

# Shaping Supramolecular Nanofibers with Nanoparticles Forming Complementary Hydrogen Bonds\*\*

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Dedicated to Christiane Dietrich-Buchecker

The secondary structures of biological systems have profound effects on their functions, as do those of synthetic organic materials, in which the arrangement of the molecular units can lead to very different properties, such as electrical conductivity.<sup>[1]</sup> Up to now, the arrangements of these blocks in macroscopic crystals have been influenced, but the situation in nanomaterials—especially those with order over a very limited scale—is still challenging.<sup>[2]</sup> In particular, the preparation of systems is required in which not only the

synthesis of individual components is important, but also the creation of dissimilar building blocks with pathways by which they can interact and influence each other in such a way that materials with distinctive characteristics are generated.<sup>[3]</sup> Thereby, the combination of the components could generate hybrid materials not only with unique organizations<sup>[4]</sup> but also with new or improved properties.<sup>[5]</sup> This approach to creating novel materials has often involved biological units as one component and inorganic nanoparticles as the other.<sup>[6]</sup> The organic part is usually used to organize the inorganic particles because of the specific noncovalent interactions that are established in naturally occurring systems. Synthetic organic systems can also control the organization of gold nanoparticles,<sup>[7]</sup> and the incorporation of colloids into materials by supramolecular approaches has been explored by several groups.<sup>[8]</sup> Here we show that the reverse is also true: Gold nanoparticles can influence the organization of an entirely synthetic nanomaterial, provided the noncovalent “programming”<sup>[9]</sup> of the particle coating is correct.

Organogels are good precursors for the preparation of conducting nanoscopic fibers.<sup>[10]</sup> Using derivatives of the  $\pi$ -electron donor tetrathiafulvalene (TTF) in these systems has been shown to provide bulk semiconductors,<sup>[11]</sup> and even nanofibers with apparently metallic conductivity.<sup>[12]</sup> In the latter case, the initial phase of the doped xerogels of **1** (Figure 1) is a semiconductor with a relatively wide band gap, but it displays a structural transition to a more conducting phase on annealing at 355 K. This phase change is a result of reorientation of the TTF residues relative to each other to give a different secondary structure to the supramolecular fibers.<sup>[13]</sup> In some materials phase change can be induced by solvent, but we sought an alternative additive to produce this effect more directly. An attractive goal for us was to employ nanoparticles to induce metal-like conductivity in these supramolecular nanowires by incorporating them into the filaments and thus avoid the need for annealing.

To this end, gold nanoparticles **2-Au** (Figure 1) were prepared in which the same amido group as in **1** is located in a TTF ligand which is linked directly to the metal through a dithiolate group.<sup>[14]</sup> The TTF derivative attached to gold in **2-Au** is compatible with compound **1** because it bears not only the same hydrogen-bonding group but also the same spacer between amido group and TTF unit as organogelator. Thus, a continuous chain of hydrogen bonds and van der Waals contacts could be formed when the particles are introduced

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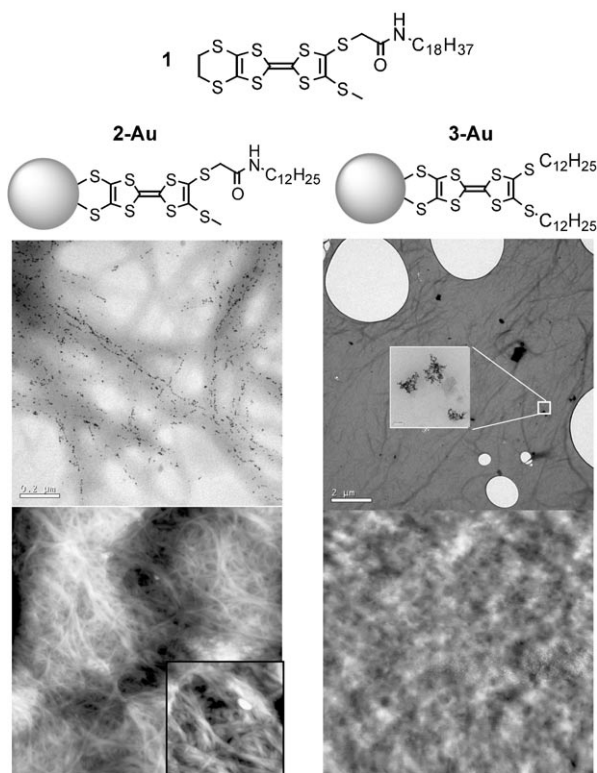
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**Figure 1.** Top: Chemical structure of gelator **1** and schematic drawings of gold nanoparticles **2-Au** and **3-Au**. Middle: TEM images of unstained xerogels of 1 wt% **2-Au** in **1** (left) and **3-Au** in **1** (right). Bottom: AFM images ( $5 \times 5 \mu\text{m}$  except for the inset, which is  $1 \times 1 \mu\text{m}$ ) of the same xerogels.

into chains of **1**. An important control experiment involves mixing **1** with nanoparticles which have no possibility for specific noncovalent interactions with the gel fibers, and hence we prepared **3-Au**, which has no amido groups. Nanoparticles **2-Au** and **3-Au** were synthesized by the standard procedure<sup>[15]</sup> involving reduction of tetrachloroaurate in a biphasic mixture in the presence of the deprotected TTF precursor (for further information and characterization see the Supporting Information).

Hybrid gels of **2-Au** and gelator **1** (referred to hereafter as **1/2-Au**) were prepared by heating 1 wt% nanoparticles with **1** in hexane to solubilize all the material with subsequent cooling to room temperature. The same type of hybrid was prepared with **3-Au** (**1/3-Au**) in which no amido unit is present in the chains appended to the TTF residue on the gold surface (Figure 1). All gels are transparent and stable for days, but vary slightly in color because of the presence of the nanoparticles. When they are exposed to the atmosphere the hexane quickly evaporates leaving transparent xerogel films of the materials on the substrate of choice.

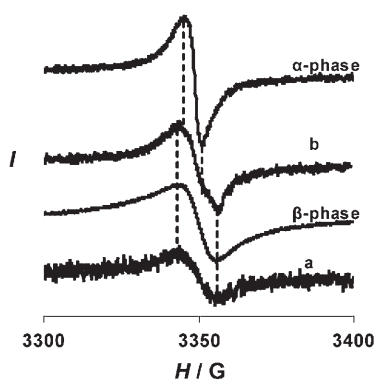
Transmission electron microscopy (TEM) images of the **1/2-Au** xerogel verify clearly the noncovalent interaction between **1** and the **2-Au** nanoparticles (Figure 1). It is evident from the TEM images that the nanoparticles are included within the fibers. Although parts of the fibers apparently contained no nanoparticles, the particles are always inside the fibers, surrounded by organic material of lighter contrast.

Furthermore, no isolated nanoparticles were seen in the many TEM measurements; all were surrounded by organic material. In contrast, when a xerogel of nanoparticles **3-Au** in **1** was imaged by TEM, no intimate contacts between the fibers and the nanoparticles could be seen. Rather, aggregates of particles and fibers of **1** are found in separate areas of the material (Figure 1). Therefore, incorporation of the amido group in the surface-attached ligand on the nanoparticles is essential to give an interaction which provides for their effective incorporation into the supramolecular nanofibers formed by **1**.

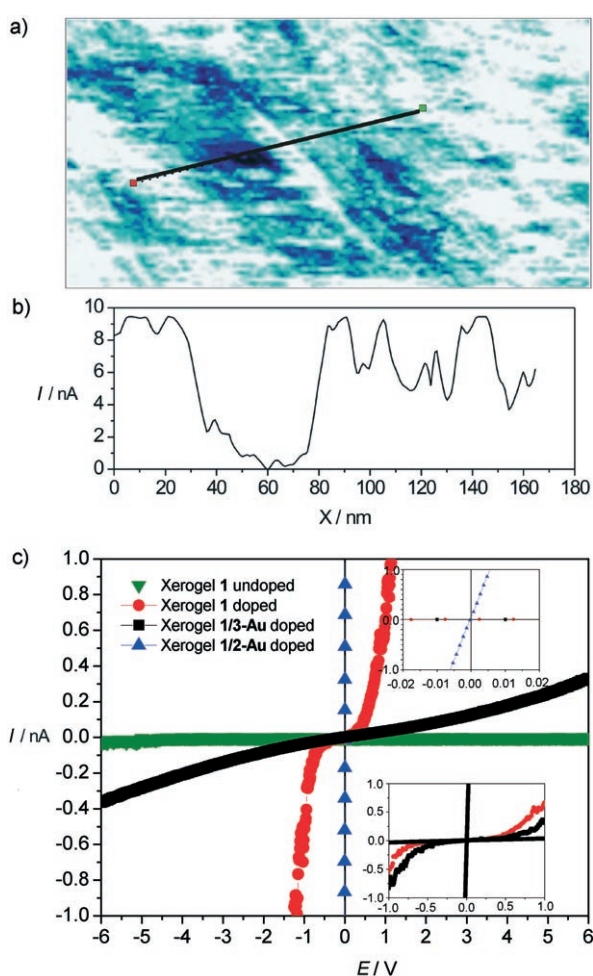
An acoustic-mode atomic force microscopy (AFM) study of xerogels **1/2-Au** and **1/3-Au** reveals distinct topographical features (Figure 1). The material formed by the xerogel **1/3-Au** is rough, with no long fibers apparent, although a short fibril structure was discernable in some images. This result is in accord with the TEM images, which show a very low homogeneity in the sample (Figure 1). On the other hand, the noncovalent interaction between the constituent components of hybrid xerogel **1/2-Au** results in a material which unambiguously exhibits long fibers when imaged by both TEM and AFM. The dimensions of the structures imaged by AFM in the case of **1/2-Au** are much longer than for **1/3-Au**, and the lateral dimensions, which range from 10 to 100 nm, are clear, while the material formed by the latter hybrid shows a very fine structure with no long fibers. The gel of pure **1** shows an intermediate texture.<sup>[12]</sup> These observations indicate that the nanoparticles **2-Au** aid in stabilizing long fibers of the organogel, while those of **3-Au** disrupt the network.

In order to oxidize the  $\pi$ -electron donor molecules to generate the conducting mixed-valent state<sup>[16]</sup> each xerogel was exposed to iodine vapor for two minutes. This procedure results in a material which has a uniform composition according to energy-dispersive X-ray (EDX) analysis (see the Supporting Information) and a morphology identical to that of the undoped (not oxidized) xerogel in the TEM micrographs, that is, no observable change in morphology of the fibers or nanoparticles occurs on doping. The organization of the donor stacks in the fibers can be characterized with a high degree of sensitivity by EPR spectroscopy,<sup>[13,17]</sup> and the morphology and electronic nature by current-sensing (CS) AFM. The iodine-doped xerogel of **1** with no nanoparticles has a peak-to-peak line width  $\Delta H_{\text{pp}}$  of its EPR signal of 6 G at 300 K (Figure 2,  $\alpha$ -phase), but when annealed at 355 K gave an irreversible increase of the line width to 13 G once cooled back to room temperature, which is evidence of a structural phase transition from the  $\alpha$ -phase of the doped xerogel to its  $\beta$ -phase (Figure 2,  $\beta$ -phase).<sup>[12]</sup> A sample of the doped **1/2-Au** hybrid xerogel gave  $\Delta H_{\text{pp}} = 13$  G at 300 K in the EPR spectrum (Figure 2a), characteristic of the  $\beta$ -phase of the mixed-valent donor assembly of the doped xerogel of **1**.

Furthermore, room-temperature  $I$ - $V$  sweeps recorded during CSAFM measurements indicated metal-like behavior (Figure 3c, blue curve), and an even more conducting and homogeneous material than pure doped **1**. From the CSAFM measurements, the estimated conductivity of the doped **1/2-Au** hybrid xerogels is  $10 \text{ Scm}^{-1}$ ,<sup>[18]</sup> approximately five times higher than the most highly conducting areas of doped **1**. In the latter, the mean conductivity estimated by CSAFM is



**Figure 2.** EPR signals of conducting doped hybrid xerogels based on **1/2**-Au (a) and **1/3**-Au (b) in comparison with the two phases formed by the pure doped xerogel of **1**.



**Figure 3.** a) CSAFM image of a doped xerogel of **1/2**-Au on highly oriented pyrolytic graphite, b) current response along the black line in (a), and c) representative spectroscopic curves of undoped xerogel of **1** (green) and doped xerogels of **1** (red), **1/2**-Au (blue), and **1/3**-Au (black). The top inset shows an expansion in  $x$  of the curves shown in the main graph to show the metallic behavior of doped **1/2**-Au, and the bottom inset shows different responses existing in a doped **1/3**-Au xerogel (black curves) in comparison to the doped xerogel **1** (red). All the curves presented for the doped materials correspond to xerogels exposed to iodine vapor for two minutes.

on the same order as that measured by the four-probe method on a bulk sample.<sup>[12]</sup> The spread in conducting behavior is also much less than for the other materials (see the Supporting Information). Clearly, the mixed-valent donor stacks in the hybrid material enter the highly conducting  $\beta$ -phase straight after doping with no need for annealing. In support of this, the EPR signal intensity of the doped **1/2**-Au xerogel is remarkably insensitive in the range from 300 to 350 K (see the Supporting Information), indicative of Pauli-type behavior seen in metallic crystalline compounds of this family of organic donors.<sup>[19]</sup> Furthermore, the low-angle X-ray diffractogram of doped **1/2**-Au hybrid is virtually identical to that of doped and annealed **1**, and different to that of doped **1** with no heat treatment (see the Supporting Information). Therefore, the **2**-Au nanoparticles induce formation of a metal-like  $\beta$ -phase with no need for heat treatment of the xerogel. The increased conductivity in the composite can be rationalized by considering the fact that the fibers in the xerogel **1/2**-Au are much longer than in pure **1** (see AFM results above), and therefore the resistance arising from fiber crossing points is lower.

On the other hand, when the doped xerogel of **1/3**-Au was studied in the same manner, EPR spectroscopy revealed two signals, with  $\Delta H_{pp}$  values of 13 and 6 G (Figure 2b). The CSAFM measurements on this material reveal an inhomogeneous surface with high contrast in the current map (see the Supporting Information). Unlike the iodine-doped **1/2**-Au xerogel, the  $I$ - $V$  curves of the doped **1/3**-Au xerogels have a wide spread in conducting behavior in different areas of the sample: In some areas the conductivity is much lower than the average of doped xerogel **1** (which gives metallic and low-band-gap semiconducting characteristics<sup>[12]</sup>), and in others metal-like behavior is witnessed (Figure 3c, inset). These results are in accord with the TEM measurements, which revealed that, in the xerogel of **1/3**-Au, negligible incorporation of the gold nanoparticles into the nanofibers results in phase separation and a breakdown of the conducting pathways. Even so, in some areas of the material the metallic  $\beta$ -phase is present, as shown by both the EPR and CSAFM measurements.

Current-sensing AFM measurements on the doped hybrid xerogel of **1/2**-Au show a fiberlike current map (Figure 3a) similar to that observed for the doped xerogel of pure **1**.<sup>[12]</sup> The measured width of the fibers is on the order of 10 nm, which corresponds to a true value of approximately 1.2 nm after the shape-deconvolution procedure. Unlike the TEM measurements (Figure 1), the individual nanoparticles cannot be identified in the AFM images, because they are incorporated into the fibers and therefore masked by the conducting yarn around them.

In conclusion, we have demonstrated formation of fibers with ohmic characteristics in a doped xerogel in which an amide-containing tetrathiafulvalene-capped gold nanoparticle (**2**-Au) induces a favorable supramolecular fiber structure of a tetrathiafulvalene-based organogelator and thus avoids the need for annealing after doping. The nanoparticle organizes the organic material into a secondary structure which shows metallic conductivity, whereas in other nanoparticle hybrids, the organic matter organizes the colloid. This

phase induction is achieved with only 1 % nanoparticles in the nanofibers, and despite the fact that areas of the organic fibers contain no particles, which perhaps indicates a cooperative structural phase induction triggered by the particles. Since the xerogels measured are from hundreds of nanometers to a few micrometers thick, we have evidence of the ability of 2-Au to guide the material into a metal-like and homogenous phase by noncovalent interactions. The 3-Au nanoparticles do not carry the correct supramolecular “code”, and therefore are not functional in the hybrid material. This strategy is not only useful for the organization of conducting materials, but may also be applicable to the organization of other fibrillar matter of natural or synthetic origin by using suitably encoded nanoparticles.

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