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Rigid organic nanotubes obtained from phenylene-butadiynylene macrocycles[†]

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Simon Rondeau-Gagné, Jules Roméo Néabo, Maude Desroches, Isabelle Levesque, Maxime Daigle, Katy Cantin and Jean-François Morin*

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Rigid organic nanotubes were prepared from six-membered phenylenebutadiynylene macrocycles through topochemical polymerization in the xerogel state. All six butadiyne units underwent polymerization, thus creating rigid nanotubes with six polydiacetylene chains lying parallel, one relative to each other.

Similar to carbon nanotubes, organic nanotubes show numerous interesting features for different applications, including host-guest chemistry and organic electronics.1 However, a reliable and straightforward synthetic strategy must be developed before they can be considered as a serious alternative to other materials. A promising strategy to prepare them is to assemble macrocyclic building blocks to obtain supramolecular nanotubes and to link them covalently to fix the tubular organization.² Among the strategies used to link supramolecular organization, topochemical polymerization of 1,3-butadiynes, yielding polydiacetylene (PDA), is particularly interesting since no metal catalyst or additive is needed to drive this polymerization.³ However, specific and strict intermolecular structural parameters are needed for this reaction to occur.⁴ Recently, we and others demonstrated that a gel state can be used to obtain such critical parameters, allowing the preparation of high molecular weight PDAs from building blocks of different sizes and shapes.⁵ We have also shown that the incorporation of specific elements of design allows the control over molecular organization in phenylacetylene macrocycle (PAM) assembly, allowing topochemical polymerization between macrocycles in the xerogel state.⁶ The material obtained after topochemical polymerization was made of soluble, PDA-walled conjugated nanorods.

In order to prepare larger, rigid and more robust PDA-walled organic nanotubes, we have chosen to prepare six-membered phenylene-butadiynylene macrocycles (**PBM1** and **PBM2**, Fig. 1) that possess six 1,4-diaryl-1,3-butadiyne units (rather than only



two in the case of PAMs), which could potentially undergo topochemical polymerization to form PDA. Compared to PAMs, PBMs are known to provide stronger π - π interactions owing to the electron-withdrawing effect of the butadiyne moiety, thus enabling the self-association of macrocycles in different solvents through gel formation.⁷ Moreover, PBMs are much larger than PAMs, which could allow the introduction of internal binding functionalities in addition to providing nanotubes with better host ability.8 Nonetheless, the controlled polymerization of PBM frameworks remains a challenging but worthy task considering that it would open the way to the preparation of non-graphitic, semi-conducting nanotubes with unique properties. In this regard, very few attempts to cross-link PBMs and related butadiyne-containing cyclic molecules through controlled topochemical polymerization have been reported but none of them lead to nanotubes that can be solubilized, handled easily and characterized as unimolecular entities.9

Herein, we report the synthesis, gelation properties and topochemical polymerization in the xerogel state of two phenylenebutadiynylene macrocycles (**PBM1** and **PBM2**). The resulting materials were characterized using Raman and UV-visible spectroscopy and transmission electron microscopy (TEM) to determine the efficiency of the topochemical polymerization and to assess the formation of nanotubes. Besides the preparation of new materials with unique properties, this study permits

Département de chimie and Centre de Recherche sur les Matériaux Avancés, 1045 Ave de la Médecine, Pavillon Alexandre-Vachon, Université Laval, Québec, QC, Canada G1V 0A6. E-mail: jean-francois.morin@chm.ulaval.ca;

Fax: +1-418-656-7916; Tel: +1-418-656-2812

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us to evaluate the versatility of our general strategy to prepare organic nanotubes with different sizes, shapes and functions.

The synthetic pathway for PBM1 is depicted in Scheme 1. Starting from N-dodecyl-3,5-diiodo-benzamide,6a TMS-protected diacetylenes were introduced by Castro-Stephen-Sonogashira coupling reaction using monodeprotected 1,4-bis(trimethylsilyl)butadiyne¹⁰ to afford compound 1 with good yield. Deprotection of diyne units with potassium hydroxide was then conducted before introduction of 1-octyl-3,5-diiodobenzene^{6a} using standard Castro-Stephen-Sonogashira coupling to obtain half-macrocycle 2 in rather low yield (28%). It is noteworthy that the low yield is due to the formation of linear oligomers, which are common side-products for this kind of statistical coupling. TIPS-protected acetylenes were then installed on the half-macrocycle by standard Castro-Stephen-Sonogashira coupling to obtain 3 in excellent yield (92%). After removal of TIPS using tetrabutylammonium fluoride (TBAF), the deprotected halfmacrocycle was directly used without purification in the ring closing reaction under modified Eglinton conditions to provide PBM1 in relatively low yield (11%).¹¹ This low yield of cyclization can be attributed to the relative instability of diyne units and the moderate solubility of **PBM1**.^{9b,12} An identical synthetic approach was used for PBM2 and it is also depicted in Scheme 1. The yields for each step are similar to those obtained for PBM1.

In order to obtain proper intermolecular orientation and distance between macrocycles prior to the topochemical polymerization, **PBM1** and **PBM2** were gelified in different organic solvents. The gelation process was chosen over crystal formation to organize molecules since it is much less time-consuming. Moreover, we have shown previously that the topochemical polymerization of 1,4-diarylbutadiyne moieties can be very efficient in the gel state compared to that in the crystalline state since the former accommodates conformational changes better.^{5c} Standard gelation tests were performed by dissolving the corresponding PBM in different solvents (1 to 10 wt per vol%). The resulting suspension was heated near the boiling point of the solvent and was allowed to cool down at room temperature. Unexpectedly, gelation was not observed in any solvents tested except for cyclohexane, which gave a translucent organogel for **PBM1** and **PBM2**. This result is surprising given that PAMs bearing the same outer decorations presented good gelation properties in a large number of solvents.⁶ We hypothesize that this significant difference in the self-assembly process between PAMs and PBMs can be attributed to the better solubility of PBMs.¹³

The distance and orientation between the macrocycles within the xerogel state were studied by powder X-ray diffraction (PXRD) analysis. The PXRD spectrum of **PBM1** is presented in ESI[†] (Fig. S18). A rather broad peak at $2\theta = 4.1^{\circ}$ (30.4 Å) is observed and can be attributed to a (100) reflection of a columnar lattice, most likely with a hexagonal symmetry. Moreover, a broad and intense peak at $2\theta = 21.5^{\circ}$ (4.3 Å) is observed and can be attributed to liquid-like order between the alkyl chains. The PXRD spectrum thus suggests that macrocycles are stacking on top of each other to form tubular assemblies as observed for similar macrocycles and discotic liquid crystals.^{8,14} Moreover, the columnar organization of PBMs suggests the presence of an inner empty cavity within the column although it was not possible to assess with certainty the presence of such a cavity based on the sole PXRD analysis.

Knowing that the macrocycles of **PBM1** in the xerogel state are stacked in a face-to-face configuration, which is an essential prerequisite for the topochemical polymerization to occur, a thin film of the xerogel obtained from a cyclohexane gel was deposited on a glass substrate and subjected to irradiation using UV light ($\lambda = 254$ nm) for a period of 48 h. Appearance of a dark blue color, associated with the formation of PDA, was observed for **PBM1** after irradiation. For **PBM2**, a slight change in color was observed after irradiation turning the white xerogel to yellow. This slight color change accounts for an incomplete polymerization and/or degradation of the supramolecular network. Surprisingly, the incorporation of external diynes did not drive the topochemical polymerization, as it was the case for the PAM family.^{6a}

The purification of cross-linked **PBM1**, thereafter called **PDA1**, was conducted using size-exclusion chromatography (SEC) (Bio-Beads SX-1) and a UV-visible spectrum of **PDA1** was recorded in CHCl₃ (see Fig. S19 in ESI†). As expected, apparition of a broad absorption band with λ_{max} at 640 nm was observed, which is characteristic of a PDA backbone. For every 10 mg of **PBM1** deposited as a gel, about 1 mg of soluble blue material can be obtained after purification by SEC, which gives a yield of about 10%.

In order to evaluate the extent of reaction of the butadiyne units, Raman spectroscopy was performed on a xerogel of **PBM1** and on purified **PDA1** and the spectra are shown in Fig. S20 (ESI[†]). The Raman spectrum of **PBM1**, recorded on the xerogel, exhibited a strong band at 2224 cm⁻¹ and a weaker one at 1593 cm⁻¹, which can be attributed to the diyne units. Unexpectedly, these bands disappeared almost completely (conversion >95%) after UV irradiation. This is confirmed by the appearance of new bands at 2112 cm⁻¹ and 1477 cm⁻¹, which can be attributed, respectively, to the stretching modes of alkyne and alkene moieties of the newly formed ene–yne functions. It is important to mention that these bands are present, at a lesser extent, in the powder spectrum of **PBM1**. This phenomenon is due to partial crosslinking of the very reactive **PBM1** induced by the Raman laser.¹⁵ However, the complete disappearance of diyne vibrational bands

Fig. 2 Structure and PDA1 in front and side views. Side groups and hydrogen atoms have been omitted for clarity. The red and blue carbon atoms represent the PDA chains and the phenyl groups, respectively.

a) b)

Fig. 3 TEM (a) and HRTEM (b) images of the nanotubes. Scale bars are 500 nm (a) and 20 nm (b).

in the **PDA1** spectrum clearly showed that all the butadiyne units contained in the macrocycles reacted to form a rigid nanoarchitecture in which six PDA chains lay parallel, one relative to each other, as presented in Fig. 2. The reaction of all the butadiyne units eliminates the possibility of incomplete polymerization or open-like structures.

TEM imaging was performed on PDA1 to visualize the resulting architecture. As shown in Fig. 3 and Fig. S21 (ESI⁺), the nanotubes appeared mostly as individualized entities, although some bundles can be found. Unlike PAMs, the PBM-based nanotubes seem to be much more rigid and their internal empty cavity can be clearly visualized. Such a high rigidity is possible only if all the butadiyne units have reacted to form PDA chains, confirming the result obtained using Raman spectroscopy. Moreover, long nanotubes (few tens of nanometers) with a very narrow polydispersity index (Fig. 3a) can be prepared, thus proving the efficiency of the topochemical polymerization of butadiynes embedded within the PBM scaffold. The exact diameter of the nanotubes (theoretical value = 2.5 nm) is very difficult to determine because of the relatively poor contrast obtained in TEM imaging for non-graphitic carbon materials on the carbon substrate. Experiments are still underway to address this issue. This result is also a clear indication that topochemical polymerization happened exclusively in an intracolumnar fashion to create a 1D nanoarchitecture.

In summary, synthesis and gelation of new phenylenebutadiynylene macrocycles bearing amide functionalities were accomplished. PXRD analysis of the resulting xerogels showed a columnar organization in which the PBMs stacked on top of each other, allowing the topochemical polymerization of the PBMs' inner butadiyne units to stabilize the supramolecular architecture. Raman spectroscopy performed on the resulting 1D nanoarchitectures confirmed that all the butadiyne units disappeared upon irradiation. HRTEM proved that the covalent nanoarchitectures thus created are rigid and possess an internal void. Thermal graphitization of this structure to create welldefined carbon nanotubes is underway.

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