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Room-temperature synthesis of soluble, fluorescent carbon nanoparticles from organogel precursors†

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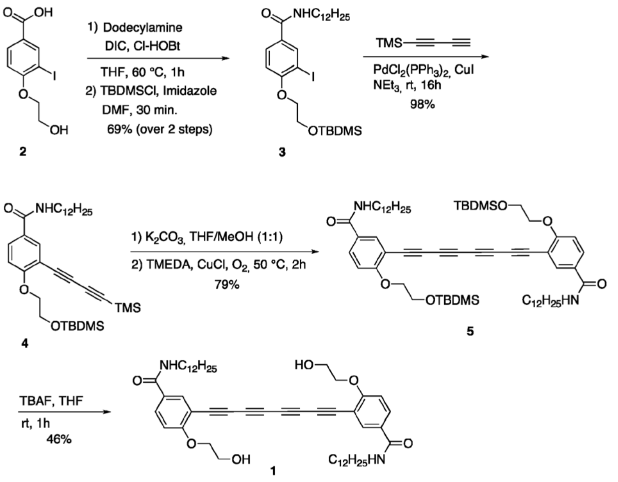
Carbon nanoparticles were obtained at room temperature by irradiating an organogel made from a 1,8-diaryloctatetrayne derivative in chloroform. During the topochemical polymerization, the morphology of the gel changes from fibers to soluble, yellow fluorescent nanoparticles in high yield. Analyses suggest that the resulting nanoparticles are made of amorphous graphitic carbon.

Carbon-rich materials like fullerenes, carbon nanotubes and graphenes have attracted a lot of attention in the past 25 years because of their exceptional electronic and optical properties.[1] Although they are recognized as being very promising materials for several electronics- and optics-related applications, many drawbacks associated with their preparation such as the use of high temperatures (pyrolysis), vacuum and metal catalysts have slowed down their use in commercial devices. Thus, a wealth of efforts has been devoted to the development of preparative methods that allow the synthesis of well-defined, carbon-rich nanostructures under milder conditions, preferably below 100 °C and without the use of metal catalysts or complex setups.

One emerging strategy to obtain carbon nanostructures at relatively low temperatures without a metal catalyst involved the use of oligoynes as highly reactive precursors.[2] In 2004, Ding and Olesik showed that an amphiphilic tetrayne derivative can be self-assembled in water to form ultrathin films that undergo a spontaneous polymerization reaction to form cross-linked polymer films.[3] These films can further be transformed into nanoparticles by heating the films suspension at 70 °C. More recently, Frauenrath *et al.* used a similar approach to prepare graphitic nanostructures from hexayne-based colloids.[4] Less ordered graphitic materials have also been prepared by Goroff *et al.* using poly(diiododiacetylene) as the carbon source and Lewis bases as a catalyst at room temperature.[5] However, to the best of our knowledge, none of the graphitic materials prepared thus far using room-temperature methods from reactive carbon-rich precursors are soluble in organic solvents. The good solubility of electro- and photoactive materials in common organic solvents represents a significant advantage for many electronics-related applications that rely on a film-forming process to cover large substrates such as light-emitting devices (LED) and organic solar cells.

Herein, we report the synthesis of soluble, fluorescent carbon nanoparticles using a room-temperature, catalyst-free process. A 1,8-diaryloctatetrayne derivative (compound **1**, Scheme 1), used as the carbon source, was self-assembled to form organogels and was irradiated under UV light at 254 nm at room-temperature. Our initial hypothesis was that by self-assembling the carbon source into a well-ordered array of molecules (organogel), the resulting graphitic materials would retain the gel morphology, namely nano- and microfibers, upon graphitization reaction at low temperatures. The possibility of morphology retention has recently been demonstrated for the graphitization of helical polyacetylene films.[6] In our case however, nanoparticles rather than the expected fibers were obtained. These nanoparticles, made of amorphous graphitic carbon, are soluble in common organic solvents and exhibit intense yellow fluorescence in solution.

The first step toward the preparation of carbon nanoparticles was the synthesis of a tetrayne derivative that bears amide groups with a long alkyl chain directly attached to the aryl groups at both ends of the molecule. We[7] and others[8] have



Scheme 1 Synthesis of the reactive 1,8-diaryloctatetrayne derivative.

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previously shown that amide groups are ideal to drive organogel formation through intermolecular hydrogen bonds while providing the optimal intermolecular distance for topochemical polymerization of butadiyne moieties. Moreover, long alkyl chains are not only necessary to make the precursors soluble and to drive the self-assembly process through van der Waals interactions, but also to make the final graphitic materials soluble in organic solvents. Thus, based on our previous study on the topochemical polymerization of 1,4-diarylbutadiyne in the gel state,[7] we designed and prepared compound **1** as depicted in Scheme 1. Starting from compound **2**,[7] an amidation reaction with dodecylamine followed by an alcohol protection reaction using *tert*-butyldimethylsilyl chloride (TBDMSCl) gave compound **3** in 53% yield over two steps. It is worth mentioning that the protection of the primary alcohol was necessary to reduce the polarity of the substrate, thus enabling further purification steps by column chromatography. Compound **3** was then subjected to Sonogashira coupling with an excess of trimethylsilyl-1,3-butadiyne[9] under standard conditions to give compound **4** in excellent yield. Afterward, the terminal alkyne was deprotected and the resulting relatively unstable product was immediately subjected to a Hay coupling without further purification to give compound **5** in good yield. Finally, the alcohol groups were deprotected using tetrabutylammonium fluoride (TBAF) to yield compound **1**.

Compound **1** shows very good gelation properties in many solvents (see Table S1 in the ESI†), especially in chloroform, toluene, benzene and chlorobenzene. In most cases, freestanding, translucent organogels can be obtained at concentration as low as 0.5 wt%. SEM images obtained after drying a toluene-based gel under ambient conditions on a metallic substrate showed a highly dense structure made of micron-long fibers (Fig. 1) indicative of very strong interfiber interactions.[7,10] To obtain better insight into the molecular arrangement, the same dried gel was subjected to XRD analysis between 1° and 20° (see Fig. S8 in ESI†). Three rather broad peaks at 2.83, 0.65 and 0.45 nm characterize the diffraction pattern, suggesting a rather disordered arrangement with a face-to-face intermolecular distance of 4.5 Å, which is consistent with intermolecular hydrogen bonds attributed to the amide groups.

The topochemical polymerization was performed on organogels of toluene and chloroform at a concentration of 10 wt% under irradiation at 254 nm for 72 hours. After only a few hours of irradiation, the gel state was lost and dark solutions were obtained in both cases. The loss of the gel state can be attributed to the conformational changes within the gel upon photopolymerization, thus disrupting the intermolecular hydrogen bond network.[7,10,11]

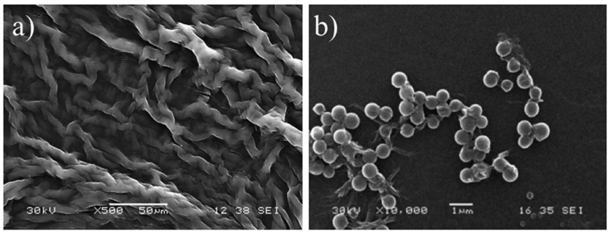

Fig. 1 SEM images of organogel from compound **1** in chloroform before (a) and after (b) irradiation (10 mg mL^{-1}). The scale bars are (a) 50 μm and (b) 1 μm, respectively.

Nonetheless, the solution was kept under UV irradiation for 72 hours before the resulting solutions were analyzed by size-exclusion chromatography (SEC) (see Fig. S9 in ESI†). Unexpectedly, the chromatogram obtained for the toluene solution is very different than that obtained for the chloroform one. On the one hand, the crude material obtained from the toluene gel contains high molecular weight fraction, but also a fairly large amount of very low molecular weight portion that could be attributed to the decomposition of compound **1** into smaller fragments, although we have no direct proof of such decomposition. On the other hand, the chromatogram of the chloroform solution does not show any trace of decomposed materials. Moreover, more than 90% of the starting compound **1** was converted to higher molecular weight materials. The decomposition of compound **1** upon irradiation in toluene is not understood at this stage. Thus, based on this result, we decided to investigate only the materials produced from the chloroform-based gel.

To assess whether or not the nano- and microfiber morphology was retained, a SEM analysis was performed on the crude material (Fig. 1b). Surprisingly, both nanoparticles and nanofibers were observed in the unpurified material. Since the nanofibers appear very similar to the ones observed in the organogel of the starting materials, we attributed the presence of fibers in the unpurified material to unreacted starting materials. To verify our hypothesis, we proceeded towards the purification of the material in order to extract the high-molecular weight fractions. The purification was achieved through successive precipitations in methanol. Since compound **1** has a similar solubility to the high molecular weight material in all the solvents we tested, we were not able to remove all the starting material from the crude product. Thus, we performed semi-preparative SEC purification using THF and collected only the desired peak. High molecular weight material with only trace amounts of starting material was thus recovered.

TEM analysis of the resulting material was performed in order to gain better insight into the morphological features of the nanoparticles (Fig. 2). Remarkably, only spherical nanoparticles with diameters between 130 and 350 nm were obtained. The change in morphology (from fibers to nanoparticles) during the course of the reaction is not yet well understood, but can partly be attributed to a decrease in the

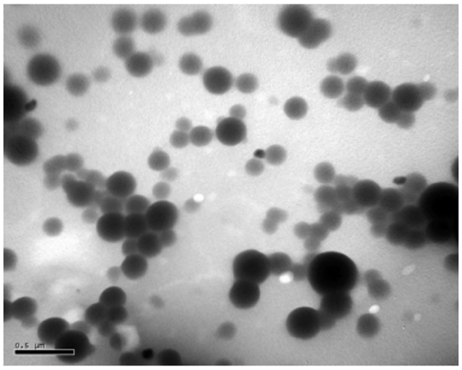

Fig. 2 TEM image of the SEC-purified material obtained after irradiation of compound **1** in the gel state for 72 hours at a concentration of 1.0 wt% in chloroform. The scale bar is 0.5 μm.

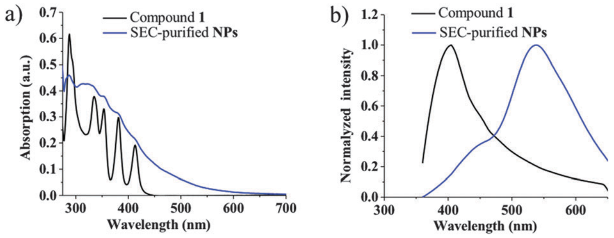

Fig. 3 UV-visible (a) and fluorescence (b) spectra of compound **1** (black) and SEC-purified nanoparticles (blue) in THF solution.

free surface energy of the material during the gel-to-solution process.

FTIR and Raman spectroscopy analyses were performed on the SEC-purified materials and the results are shown in Fig. S10 in ESI.† The bands at 2199 and 2126 cm^{-1} associated to the internal alkyne units in the FTIR spectrum of compound **1** vanished with time upon irradiation meaning that the sp carbon atoms were progressively transformed into other types of carbon, presumably sp^2 carbon atoms. However, the complete disappearance of those peaks has never been observed under the reaction conditions used to make these carbon nanoparticles. The strong peaks associated to alkyl chains at 2918 and 2849 cm^{-1} are still present in the nanoparticles spectrum, proving that our approach is useful for the preparation of soluble, carbon nanoparticles bearing alkyl chains.

Raman spectroscopy was performed to assess the presence of graphitic carbon in the nanoparticles. The band associated to the tetrayne moiety at 2105 cm^{-1} disappeared and was replaced by two very broad and intense bands at 1352 cm^{-1} and 1581 cm^{-1}, associated to the D and G bands of graphite-like materials, respectively (see Fig. S10 in ESI†). The rather broad signals suggest that nanoparticles are mostly composed of amorphous, disordered graphitic materials and that the graphitization reaction is probably incomplete as observed by FTIR analysis.[5,6,12]

The optical properties of the carbon nanoparticles were also determined and the results are shown in Fig. 3. A diluted solution of carbon nanoparticles in THF exhibits a yellowish orange color with a featureless UV-visible spectrum peaking at around 300 nm (Fig. 3a). This is consistent with other graphitic nanomaterials reported recently.[13,14] This solution also presents intense yellow fluorescence peaking at 541 nm when excited with UV light at 350 nm, representing a Stoke shift of *ca.* 140 nm (Fig. 3b). The longer wavelength emission of our materials can be attributed to their bigger size compared to those already published ($<$100 nm). Nonetheless, the width of the emission band (FWHM $\approx$ 100 nm) is very similar to the ones observed for similar materials.[13]

In conclusion, soluble graphitic nanoparticles exhibiting yellow fluorescence in solution were prepared at room temperature through topochemical polymerization of an amide-containing 1,8-diaryloctatetrayne in the gel state. Studies are currently underway to prepare nanoparticles with different sizes and shapes by changing the organogel morphology.

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