Supramolecular and core–shell materials from self-assembled fibers†

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The present study reports on the formation of supramolecular fibers from a novel cyclen-based ligand and metal salts. In particular, the fibers were shown to stabilize supramolecular porous materials of low density. It was also demonstrated that these fibers could be functionalized by radical polymer growth on their surface. Such new supramolecular fibers constitute a simple and tunable starting material for the synthesis of 1D core–shell objects.

Organic micro- and nano-fibers are the key to numerous innovative materials, both for academic research and industrial development. Considerable advances have been made in the technology concerning 1D objects in recent years and these objects are the starting materials for many applications in the fields of optoelectronics, sensors, filtration, medicine and catalysis.[1] A powerful approach to enlarging the application field of 1D objects involves functionalizing their surfaces, for example by polymer growth.[2] This approach, known as a core–shell or core sheath method, is well known in the field of polymer fibers developed by electrospinning. However, when starting from 1D supramolecular objects, using such a core–shell approach is less common, despite the fact that supramolecular fibers offer many advantages in terms of composition, nanostructure, shape (ribbon, wire, helix, network, *etc.*), physico-chemical properties and ease of access (self-assembly).[3]

The study presented here reports on the formation of a supramolecular fiber from a new cyclen-based ligand and metal salts, and demonstrated that these supramolecular fibers can be functionalized by radical polymers grown on their surfaces.

The new ligand, that we have called "tetrastyrylcyclen" (TSC, 2), was synthesized in a single step, starting from cyclen (1) and 4-vinylbenzyl chloride. The synthesis pathway is presented in Scheme 1. In most cases, cyclen, 4-vinylbenzyl chloride and triethylamine were refluxed in the presence of acetonitrile and dichloromethane. After 24 h of reflux, the TSC that had precipitated in the medium was isolated by filtration, washed with acetonitrile and methanol, and dried under vacuum. The TSC was thus obtained as a white powder at a 60% yield and was subsequently characterized by nuclear magnetic resonance (NMR), mass spectroscopy and by X-ray crystallography.†[4]

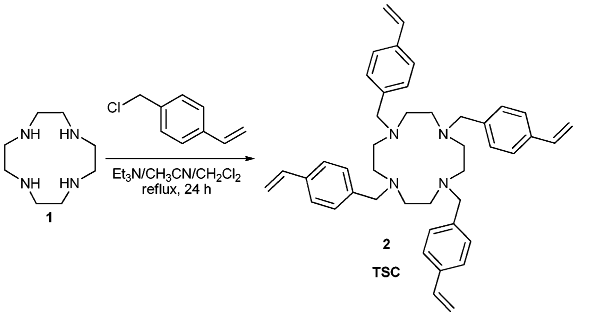
In the presence of metal salts such as cupric chloride, zinc chloride, nickel(II) chloride or cobalt(II) chloride, and together with a polar solvent such as an aliphatic alcohol, TSC self-assembled to become a gel. Such gels can also be obtained starting from a total mass concentration of 1%. For instance, 1.85 mL of a cupric chloride solution (0.02 M) in 96% ethanol was added to 0.15 mL of a solution of TSC in THF (0.31 M), preheated at 50 °C. The medium was stirred for several seconds and then stored at room temperature and the formation of a fibrous gel (Fig. 1a) was observed after a few minutes. In order to dry this gel, it was first immersed in cyclohexane, and then when all the solvents had become exchanged with cyclohexane, the gel was frozen and freeze-dried.

This method provided supramolecular objects that were robust enough to be unmolded and handled despite their low density. Fig. 1b shows a photograph of these objects. Moreover, scanning electron microscopy (SEM) observations of the objects showed that they consisted of an interlaced fiber network (Fig. 1c and 1d).

The metal presence and homogenous repartition as fibers constitutive elements was confirmed by STEM (scanning transmission electron microscopy) analysis. As we can see in Fig. 2, the elements chlorine (2b) and copper (2c) are present and uniformly distributed inside all the fibers.

The fibers were in the form of ribbons, with thicknesses of a few tens of nanometres and widths ranging from 0.1 to 2 micrometres. However, all fibers were very long, *i.e.*, in the millimetre range.

Isolated fibers were obtained by dispersion of the gel in a polar solvent such as an aliphatic alcohol. The fibers were then isolated by filtrating the suspension. Pure fibers were obtained



Scheme 1 Synthesis scheme of TSC from cyclen and 4-vinylbenzyl chloride.

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† Electronic supplementary information (ESI) available: X-ray crystallography of TSC and TSC.Cu. CCDC 702134 & 744758. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b917279c

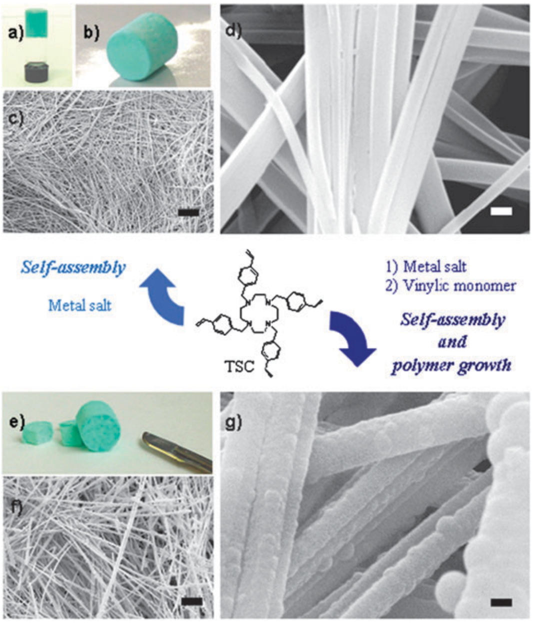


Fig. 1 Development of supramolecular materials from TSC in the presence of cupric chloride: (a) photograph of the supramolecular gel; (b) photograph of the supramolecular object obtained after drying the gel; (c) and (d) SEM images of the supramolecular object (scale bars are 20 μm and 0.5 μm, respectively); (e) photograph of dried supramolecular object obtained after radical polymerization in the presence of DVB; (f) and (g) SEM images of the dried supramolecular object (scale bars are 20 μm and 0.5 μm, respectively).

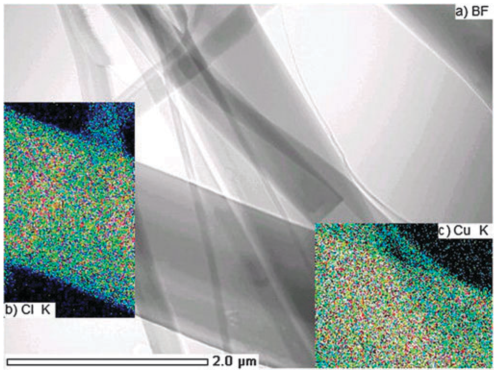
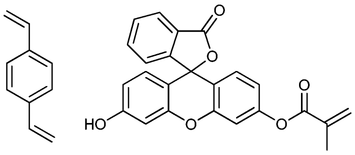


Fig. 2 (a) TEM BF image of fibers obtained from TSC and cupric chloride. (b) STEM image of chlorine. (c) STEM image of copper.



Scheme 2 Chemical structures of the monomers used for polymer growth on the fibers: divinylbenzene (DVB) (3) and fluorescein methacrylate (4).

only when the TSC/metal salt ratio = 1. Furthermore, high resolution ESI-HRMS analysis of the fibers demonstrated that the cation was TSC.CuCl+ ($C_{44}H_{52}N_4CuCl+$, m/z = 734.3171) in the case of cupric chloride-based fibers and TSC.ZnCl+ ($C_{44}H_{52}N_4ZnCl+$, m/z = 737.3148) when the fibers were based on zinc chloride. These values confirmed that the ligand/metal ratio was 1/1 in the fibers, which corresponded to the stoichiometry generally observed in copper- and zinc-based cyclen derivative complexes.[5] The structure of the complex with TSC and $CuCl_2$ was confirmed by X-ray crystallography.†

Production of a gel under the same conditions, but in the presence of a polymerizable monomer such as divinylbenzene (DVB, Scheme 2) and AIBN, provided an identical material. When this gel was heated for 5 h at 70 °C, a solid was obtained which could then be dried easily under vacuum, without mechanical deformation, providing a robust material capable of being unmolded and machined. SEM observations of this material showed that it consisted of fibers covered with small points of growing polymer.

The fibers were covered with polymer to greater or lesser degrees according to the quantity of DVB used. The same experiment, but this time mixing the DVB and the AIBN with already formed fibers, also provided fibers coated with polymer. Similar results were obtained with various vinyl monomers and other metal-based supramolecular fibers.

For example, Fig. 3 shows fibers consisting of TSC and zinc chloride, onto which a fluorescent dye monomer (*i.e.*, fluorescein methacrylate) was polymerized in diluted medium (Scheme 2). As in the case of DVB, SEM demonstrated that the fibers were coated with polymer after polymerization. Optical fluorescence microscopy showed green fluorescent fibers, which clearly confirmed that the dye had polymerized on the surface.

These experiments reveal that the new supramolecular fibers can be functionalized by radical polymerization of vinyl monomers on the fibers surface. The fiber surface probably presents reactive vinyl bonds which permit the growth of polymer chains. In fact, in the case of polymerization of

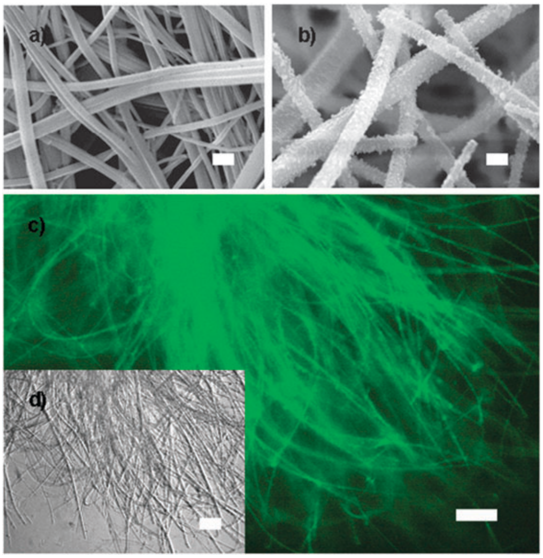


Fig. 3 (a) SEM micrograph of fibers obtained from TSC and zinc chloride (scale bar = 1 μm). (b) SEM micrograph of fibers based on TSC and zinc chloride after radical polymerization in the presence of fluorescein methacrylate (scale bar = 1 μm). Optical micrographs of the same fibers under (c) blue light (λ = 485 nm, scale bar = 100 μm) and (d) white light (scale bar = 100 μm).

non-reticulating monomers, the polymer chains obtained on the fiber surface were shown to be non-soluble in organic solvents such as THF. This suggests a covalent link between the fibers and the polymers.

In addition, this supramolecular/covalent hybrid strategy, resulting in self-assembled materials hardened by polymerization, is an efficient way to obtain metal-doped materials of low density (as low as to 15.10–3 mg/cc) with good mechanical properties compatible with micromachining. The simple self-assembly of TSC/metal yielded materials with high metal atom levels (0.97%). In fact, TSC contains precisely 100 atoms and the metal two ions. The growth of polymers on the fibers constituting the materials may make it possible to vary the levels of contributing metal by the addition of other elements (carbon, hydrogen, or other metals) according to the monomer used.

The latter characteristics are very promising for the fabrication of laser target components intended for inertial confinement fusion (ICF) experiments.[6]

In terms of application, the fibers obtained by self assembly starting from various metals constitute a novel, simple and tunable means of developing organic core–shell materials.

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4 Cyclen (2 g, 1 eq, 11.6 mM), 25 mL of anhydrous acetonitrile, 25 mL of anhydrous dichloromethane, 4-vinylbenzyl chloride (12.4 g, 7 eq, 81.3 mM) and triethylamine (17.6 g, 15 eq, 170 mM) were charged in a round bottom flask under argon atmosphere. The medium was stirred and heated at reflux for 24 h. The reaction was stopped, cooled at room temperature and the medium filtered. The crude solid was washed with 20 mL of acetonitrile and three times with 50 mL of methanol. The solid was dried under vacuum and 4.21 g of pure product was isolated as a white powder. ^{1}H NMR (CDCl$_3$) δ 7.33 (m, 16H, aromatic), 6.73 (dd, 4H, J = 10.8/17.6 Hz, vinyl), 5.75 (d, 4H, J = 10.8 Hz, vinyl), 5.24 (d, 4H, J = 17.6 Hz, vinyl), 3.44 (s, 8H, CH_2-Ph), 2.71 (s, 16H, CH_2-cyclen). ^{13}C NMR (CDCl$_3$) δ 139.84, 136.77, 135.85, 129.06, 125.89, 112.99, 59.78, 53.12. ESI(+)-HRMS calcd for $C_{44}H_{53}N^+$ $[M+H]^+$: 637.4265; found: 637.4265.

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