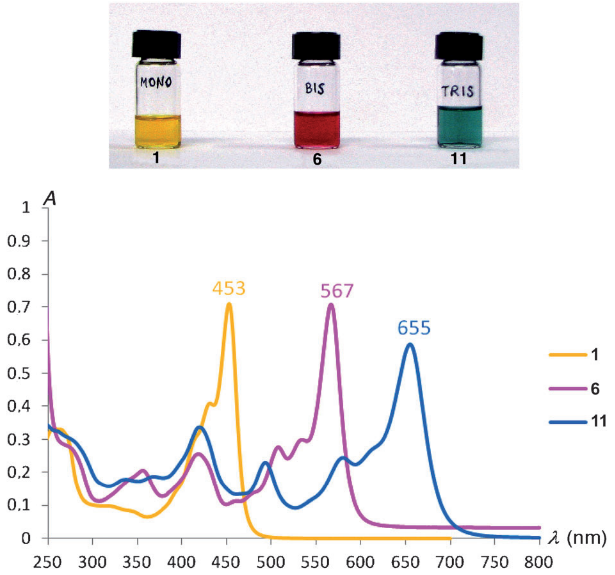


Figure 4. Absorption spectra of the monomeric, dimeric, and trimeric 1,4-PTAs **1**, **6**, and **11** in $CHCl_3$ solution, respectively (bottom), and corresponding photographs of diluted solutions in CH_2Cl_2 (top). The spectrum of **11** was recorded at 0 °C after rapid preparation of a diluted solution of undetermined concentration.

to elemental analysis, which indicated that the mixture was actually composed of a 10% molar ratio of **11**, corresponding to a **11**/$SnCl_2$ ratio of 38:62 by weight. The yield of the reductive elimination process from **10** to **11**, isolated as a mixture with $SnCl_2$, was thus estimated to be 48% (Scheme 4; 10 equiv of $SnCl_2$ was used). However, all attempts to separate **11** from the $SnCl_2$ matrix (by chromatography or any method requiring dissolution) failed because of the instability of the tris-butatriene in solution. This also prevented selective crystallization of **11** (all the deposited single crystals submitted to XRD analysis to date turned out to be $SnCl_2$ crystals).

These results indicate that perphenylated 1,4-PTAs are less stable than 1,2-PTA congeners, which were described to be stable and soluble, even for quite large oligomers.[13] Whereas all the known 1,2-PTAs are described as yellow solids irrespective of their length, the three 1,4-PTAs **1**, **6**, and **11** are dark solids, giving yellow, pink, and blue solutions, respectively (Figure 4). The corresponding UV/Vis spectra present systematic bathochromic shifts of ca. 100 nm along the series **1**→**6**→**11**, reflecting the parallel increase of the extent of conjugation from monomer **1** to trimer **11** (Figure 4).

Whereas the extinction coefficients of **1** and **6** were calculated to be quasi-identical (ca. 50000 L mol^{-1} cm^{-1}), that of **11** could not be determined because of its instability in solution. When the degradation of **11** was monitored at room temperature (Figure 5), it was observed that the initial most intense band at 655 nm almost disappeared after 22 min and was replaced by an intense band at 419 nm, while the initially blue solution turned progressively to green, then yellow, and finally to pale-brown.

Continuing to monitor the solution, it was observed that the band at 419 nm reached a maximum intensity after nearly one hour, then began to decrease, and disappeared after two days. Although the structure of products could not be determined (the ^1H NMR spectrum of the degradation material was not characteristic), the monitoring suggests that the evolution of **11** proceeds quite selectively through an intermediate of shorter maximal π-conjugation extent (419 vs. 655 nm for **11**), roughly corresponding to that of dialkynyldiphenylbutatrienes such as **1** (453 nm). By comparison to **6**, the sensitivity of **11** might thus be attributed to the possibility of intramolecular reactions between facing external butatriene units in some *cisoid*-folded conformations of stereoisomers of **11**

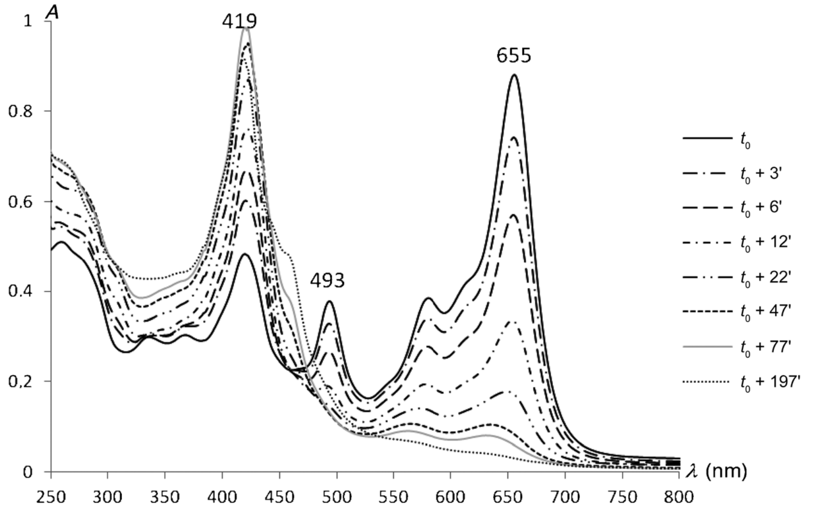
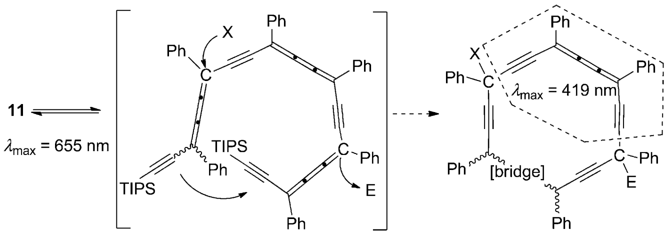


Figure 5. UV/Vis monitoring of the decomposition of the 1,4-PTA trimer **11** in $CHCl_3$ solution at room temperature. The time intervals are provided between the successive spectra (min) versus the initial time t_0.

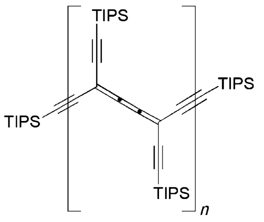


Scheme 5. Putative intramolecular process triggered at the benzylic carbon vertices and allowed by the specific stereochemical/conformational features of **11** compared to **6**, accounting for the higher stability of the latter. The dotted line encompasses a dialkynyldiphenylbutatriene motif, the maximum absorption of which should occur in the range 400–450 nm.

featuring a *cis*-configured central butatriene unit (Scheme 5). Such a transformation might also be facilitated by traces of $SnCl_2$ in solution. The use of other reductants has been attempted,[14] but although $SnCl_2$ alone (in the absence of HCl) proved to be less efficient, the strongly acidic KI/H_2SO_4 system produced black polymeric materials. The classical $SnCl_2/HCl$ system thus appears to act in a manner that is a trade-off between acidity and reductive efficiency for **10**.

Conclusion

The first examples of the 1,4-PTA family have been described in the perphenylated series up to the oligomeric order three. By comparison to 1,2-PTAs, which are stabilized by the noncumulenic representative resonance form **a** (Figure 1), the poor stability of the 1,4-PTA trimer **11** in solution can be primarily attributed to two features: i) the unique resonance form involving a [3]cumulenic motif (Figure 1), and ii) the occurrence of *cis*-configured dialkynylbutatrienes motifs, which are both kinetically and thermodynamically allowed (in 1,2-PTAs, the *cis* configuration of the olefinic bonds is thermodynamically disfavored by steric factors). Nevertheless, the reactivity of **11** might also be due to the benzylic nature of the sp^2-vertices (Scheme 5), and steric stabilization of these centers could be envisioned by replacement of the phenyl substituents with hindered aryl groups, such as mesityl or 2,6-diisopropylphenyl groups, or even Tokitoh's "Tbt" groups.[15] The sensitivity of **11** is also possibly related to its poor solubility, preventing its separation from the $SnCl_2$ matrix. The next challenge is therefore the synthesis of diversely substituted 1,4-PTA oligomers, and, in particular, the likely highly soluble TIPS-protected total *carbo*-mer of oligoacetylenes, for which C_2 units are also inserted into the C–H bonds (Scheme 6). Functional 1,4-PTA oligomers are the ultimate targets.[16]



Scheme 6. The challenging soluble 1,4-PTA targets: TIPS-protected total *carbo*-mers of oligo-acetylenes.

Acknowledgements

In addition to the Ministère de l'Enseignement Supérieur de la Recherche et de la Technologie and the Paul Sabatier University, thanks are due to the Centre National de la Recherche Scientifique and to the ANR program (ANR-11-BS07-016-01) for post-doctoral fellowships to A.R.

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[12] Crystal data and structure refinement for **6**: $R=0.06$. Ellipsoids are set at 50% probability. Space group: $P\bar{1}$. Selected bond lengths in Å: Si1−C1 1.840(2), C1−C2 1.207(3), C2−C3 1.432(3), C3−C4 1.351(3), C4−C5 1.237(3), C5−C6 1.354(3), C6−C7 1.418(3); Selected bond angles in degrees: C2-C1-Si1 172.3(2), C1-C2-C3 176.9(2), C2-C3-C4 116.73(19), C3-C4-C5 179.3(2), C4-C5-C6 179.5(2), C5-C6-C7 117.88(19). CCDC-878530 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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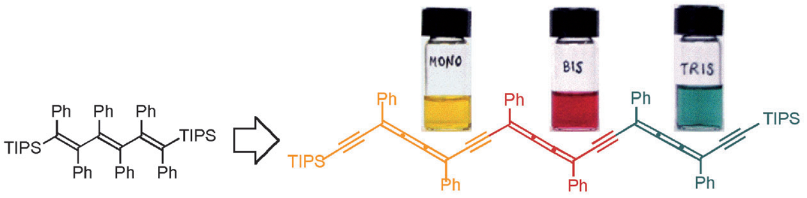
Received: May 4, 2012
Revised: July 23, 2012



Colorful chain *carbo*-mers of polyacetylenes are isomers of the well-known polytriacetylenes (PTAs). The three first representatives are shown to exhibit continuously but markedly varying chromophoric properties (see figure).

Polyacetylenes

*A. Rives, V. Maraval,**
N. Saffon-Merceron,
*R. Chauvin** .... ■■■■–■■■■

First Perphenylated *carbo*-oligoacetylenes: An Extension of the Polytriacetylene Family