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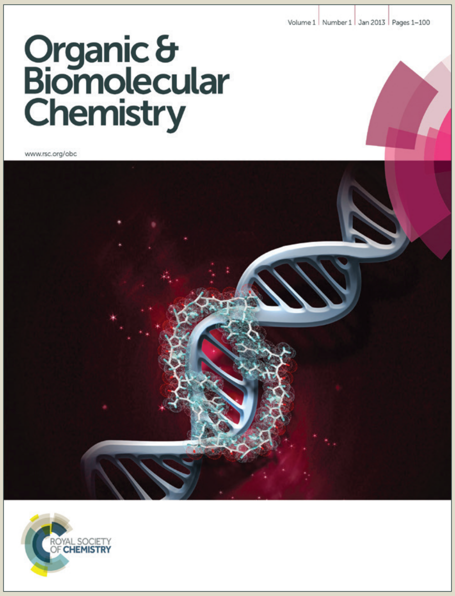

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ARTICLE

Synthesis, Gelation and Topochemical Polymerization of *meta*-Linked Oligophenylenebutadiynylene Derivatives

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Abstract: Rational design of *meta*-linked oligophenylbutadiynylene (OPBDs) derivatives has been conducted in order to gain insights on their gelation properties and reactivity toward topochemical polymerization to yield polydiacetylenes (PDAs). Different structural parameters influencing the gel formation such as the presence of peripheral 2-hydroxyethoxy side chains and the position of amide functionalities, responsible for intermolecular hydrogen bonds, have been studied. Topochemical polymerization of butadiynes units contained within the OPBDs was performed and the resulting PDAs were characterized using electron microscopy and spectroscopy.

Introduction

Interest in polydiacetylenes (PDAs) has grown significantly among the scientific community. These organic semiconductors showed great potential for many applications in several important areas such as organic electronics[1-4], nanomaterials chemistry[5], biotechnology[6-8] and so on. These polymers possess interesting optical and chromic properties, such as unique blue-red transitions, which make them interesting candidates for the sensing of various analytes and ions.[9-11] Initially reported by Wegner et al. in the early 70s, these semiconductors are mainly obtained by topochemical polymerization of butadiynes-containing monomers.[12-15] The butadiyne functionalities, when pre-assembled according to specific structural parameters, can undergo a series of 1,4-addition to form polydiacetylenes. Traditionally, the requisite parameters needed for the reaction, namely an angle of 45° and a distance of 3.9 Å between the butadiynes, are obtained in the crystalline state.[16-18] Despite the efficiency of the polymerization on single crystals, this approach has several drawbacks. As a matter of fact, preparation of single crystals through slow evaporation of solvents can be time-consuming and usually requires a well-controlled environment that is often unsuitable for large-scale production of materials. To overcome these drawbacks, a different approach using self-assembly of butadiyne-containing monomers in the gel state, in which the critical parameters for the 1,4-addition can also be obtained, was developed.[19-31] This method allows for the preparation of large quantities of PDA in a much faster process without the need for the "perfect" solvents system as needed for crystals formation. Thus, it is not surprising that the polymerization in the gel state is an increasingly popular avenue to prepare various types of PDAs.

Among the plausible applications of PDAs, their use as precursors for the preparation of well-defined carbon-rich nanostructures is particularly interesting.[32-38] Because of their unique structure of alternating double and triple bonds, aryl-appended PDAs present all the characteristics needed to become excellent building blocks for the preparation of carbon-rich nanoarchitectures with unique properties. Thus, by self-assembly and topochemical polymerization of monomers with well-defined structures, it was possible to obtain various architectures such as nanorods,[39, 40] nanotubes,[41-44] nanoparticles[45, 46] and, more recently, two-dimensional layered graphite-like materials.[47] For the later, linear, *para*-linked oligophenylenebutadiynylenes (OPBD) containing at least two butadiyne units have been self-assembled and submitted to irradiation to yield a 2D PDA. Surprisingly, this PDA underwent a rapid chemical transformation upon exposure to ambient UV light or gentle heating. The transformation involved the enyne moieties and the phenyl groups of the PDA and further characterization indicated that a cycloaromatization occurred, yielding to 2D layered, graphite-like materials. In order to obtain more insights on the graphitization mechanism occurring for this particular PDA, we undertook the preparation of different OPBDs with different shapes and sizes. The first question we sought to answer is whether the observed chemical transformation of the PDA to partially graphitized materials is specific to the linear OPBD we used in the previous study or if it can be applied for OPBDs with different chemical nature, sizes and shapes, thus opening the way to the modulation of the properties of the graphitized materials through chemical functionalization and modification of the OPBDs.

Herein, we report the synthesis, self-assembly and topochemical polymerization of new *meta*-linked OPBDs possessing specific structural elements promoting gelation such as amide functionalities, aliphatic chains and polar 2-hydroxyethoxy side-chains. We show that by varying the position and the amount of these elements on the π-conjugated scaffold, it is possible to significantly influence the self-assembly in the gel state. The reactivity of OPBDs toward the topochemical polymerization of butadiyne units was also studied and correlated with the gelation properties. Since two butadiyne units are incorporated within the OPBDs scaffold, the materials obtained after irradiation are expected to be two-dimensional (2D) PDAs (Figure 1) in which the simplest form is a nanoribbon,[48, 49] although more complicated 2D architectures are also expected based on previous report.[47] Attempts to transform these 2D PDAs into graphitic materials have also been conducted and the results obtained for this transformation are compared to those obtained for the linear OPBD analogues.

Results and Discussion

The self-assembly mode of small molecules in the gel state relies on a delicate balance of weak forces such as π-stacking, hydrogen bonds and van der Waals interactions. The strength of these interactions is highly dependent on several electronic and steric parameters, which makes the design of organogelators with the optimal structural parameters for the topochemical polymerization very difficult. Recently, we and others have studied the influence of some structural parameters on the self-assembly in the gel state.[50-53] For example, variation of the configuration of amide groups (mostly hydrogen bonds) and addition of various polar side chains contained in different building blocks allow to greatly influence the assembly.[54, 55] Nonetheless, the precise structural parameters obtained within organogels are still very difficult to predict accurately. Thus, we decided to prepare various OPBDs in order to establish general rules that will guide us toward well-defined PDAs and, eventually, to carbon-rich materials with precise sizes and shapes. For this study, four OPBDs have been prepared and the structures are shown in Figure 1.

From a structural point of view, **T1** and **T2** differ only by the presence of a polar 2-hydroxyethoxy side-chain on the main skeleton of **T2**. This variation allowed us to gain information on the effect of this side-chain on the gelation properties and on the reactivity of these compounds upon irradiation.

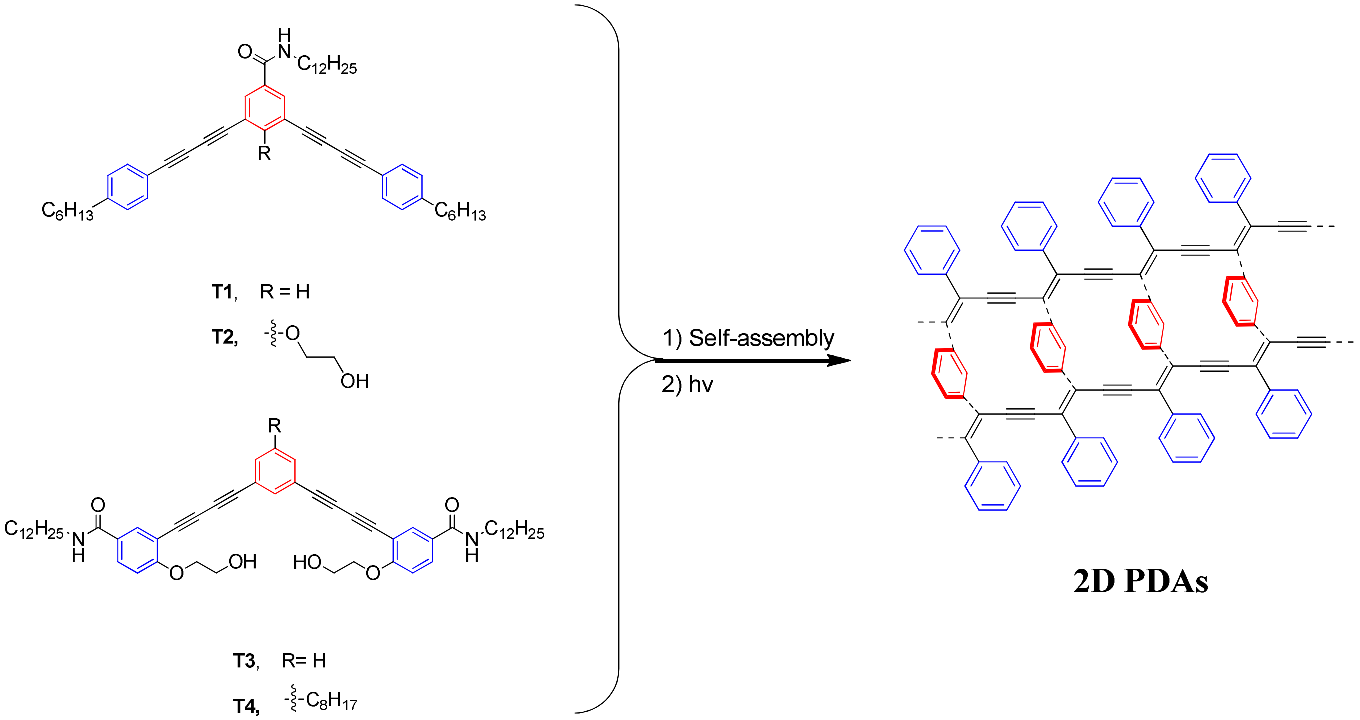

Figure 1. General approach toward 2D PDAs from *meta*-linked PBD precursors.

Both compounds are bearing an amide group to allow the intermolecular hydrogen bonding necessary for gelation. Hexyl chains have also been inserted in order to promote van der Waals interactions. Although the *para*-hexylbenzene moiety is an electron donor, which slightly decreased the strength of π-stacking interactions,[56] this substitution was used for synthetic convenience. Meanwhile, **T3** and **T4** possess two amide functions and two 2-hydroxyethoxy side-chains to increase the strength of hydrogen bonds and to assess the influence of the number of polar chains on the gelation properties of OPBDs. **T3** and **T4** differ only by the presence of an octyl aliphatic chain, resulting in an increased of van der Waals interactions and solubility for **T4**. Thus, by comparing the first series (**T1** and **T2**) with the second (**T3** and **T4**), we expected to gain information on several elements of design influencing the self-assembly in the gel state.

The synthetic pathway toward OPBDs **T1** to **T4** is shown in Figure 2. Starting from 1-bromo-4-hexylbenzene,[57] an asymmetric butadiyne moiety was installed using modified Castro-Stephen-Sonogashira[58] conditions with 1-(trimethylsilyl)butadiyne, obtained by the monodeprotection of 1,4-bis(trimethylsilyl)butadiyne[59] (32% yield over 2 steps). Afterward, removal of the silyl protecting group was performed using tetrabutylammonium fluoride and the resulting compound was directly coupled to *meta*-diiodo aryl moieties under standard Castro-Stephen-Sonogashira coupling conditions to afford OPBDs **T1** (27% yield) and **T2** (28% yield). The synthetic pathway for the synthesis of **T3** and **T4** is started from previously reported compound **3**.[45] Removal of the silyl protecting group was carried out using tetrabutylammonium fluoride and the resulting compound was directly coupled to 1,3-diiodobenzene (for **T3**) and 1,3-diiodo-5-octyl-benzene (for **T4**) under standard Castro-Stephen-Sonogashira coupling conditions to afford OPBDs **T3** (76%) and **T4** (22%), respectively.

In order to determine the influence of the substituents on the self-assembly, gelation properties were determined in several commonly used organic solvents.[60] Gelation properties are summarized in Table 1. For **T1** and **T2**, which differ only by the presence of a polar 2-hydroxyethoxy side-chain at the center of the OPBD, the gelation properties are similar. Both OPBDs have a good solubility in most of the solvents, which limits the gel formation. However, **T1** and **T2** tend to form very opaque gels in hydrocarbons such as *n*-decane and *n*-octane. Furthermore, they both formed a gel in methanol, despite the high polarity of this solvent. The presence of a polar chain (**T2**) also seems to provide stronger assembly in chlorinated solvents such as chloroform, unlike its counterpart without side-chain (**T1**). Based on these results, we thus hypothesize that, in the cases of **T1** and **T2**, the addition of a 2-hydroxyethoxy chain only brings subtle changes to the gel formation properties. **T3** and **T4**, which differ by the presence of an octyl chain at the top of the OPBDs, showed good gelation properties in most of the solvents tested. Both OPBDs formed gels in aromatic solvents, ethyl acetate and phenyl ether. The presence of two side-chains and two amides seems to increase the strength of intermolecular interactions. Interestingly, the addition of an octyl chain on the central phenyl of the OPBD (**T4**) increased its gelation abilities and organogels have been formed in solvents such as acetonitrile and cyclohexane, demonstrating that, despite the increased solubility, van der Waals interactions seem to favor the self-assembly. However, thermal analysis suggests that organogel obtained from **T4** are less stable than those obtained from **T3** (*vide infra*). By comparing the first series of OPBDs (**T1** and **T2**) with the second (**T3** and **T4**), we observed that the gel formation ability is significantly increased by the introduction of amide groups and polar side-chains. Moreover, the addition of aliphatic chains allowed the gelation of OPBDs in a wider range of solvents despite the better solubility.

For each compounds, the critical gelation concentration, melting temperature and crystallization temperature of the solvent trapped in the assembly have been determined in order to gain insights on the stability of the gel and on the strength of the supramolecular networks. These properties are summarized in Table 2. *n*-Octane was chosen as solvent for **T1** and **T2** given the good gelation properties of the compounds in this non-polar solvent while toluene was chosen for the same reason for **T3** and **T4**. Organogels from **T1** and **T2** showed similar thermal properties, indicating that the introduction of a 2-hydroxyethoxy chain on the central phenyl does not significantly affect the gel stability. It is important to note that the critical gelation concentration and the melting temperature have not been determined for **T2** since a robust, free-standing gel has never been obtained.

Table 1. Gelation properties of OPBDs **T1** to **T4**, S = soluble, P = precipitate, I = insoluble and G = Gel

Solvent	**T1**	**T2**	**T3**	**T4**
toluene	S	S	G	G
benzene	S	S	G	G
chloroform	S	G	G	S
n-octane	G	G	I	I
n-decane	G	G	I	I
cyclohexane	S	S	I	G
ethyl acetate	S	S	G	S
phenyl ether	S	S	G	G
o-dichlorobenzene	S	S	G	G
1,4-dioxane	S	S	S	S
acetonitrile	P	P	P	G
methanol	G	G	P	P

For **T3** and **T4**, the main difference is the melting temperature of the gel. used organic solvents. Indeed, the gel of **T3** in toluene presented a melting temperature of 115 °C while **T4** presented a melting temperature of 76 °C. This significant difference indicates that the addition of octyl chain weaken the supramolecular network and, thereby, the stability of the gel.

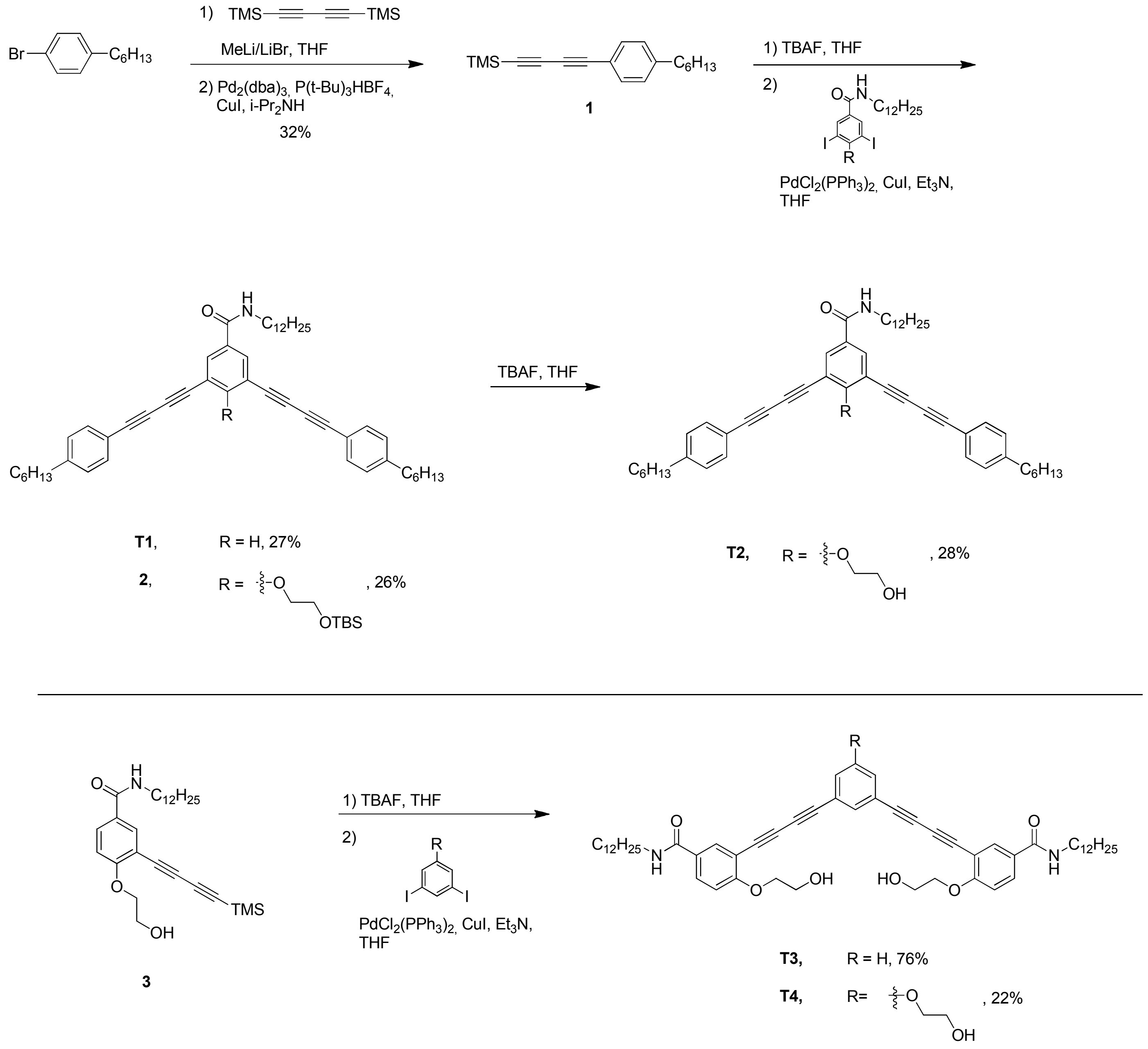

Figure 2. Synthetic pathway to *meta*-linked oligomers **T1-T4.**

Table 2. Properties of OPBDs-based organogels

Compound	CGC[a] (mg/mL)	T_c (°C)[b]	T_{gel} (°C)[c]
T1 (octane)	3	- 63.3	43
T2 (octane)	-	-62.5[*]	-
T3 (toluene)	2	-135.4	115
T4 (toluene)	2	-127.8	76

[a] Critical gelation concentration. [b] Crystallization temperature of the solvent trapped in an organogel at 10 mg/mL. [c] Melting temperature for the organogel in toluene and octane at 10 mg/mL using the drop-ball method.[61] [*] Since no robust gel was obtain from **T2**, this data was estimated when apparition of an opaque phase was observed

To study the three-dimensional network of the gel matrix at the microscale level, scanning electron microscopy (SEM) images were recorded on the dried organogels (xerogels) of **T1**-**T4**. Organogels from *n*-octane were prepared for **T1** and **T2** while toluene was used for **T3** and **T4**. The results are shown in Figure 3. As previously observed for other type of organogelators,[23, 50, 62, 63] all organogels prepared have a fibrillar structure at the micron scale. **T1** forms large well-aligned fibers while **T2** presents a more disorganized 3D network. For **T3** and **T4**, the fibrillar network is less defined than **T1** and **T2**, probably due to the difference of solubility.[50, 64, 65]

The topochemical polymerizations of butadiynes units were carried out using UV irradiation at 254 nm for 24 hours on the xerogels of **T1**-**T4** prepared from various solvents (Supporting Information). The results obtained for the formation of PDAs are presented in Table S1. For **T1** and **T2,** which presented a rather inefficient gelation in most of the solvents tested (except hydrocarbon solvents), no PDA formation was observed, even after long period of irradiation, which indicates that the supramolecular assemblies are probably too disordered and that the proper stacking parameters of butadiyne units to allow the 1,4-addition was not obtained. In the case of **T2**, a greenish color, generally associated with incomplete formation of PDAs, was observed in *n*-octane. The addition of a polar side-chain to the center of the OPBD therefore appears to allow self-assembly approaching optimal conditions, unlike its counterpart bearing no side chain. However, the formation of PDA remains quite difficult and not effective enough to be further investigated. For **T3** and **T4** that possess good gelation properties in various solvents tested, the formation of PDA was observed in many conditions with toluene and benzene giving the best results. In the case of phenyl ether, the polymerization was incomplete, resulting in the appearance of a greenish color rather than the characteristic blue color associate to PDAs. All further characterizations discuss below were performed on organogels of **T3** and **T4** obtained from toluene. Toluene was chosen because of the rapid appearance of an intense blue color during the irradiation of the xerogel, which may be correlated to good polymerization yield.

UV-visible spectroscopy was used to confirm the presence of PDA upon irradiation of xerogels (see Figures S1 and S2 in Supporting Information). For **T3** and **T4**, the appearance of a band associated with PDA, with a maximum at 635 and 633 nm for **T3** and **T4**, respectively, was observed. It is important to mention that all PDAs that were characterized were previously purified using a Soxhlet apparatus (acetone as solvent) in order to remove unreacted precursors and low molecular weight fractions.

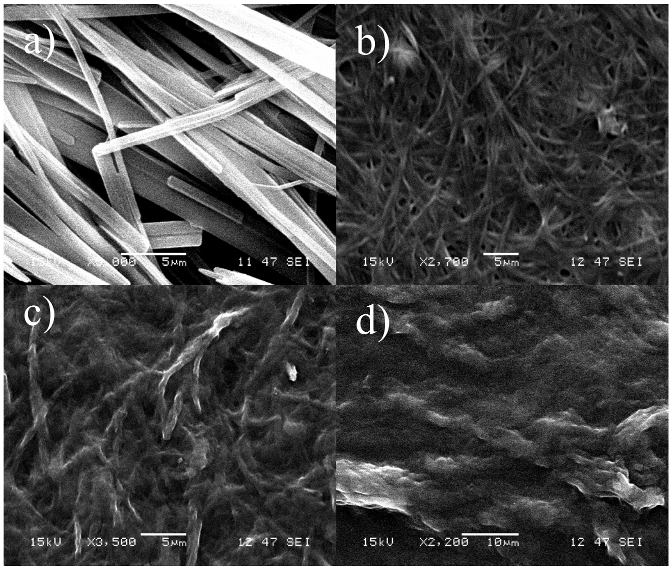

Figure 3. SEM images of a 10 mg/mL xerogel of a) **T1** (octane), b) **T2** (octane), c) **T3** (toluene) and d) **T4** (toluene). Scale bars are 5 µm (a to c) and 10 µm (d).

Raman spectroscopy was used to assess whether all the butadiyne units have reacted upon irradiation and the results obtained are presented in Figure 4. Both **T3** and **T4** possess an intense band at 2217 cm^{-1} (**T3**) and 2227 cm^{-1} (**T4**) associated with the unreacted butadiyne moieties. After irradiation of the xerogel, the disappearance of this band is observed as well as the appearance of two new bands associated with new triple and double bonds of PDA. **PDA3** has two new bands at 2109 and 1457 cm^{-1} while **PDA4** presented two new bands at 2109 and 1470 cm^{-1}. These new bands can be respectively associated to the alkyne and alkene moieties of the PDA, respectively.

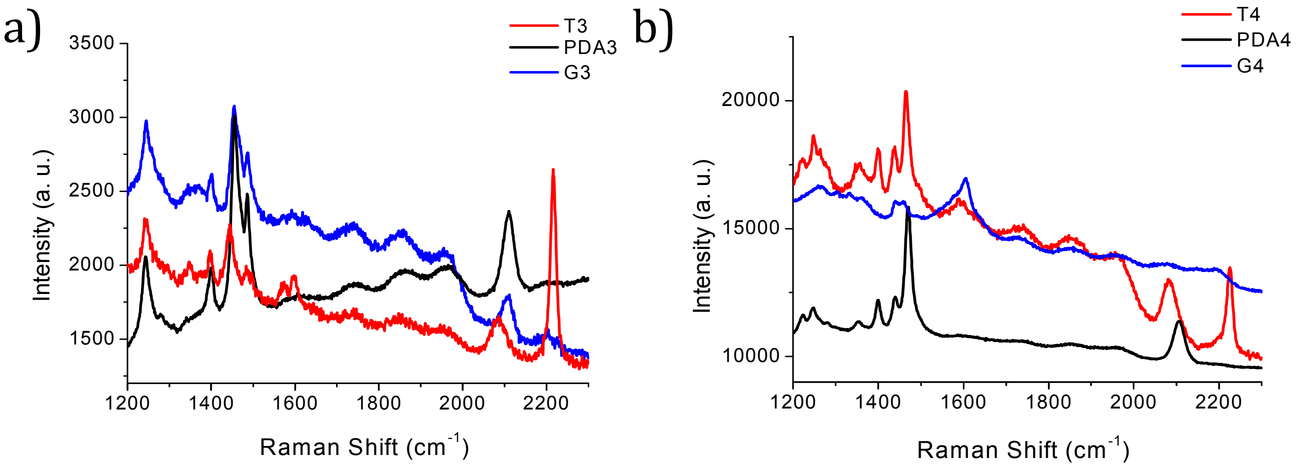

Figure 4. Raman spectra for a) **T3** and **PDA3** and b) **T4** and **PD4**.

The absence of residual bands associated to butadiyne confirms the complete reaction of **T3** and **T4** to form PDAs. It is important to note that the presence of bands associated to PDA around 2100 and 1470 cm^{-1} in the spectra of the **T3** and **T4** can be observed. These bands originate from the partial polymerization of butadiyne units while the Raman spectra are recorded due to the use of focalized laser beam.

As already reported by our group, some PDAs obtained from linear OPBDs can undergo a chemical reaction in solution when heat or light is applied to form layered graphite-like materials.[47] To test if the *meta*-linked monomers can undergo such a reaction like their linear analogues, samples of **PDA3** and **PDA4** were dissolved in THF and heated at 150 °C (microwave oven) for one hour, leading to new materials thereafter called **G3** and **G4**, respectively. Following the heat treatment, the blue color associated to PDA completely disappeared. In order to confirm that the color change is the result of a chemical transformation and not an indication of irreversible thermochromism, UV-visible spectrum was recorded on **G3** and **G4** and the result in shown in Figure S3 and Figure S4. As expected, the complete disappearance of the absorbance bands associated with PDA was observed, indicating that the enyne moieties within the PDA backbone have been chemically transformed. However, this chemical transformation is not complete, as determined by the Raman spectrum in which bands associated to the initial PDA are still present after the heat treatment (Figure 4). This observation suggests that the reactivity of *meta*-linked OPBDs is lower than their linear analogues. This can be explained by the assumed non-planarity of the *meta*-linked central phenyl ring relative to the PDA backbone, preventing efficient intramolecular cycloaromatization. Interestingly, heating **PDA3** and **PDA4** results in green emissive materials. The emission peaked at 490 and 503 nm for **G3** and **G4**, respectively, which are about 30 to 40 nm blue-shifted compared to the layered graphitic materials prepared from *para*-linked oligomers (Figures S5 and S6 in Supporting Information).[47] The slightly higher energy emission is indicative of less conjugated materials, which is expected for *meta*-linked oligomers. Although the difference between the *para*- and *meta*-linked oligomers might not seem significant, it shows that the optical properties of the layered graphitic materials can be modulated through molecular design. Study of the cycloaromatization reaction on model compounds is currently underway to understand the exact nature of the chemical transformation occurring when aryl-appended PDAs are heated.

Transmission electron microscopy (TEM) analysis was performed in order to obtain information on the nanostructure of these materials. The resulting images are shown in Figure S28. Both **G3** and **G4** obtained showed a fibrillar structure. For **PDA3,** few microns-long, large fibrils can be observed, indicating that the initial gel morphology has been retained during the topochemical polymerization. **PDA4** showed similar behaviour, although the morphology retention seems less efficient. After heating **PDA3** and **PDA4**, not much change was observed in their morphology, although **PDA4** seems to undergo partial morphology change from fibrillar to layered structure as we observed previously for the linear OPBD.[47]

Conclusion

The design and synthesis of new *meta*-linked OPBDs was realized. OPBDs with the proper elements of design can self-assemble in the gel state to form supramolecular, well-defined nanoarchitectures. By varying the number of amide functionalities (hydrogen bonding), adding long aliphatic chains promoting van der Waals interactions and varying the number of 2-hydroxyethoxy polar side-chains, it was possible to somehow modulate the gelation properties in several organic solvents. The topochemical polymerization of the OPBDs in the xerogel state was accomplished under UV irradiation and the formation of PDAs was observed for **T3** and **T4**. These PDAs underwent partial chemical modification upon heating, resulting in carbon-rich materials. Interestingly, the resulting PDAs are less reactive toward light or heat than the PDAs obtained from *para*-linked analogues. The chemical transformation that occurred during the thermal treatment is currently under investigation.

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