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COMMUNICATION

H-Bonding-driven gel formation of a phenylacetylene macrocycle†

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An amide-containing phenylacetylene macrocycle (PAM) has been synthesized and its gelation properties were studied in different solvents. Surprisingly, this macrocycle forms organogels at low concentration in many polar and apolar solvents. XRD and FTIR analysis suggest that this macrocycle forms stable supramolecular assemblies owing to H-bonding. Scanning electron microscopy analyses show the formation of bundles of nanofibrils, demonstrating the long-range organization of this material.

The face-to-face stacking of π-conjugated systems is a convenient and elegant way of building well-ordered molecular architectures that could be used as efficient active components in electronic devices. In fact, high levels of organization in organic semiconducting materials can help in improving charge mobility in bulk and thin-film configurations. Rigid, 1D conjugated building blocks that have been used to create such ordered arrays in the solid state are hexa-*peri*-hexabenzocoronene,[1] perylenes,[2] porphyrins,[3] phthalocyanines,[4] π-conjugated oligomers[5] and macrocycles.[6] Among others, macrocycles, especially phenylacetylene macrocycles (PAMs), have attracted a lot of attention in the past ten years because supramolecular assemblies of PAMs in a face-to-face configuration can lead to porous materials analogous to carbon nanotubes. However, a good and reliable method to assemble PAMs in a face-to-face configuration still needs to be developed, the biggest challenge being to find a good balance between PAMs' solubility and intermolecular interactions. Self-association of PAMs in solution has been demonstrated several times,[5] but relatively low binding constants have been reported and the architectures thus formed through this process are usually made of dimers or trimers at most.

Recently, Moore *et al.* have developed an efficient way of assembling carbazole-based PAMs using the sol–gel process in cyclohexane.[7] The gel thus obtained was made of microns-long nanofibrils owing to π–π and hydrophobic interactions. In order to extend the scope of this strategy to other types and sizes of PAMs, we have undertaken the preparation of PAMs containing chemical functions that are expected to improve intermolecular interactions, our ultimate goal being to prepare more robust organic nano-objects for further utilization in devices. We report herein the synthesis and gelation properties of a new PAM (**1**, Fig. 1) showing excellent gelation properties in many organic solvents owing to the presence of two amide groups that increased intermolecular interactions through H-bonding. H-bonding has proven to be an efficient strategy to increase intermolecular interactions between macrocycles.[8]

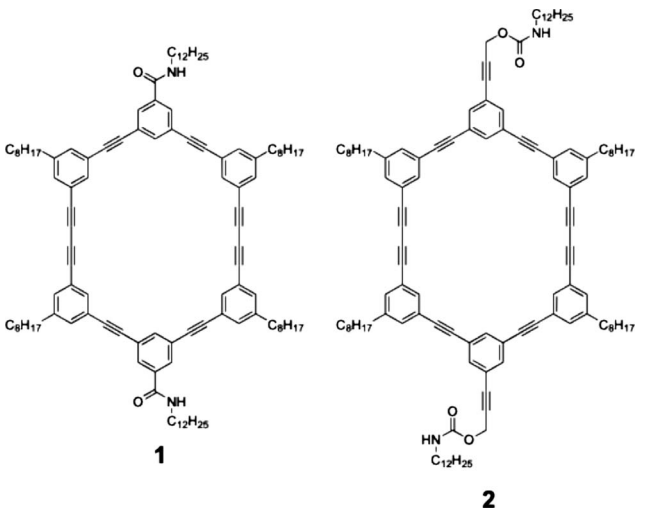

Fig. 1 Phenylacetylene macrocycles **1** and **2**.

The structures of the two PAMs prepared for this study are presented in Fig. 1. The only structural difference between PAMs **1** and **2** is the functional group introduced onto the head and the tail of the macrocycle to generate intermolecular H-bonding. In PAM **1**, a very common amide group was introduced while urethane was used for PAM **2**. Because our long-term goal is to prepare covalently linked nanotubes from these architectures, diyne unit was introduced within the structure of the PAMs to allow further photopolymerization to form polydiacetylene (PDA).[9] Four octyl chains per PAM were also added to increase the solubility and van der Waals intermolecular interactions of the resulting PAMs.

Macrocycles **1** and **2** were prepared using similar synthetic pathways, which involved a ring closing reaction by the Eglinton–Glaser coupling between identical symmetrical *meta*-substituted trimers in highly diluted conditions.[10] The synthetic strategies for the synthesis of **1** and **2** are depicted in Scheme 1 and in Scheme S1 in the ESI,† respectively. For **1**, the amide

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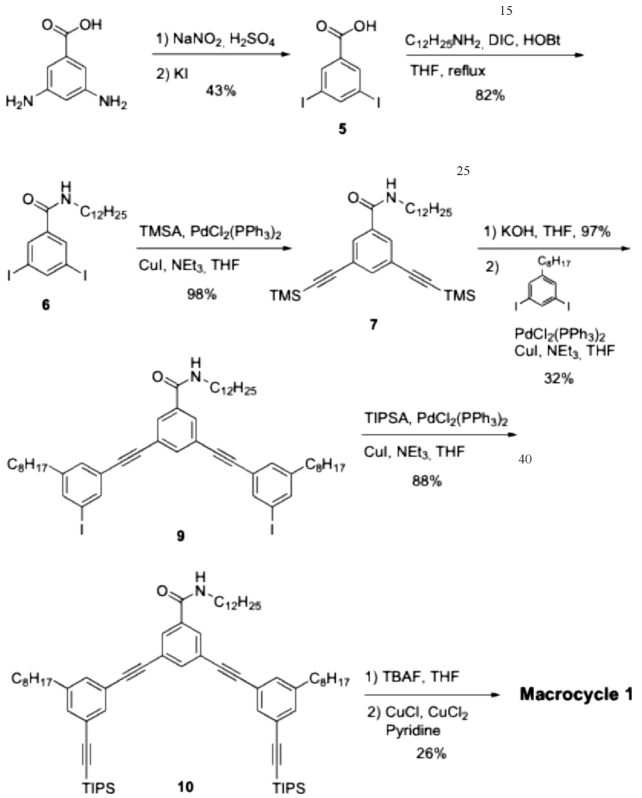
† Electronic supplementary information (ESI) available: Experimental procedures and characterization data for all the new compounds, synthetic scheme for PAM **2** and X-ray diffractograms. See DOI: 10.1039/c1ob05441d



Scheme 1 Synthesis of PAM **1**.

groups were place at the "top" and "bottom" junctions of the macrocycle. Starting from 3,5-diaminobenzoic acid, the amino groups were replaced by diazonium intermediates using sodium nitrite in acidic conditions. The bis(diazonium) salt was then reacted with potassium iodide to provide compound **5** in 43% yield.[11] Amide was formed by reacting compound **5** with dodecylamine using *N*,*N*′-diisopropylcarbodiimide (DIC) and 1-hydroxybenzotriazole (HOBt) to provide compound **6** in good yield (82%). It is noteworthy that in our hands, the coupling reaction using dicyclocarbodiimide (DCC) and *N*,*N*′-dimethylaminopyridine (DMAP) gave only a poor yield of compound **6** since the DCC-activated carboxylic acid derivatives cannot be converted to the final product efficiently. Standard Castro–Stephen–Sonogashira[12] coupling, using trimethylacetylene (TMSA), $PdCl_2(PPh_3)_2$ and CuI, was then used to install protected alkynes in the *meta* positions to give compound **7** in excellent yield (98%).

The two alkyne groups were then deprotected using potassium hydroxide in tetrahydrofuran (THF) and directly coupled to 1-octyl-3,5-diiodobenzene by Castro–Stephen–Sonogashira reaction to give compound **9** in 32% yield. Because the use of an excess of 1-octyl-3,5-diiodobenzene was not sufficient to avoid the formation of longer oligomers, the yield obtained for this reaction was quite low. The alkyne groups used for the Eglinton ring closing reaction were introduced using Castro–Stephen–Sonogashira reaction using triisopropylsilylacetylene (TIPSA) to yield compound **10** in 88% yield. In the final step, the two alkyne groups were deprotected using tetrabutylammonium fluoride (TBAF) in THF, followed by the Eglinton–Glaser ring closing reaction in high dilution conditions (10^{-3} M) as adapted by Höger

Table 1 Gelation properties of PAM **1** at 1.0 w/v%

Solvent	Observation[a]
toluene	G
1,2-dichlorobenzene	S
benzene	G
p-xylene	G
chlorobenzene	G
pyridine	S
tetrahydrofuran	S
methanol	P
acetone	P
ethyl acetate	G
dimethylformamide	S
acetonitrile	S
cyclohexane	G
1,4-dioxane	G with precipitate
hexanes	G
1,2-dichloroethane	G
chloroform	S
carbon disulfide	S
2-propanol	P
ethanol	P
dichloromethane	P
decalin	G
methyl *tert*-butyl ether	P

[a] G = gel; S = soluble; P = precipitate.

et al.[13] As reported by Breslow *et al.*,[14] the high-dilution conditions usually needed to perform macrocyclization reactions can be avoided when Cu(I) and Cu(II) are used in anhydrous pyridine, making the reaction mixture easier to workup. The macrocycle **1** was thus obtained in 26% yield, which is low but comparable to other non-templated ring closing reactions using this method. The macrocycle **1** is readily soluble in THF and chloroform and partly soluble in all the other common organic solvents.

For the gelification process, powder of **1** and **2** was dissolved in solvent (1.0 w/v%) by heating the solvent near its boiling point and the clear solution thus obtained was allowed to cool down at room temperature, resulting in a gel which was either opaque or translucent depending on the solvent used for the gelification process. The gelification properties of PAM **1** are summarized in Table 1. Surprisingly, PAM **1** formed a gel in 10 out of the 23 solvents tested, which included aromatic as well as polar (ethyl acetate) and apolar (hexanes) solvents. The astonishing ability of PAM **1** to form a gel in different solvents can be ascribed to its ability to participate in different kinds of intermolecular interactions, presumably H-bonding, van der Waals and π–π interactions.

PAM **2** shows much better solubility in most of the solvents listed in Table 1 compared to PAM **1**, resulting in very poor gelation ability at the concentrations tested (1–10 w/v%). This can be explained by the lower ability of the urethane function to participate in H-bonding compared to amides and by the higher rigidity of chemical functions surrounding the amide groups in PAM **1**. This result demonstrates how important the structural parameters are for the gelification process and how difficult it is to predict self-assembly behavior based on structural analysis.

In order to study the nanoscale morphology of the organogel of PAM **1**, a small portion of it was slowly dried in ambient conditions onto a metallic substrate and subjected to scanning electron microscopy (SEM) analysis. As shown in Fig. 2a, organogel of

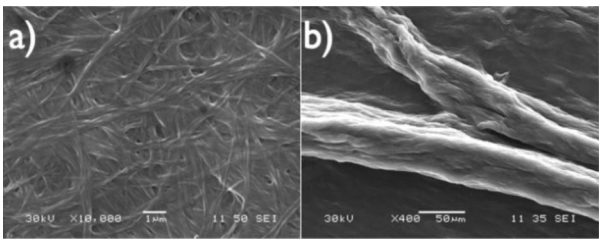


Fig. 2 SEM images of the organogel from PAM **1** (a) in toluene, scale bar = 1 μm, and (b) in cyclohexane, scale bar = 50 μm.

PAM **1** in toluene (1.0 w/v%) is made of microns-long 1D wirelike fibers with diameters of few tens to few hundreds of nanometres. These nanofibers assembled into much larger bundles, which is indicative of strong interfiber interactions. Interestingly, the size of the fiber obtained after the gelification process is dependant on the nature of the solvent. As shown in Fig. 2b, much larger fibers than those obtained from toluene gel (Fig. 2a) are observed when cyclohexane is used at the same gel concentration (1.0% w/v). In this particular case, microns-wide fibers are obtained, and although the internal structure of the fibers is difficult to observe, one can argue that the fibers are made of aligned smaller fibers. At this point, the parameters that lead to different assembly from one solvent to another are not well understood and a systematic study of fiber width–solvent dependence is being conducted.

To assess whether or not the amide groups allow the formation of intermolecular H-bonding, Fourier transform infrared (FTIR) spectra were recorded on a gel of PAM **1** at different temperatures. The results are shown in Fig. 3. For this study, the gel was prepared in decalin because a high boiling point solvent was needed to avoid solvent loss during the experiment.

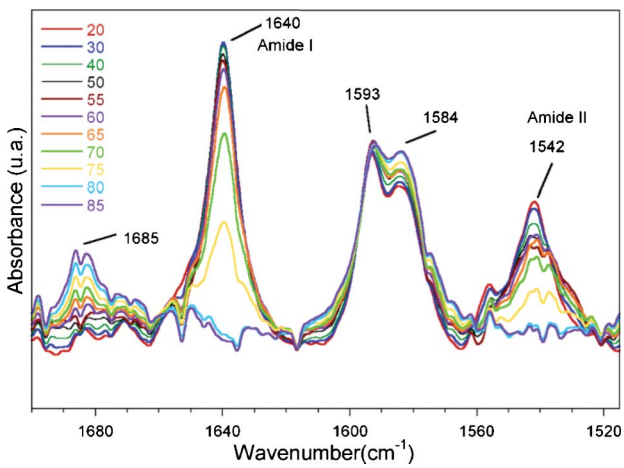


Fig. 3 FTIR of a 1.0 w/v% organogel of PAM **1** in decalin as a function of the temperature.

At 20 °C, the associate Amide I and Amide II bands were observed at 1640 and 1542 cm^{-1}, respectively. Upon heating, the bands gradually disappeared, as the H-bonds broke, and a new band at 1685 cm^{-1} attributed to the free Amide I band appeared. Unfortunately, the band associated with the free Amide II band was hidden by the decalin peak in the 1400–1520 cm^{-1} region. These spectral changes strongly support the formation of intermolecular H-bonding that contributed to the gelation ability of PAM **1** in addition to possible π–π and van der Waals interactions.

To study the molecular organization that leads to the fibrillar structure observed in the SEM images, X-ray diffraction (XRD) analyses were performed on films of PAM **1** obtained from a cyclohexane gel (1.0% w/v) and compared to a film made from PAM **1** in a THF solution for which no gelation was observed at this concentration. The diffractogram (see Figure S2 in the ESI†) of the dried gel showed a sharp intense peak at 2θ = 2.5, which corresponds to 3.52 nm. The data extracted from the diffractogram are not clear enough to confirm any particular arrangements within the gel. Nonetheless, based on other reports on PAM assemblies,[6,15] it can be hypothesized that the macrocycles stacked on top of each other to form columnar assemblies with an intercolumnar distance of *ca.* 4 nm, which is in good agreement with the calculated width of PAM **1**. The columnar arrangement is also in good agreement with the fibrillar structure observed by SEM. Interestingly, no feature except a broad band centered at 2θ ≈ 24, which is representative of an amorphous material, was observed when a film of PAM **1** was formed from a THF solution. This is indicative of the importance of the gelification process for obtaining a well-ordered array of macrocycles.

In summary, we have prepared a phenylacetylene macrocycle that shows excellent gelation properties in many organic solvents. Characterization reveals the formation of nanofibrils that consist of stacks of macrocycles owing to intermolecular hydrogen bonding as showed by the FTIR analysis as a function of temperature. The interactions strengthen the supramolecular organization and open the way to the utilization of PAMs as robust building blocks for the preparation of nanoscale functional materials. PAM **1** is now being studied as a potential precursor in topochemical polymerization to build covalently linked organic nanotubes.

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