

# Organic Fluorescent Nanofibers and Sub-micrometer Rods

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## 1. Introduction

Luminescent nanofibers are a particular class of nanofibers. Like the other members of this family, they are very small objects whose typical diameters range between 50 to 500 nm (it is noteworthy that beyond these values, the term of microfibers is more appropriate) and lengths can reach several hundred micrometers. Besides, they display special photophysical behavior. By definition, fluorescent nanofibers have the property to emit light after absorption of UV or visible radiations, and electroluminescent nanofibers emit light upon electrical excitation. Passive properties are also encountered. This is the case in particular for waveguiding, light being guided along the long axis when the fiber width is above a minimum critical value. It is thus easy to understand why these fibers are presently attracting increasing attention. One of the most promising applications is their use in nanotechnologies. This field has developed tremendously during the last few years and sub-micrometer organic materials that exhibit specific optical properties are now of high demand. Among them, luminescent nanofibers occupy a very special position, because their morphology makes them unique for use in miniaturized systems, especially photonic devices, where they can be incorporated individually and act as active component to generate or transmit light from one point to another (Schiek et al., 2008). Their use has been proposed as frequency doublers (Brewer et al., 2006) and nanolasers (Quochi et al., 2006). They are also prime candidates for applications in the fields of photovoltaic cells and organic light-emitting diodes (OLEDs) for color displays or white light illumination (Ner et al., 2008; Ner et al., 2009). Other original uses can be found. For example, some fluorescent nanofibers have been shown to act as chemosensors to detect traces of amine vapor (Che et al., 2008; Che & Zang, 2009), explosives (Long et al., 2009; Naddo et al., 2007; Naddo et al., 2008; Tao et al., 2007; Wang et al., 2001; Wang et al., 2002; Zang et al., 2009) and metal ions (Wang et al., 2001; Wang, Drew et al., 2002). As biosensors, nanofibers reveal the presence of pathogen bacteria (Memisevic et al., 2009) and proteases (Law et al., 2007), and could be used for diagnostic purpose. Generally, the sensing performance is improved by the extended effective surface area of the nanofibers. These structures could also play the role of antennae in light-harvesting nanomaterials (Channon et al., 2009; Channon et al., 2009;

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Desvergne et al., 2006). More simply, nanofibers can also be stamped onto precious documents, such as banknotes, where they form a blue-light emitting mark, which appears more brilliant when seen from the side than from above, due to the particular waveguiding properties of the fibers (Schiek et al., 2008).

The advantage of using organic molecules instead of inorganic compounds to fabricate nanofibers is obvious. Organic compounds offer more variability and flexibility in molecular design than their inorganic homologues. A large number of chemical modifications can be introduced via synthesis to modulate or totally change the physical properties, and especially the photophysical properties that are of concern here. Besides, nanostructures based on organic molecules are able to provide high luminescence efficiency for quite a low material density, and easy and cheap processing since controlled self-assembled growth can be implemented.

It must be stressed that there is a special interest in crystallized organic materials. Actually, waveguiding is favored when the nanofibers present a high degree of crystallinity and preferential orientation of the molecules (Brewer & Rubahn, 2005). This is also the case for other photophysical processes, such as energy migration and energy transfer. These phenomena are encountered in materials that perform a light-harvesting function and, more simply, in materials where the color emission is tuned by energy transfer between two different types of molecules. Another consequence of crystallinity is that absorbance and fluorescence strongly depend on the polarization of the incident light with respect to the transition dipole of the molecules, and thus to the fiber axis. Finally, electrical conduction is also favored by a high crystal order (Henrichsen et al., 2007), which is of great interest for electroluminescent compounds.

## 2. Photophysical behavior and design of fluorescent nanofibers

The main problem in the design of fluorescent nanofibers is linked to the photophysical behavior of dyes in the solid state. Generally speaking, most dyes are strongly fluorescent when dissolved in their good solvents, but they lose their fluorescence upon aggregation. This is due to the intermolecular interactions that take place in the solid state and open deactivation pathways that compete with the fluorescence process (Birks, 1970; Silinsh, 1980). In particular, the frequently encountered plane-to-plane stacking of fluorophores (similar to *H*-aggregates) generates intermolecular coupling of electronic transition dipole moments and leads to virtually non-fluorescent solids. Particular excited species called excimers and excitons can also be formed between neighboring dye molecules, and often result in the loss of excitation energy in non-radiative processes. This behavior is not specific of fibers and is encountered in all other types of solids.

In these conditions, how can highly fluorescent nanofibers be obtained? All depends on the complexity degree that is sought after. The simplest approach is to get the fluorophores dispersed in a solid medium. As will be seen below, a good example is given by dye-doped polymers. In this case, the first requirement is to choose a highly fluorescent dye and to make sure that its fluorescence is not quenched by the surrounding medium. Many organic dyes can be dispersed in an organic medium and using them at low concentrations allows aggregation to be prevented. The dye molecule can also be individually inserted in a cage molecule before being incorporated in a solid matrix.

Another strategy is to take advantage of the fiber structure to drive the arrangement of the fluorophore molecules. This is the case for bionanofibers and some other fibers where the dye moiety is linked to an extensive alkyl moiety. Ideally, the dye molecules are arranged in the fibers as *J*-aggregates, forming a head-to-tail arrangement (Kobayashi, 1996). The arrangement of the dye molecules favors very interesting photophysical phenomena (actually quite close to those that quench fluorescence in the solids when they are not controlled). For instance, when the dye molecules are of the same chemical nature and placed in an identical environment, all of them have the same energy level. The excitation energy can then migrate from one molecule to the other. When two different types of molecule are used, the excitation energy is finally transferred to the molecule whose energy level is the lowest. If the molecule that collects the excitation energy is fluorescent, it readily emits light (Fig. 1). This phenomenon is known as a light-harvesting or antenna effect. In practice, pairs of fluorophores must be chosen so that the emission spectrum of the "donor" overlaps the absorption spectrum of the "acceptor". The process efficiency closely depends on the fluorophore separation distance and the orientation of their transition dipoles.

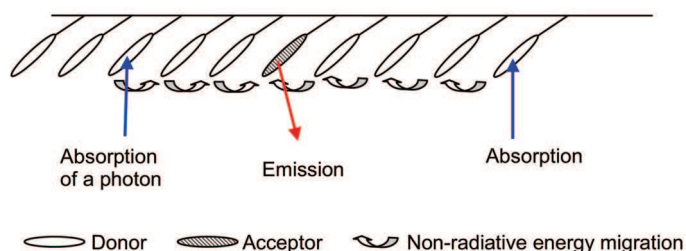


Fig. 1. Schematized energy transfer between donor and acceptor dyes: light-harvesting effect.

Maximum difficulties are probably encountered with crystallized dye materials. Actually, aggregation strongly affects fluorescence, but crystallization makes the things even worse. In a crystal, the molecules are closely packed, well aligned, and intermolecular interactions are very strong. The formation of excimers is favored and that of excitons, followed by the migration of the excitation energy to impurities traps or surface defects, also reduces drastically the emission efficiency. This is true for all organic solids, but takes a particular importance for submicron-sized solids. It has been shown recently that photophysical properties such as the photoluminescence quantum yield strongly differ according to the way the particles have been prepared (Katoh et al., 2009). The differences have been attributed to surface defects and impurities. It can be deduced that surface defects play a prominent role in nanofibers, whose surface area is wide by comparison with that of more compact structures. It must be noted that in the smallest nanocrystals, the number of surface molecules –in contact with the outer medium– is high enough not to be negligible with respect to the number of core molecules, and consequently, two populations of molecules can be distinguished from a spectroscopic viewpoint. But, this particular case will not be evoked here.

The best way to insure good fluorescence efficiency to crystallized nanofibers would be to choose a dye that is highly fluorescent in the solid state. Fortunately, although rare, this

type of dyes exists. A small number of structures are already known and there is active research for creating new ones. These molecules generally display a particular molecular arrangement. For example, they form a brick-wall-like architecture (Cornil et al., 2000), are separated by bulky groups, or undergo cross dipole stacking (Xie et al., 2005). In fact, many requirements must be taken into account for the rational design of fluorescent crystallized nanofibers. Molecules must have the conjugated system of good fluorophores, spontaneously self-organize into nanofibers, and lead to a high degree of crystallinity with a special molecular arrangement, compatible with fluorescence. For the moment, very little is known about molecules that could satisfy all these specifications.

### 3. Overview of the different types of fluorescent nanofibers and their preparation methods

As for other nanomaterials, two main approaches are used to fabricate nanofibers. In the “top-down” approach, fibers are constructed from larger entities without atomic-level control. In the “bottom-up” approach, they are created through self-assembly processes of molecular components, according to the principles of molecular recognition. The chosen approach closely depends on the nature of the nanofibers.

#### 3.1 Polymer-based nanofibers

The “top-down” approach is widely used for the fabrication of polymer-based nanofibers. Polymers can be intrinsically fluorescent due to an extended conjugated system (Chen et al., 2009; Kang et al., 2007; Long et al., 2009; Samitsu et al., 2009; Xin et al., 2009; Zhang et al., 2007; Zhao et al., 2007; Zhu et al., 2009). A good example is that of poly(phenylene vinylene) (PPV) derivatives, which emit from blue to yellow-green. Fluorescent polymers can sometimes be combined with nonfluorescent ones (Yoon & Kim, 2008). Polymers can also be dye-doped. In this case, the dye molecules can be either covalently fixed or simply dispersed in the bulk (Camposo et al., 2007; DiBenedetto et al., 2008; Fantini & Costa, 2009; Lee et al., 2002; Liang et al., 2008; Lv et al., 2008; Tomczak et al., 2006; Tao et al., 2007; Yang et al., 2009; Wan et al., 2006; Wang et al., 2001; Wang, Drew & et al., 2002; Wang et al., 2007; Wang et al., 2008), incorporated in zeolite embedded in the polymer structure (Cucchi et al., 2007; Vohra et al., 2009), or even forming a distinct phase (Lee et al., 2006; Li et al., 2009).

Electrospinning is the most currently used fabrication method. It consists in exposing a polymer solution droplet to a high voltage, so that a fine liquid jet is formed, finally resulting in submicron or nanometer scale fibers. It has an advantage with its comparative low cost and relatively high production rate. However, other methods can be useful, for example the photopolymerization of an organogel (Kang et al., 2007) or the whisker method, according to which a nematic liquid crystal promotes the self-assembly and anisotropic crystallization of conducting polythiophene nanofibers (Samitsu et al., 2009). Polymer nanofibers were also fabricated via vapour deposition polymerization (VDP) using a porous aluminium oxide membrane as template. The treated template was then dipped in organic dye solution before additional VDP was carried out. The process results in encapsulating the dye molecules in the polymer and interesting energy transfer occurs when multiple organic dyes are used (Lee et al., 2006). Many polymer-based nanofibers display interesting optical properties. In particular, they open new perspectives in the field of low-cost fabrication technology of flexible nanoscale OLEDs.

### 3.2 Bionanofibers

Biological molecules that spontaneously assemble via non-specific hydrogen-bonding interactions offer an attractive starting point for the preparation of fluorescent nanofibers. They often allow a level of control over the distribution and orientation of the chromophores. They are relatively simple to produce and can be tailored to provide a wide range of photophysical functionality. Various preparation methods have been reported, pertaining either to the “top-down” approach or to the “bottom-up” approach.

For instance, nanofibers made of natural polymers such as DNA can be produced by electrospinning. This is the case for DNA molecules mixed with intercalating fluorescent dyes, the obtained fibers having a diameter of about 27 nm (Bellan et al, 2007). More elaborated systems, such as DNA complexed with a cationic surfactant, can be processed by the same method. This complex has unique material properties including thermal stability and solubility in organic solvents. It has been used as a matrix to allow homogeneous distribution of encapsulated multiple chromophores. Chromophores were chosen so that they act as pairs of energy donor and acceptor. In the present case, the optimized spatial organization provided by the DNA matrix favors efficient energy transfer and the simultaneous emission of various fluorophores results in white light, particularly interesting for use in OLEDs (Ner et al., 2008; Ner et al., 2009).

Another strategy is to synthesize labeled precursors that self-assemble spontaneously. For instance, a thymidylic acid derivative labeled with an anthracene dye arranged in a single-strand oligomer. The assembly with a complementary single-strand oligomer resulted in a helicoidal nanofiber of about 5 nm in diameter, presenting the spectral characteristics of *J*-aggregates (Iwaura et al., 2009).

Peptides are also very useful to drive the organization of chromophores. They are known to assemble into fibrillar “amyloid-like” architectures, which are generally about 10 nm in diameter and a few micrometers long. Various precursors containing a peptide component and an organic fluorophore were synthesized. They were allowed to self-assemble and gave fibrils that exhibited a  $\beta$ -sheet signature. In the cases where the fibrils were decorated with a single fluorophore, energy migration was shown to occur (Channon et al, 2008). When two types of well-selected fluorophores were used to label the peptide segments, the mixing of these precursors resulted in a fiber that bore both donor and acceptor groups. An efficient energy transfer process took place, so that the system was proposed as a route to light-harvesting nanomaterials (Channon et al., 2009; Channon et al., 2009). Finally, dye-labeled peptides were also incorporated into assemblies with nonfluorescent peptides able to bind with heparin, a biologically important macromolecule. When the system was put in the presence of fluorescein-tagged heparin, a selective transfer of energy was observed. The fluorescent peptide fibrils were then proposed as energy donors to study a range of interactions with biological molecules (Behanna et al., 2007).

### 3.3 Dendrimer-based nanofibers

Curiously, another class of macromolecules, specifically dendrimers, exhibits a facile one-dimensional self-assembling ability. Acetylene-linked stiff dendrimers were expected to assemble into high-order structures, due to intermolecular  $\pi$ - $\pi$  stacking. They were composed of a pyrene core and carbazole/fluorine dendrons, with fluorinated groups at the periphery. The dendrimers were dissolved in a mixture of organic solvents. Since the “good” solvent evaporated faster than the “poor” solvent, the solubility of the dendrimer molecules was decreased and this induced aggregation. One of the compounds assembled

in nanofibers of heterogeneous size. Interestingly, the fluorescence of the fibers was blue-shifted with respect to that of the isolated dendrimer molecule (Zhao, Lee et al., 2008). The formation of micrometer-long fluorescent nanofibers was also reported for polyphenylene dendrimers functionalized with one or multiple peryleneimide fluorophores. The fibers were prepared by simple evaporation of a solvent on various substrates such as silicon, glass or mica. The morphology of the fibers depends on the preparation method. When the fluorophore is embedded in the dendrimer core, the emission of the fiber is similar to that of the isolated chromophores, due to shielding effect. In contrast, when the fluorophore is attached to the surface of the dendrimer, it suffers interactions with other peripheral fluorophores (Liu et al., 2003).

### 3.4 Nanofibers made of low-molecular-weight molecules with appended fatty moieties

Let us now turn our attention on nanofibers made of low-molecular-weight molecules. The “top-down” approach used for organic macromolecules is not adapted. Besides, the fragile organic molecules are generally damaged by the microfabrication techniques, such as electron-beam/focused ion beam deposition, traditionally used for inorganic compounds. Thus, the best strategy to prepare quantitative amounts of nanofibers is probably the “bottom-up” approach, which turns to good account the self-association properties of the organic molecules.

From a general viewpoint, several organic systems have been reported to self-organize in solution into micro- or nanofibers (Shimizu et al., 2005). It must be noted that the fibers of concern here are potentially fluorescent, although this property is not always reported. The molecules generally contain a large aromatic moiety that is prone to stacking, and a lipophilic moiety that provides supplementary van der Waals attractions between adjacent molecules within the stacks, and between neighboring stacks to give nanostructures (Hoeben, 2005).

Some organic gelators spontaneously give fluorescent fibers in organic solvents. Among them are rod-shaped alkoxy-tetracene (**1**) and alkoxy-anthracene (**2**) (Del Guerzo et al., 2005; Desvergne et al., 2006; Shklyarevskiy et al., 2005; Reichwagen et al., 2005), and the cholesterol-appended derivatives of phenanthroline (**3**) (Sugiyasu et al., 2005) and salicylideneaniline (**4**) (Xue et al., 2007) (Fig. 2).

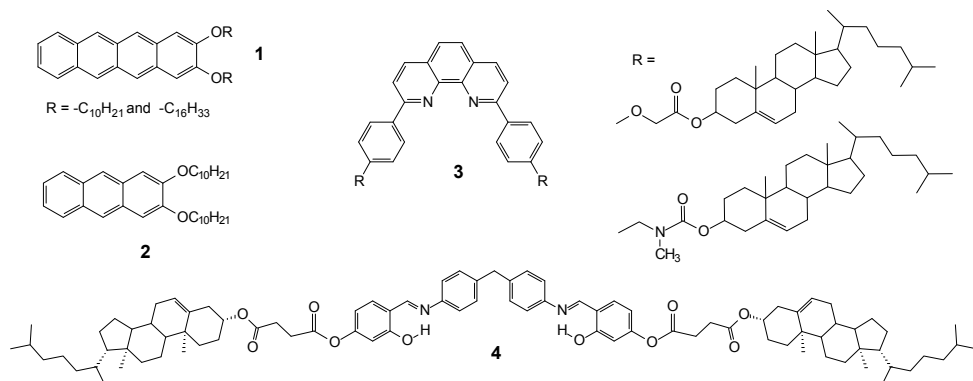


Fig. 2. Chemical structure of compounds 1-4

Highly dipolar merocyanine dyes (**5**) (Würthner et al., 2003; Yao et al., 2004), *p*-phenylenevinylene (**6**) (Jeukens et al., 2005), perylene diimide trimers (**7**) (Yan et al., 2005), and a bi-oxadiazole derivative (**8**) (Qu et al., 2009), all associated to long alkyl chains, were also reported to give helical stacks, although the molecular arrangement is different for each of these compounds (Fig. 3).

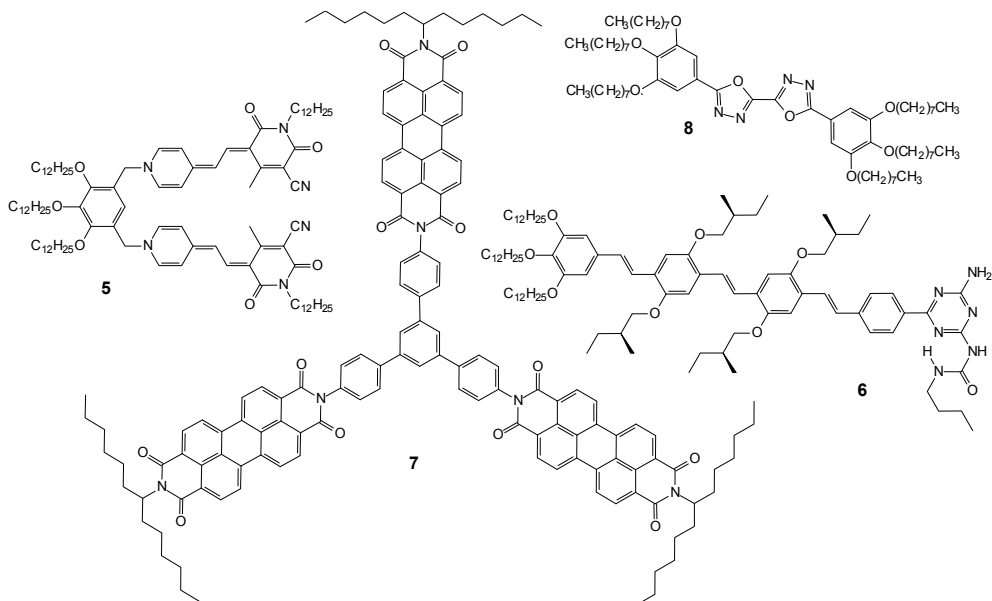


Fig. 3. Chemical structure of compounds 5-8

For molecules like the carbazole-cornered tetracycle (**9**),  $\pi$ - $\pi$  stacking between molecules is extremely effective and micrometer-long nanofibers can be easily fabricated via surface casting (Balakrishnan et al., 2006; Naddo et al., 2007). For **10**, in contrast, the formation of fibers is driven by multiple hydrogen bonds between the six organic acid groups that are situated at both ends of the molecule. These rigid molecules favor high fluorescence efficiency in the solid state (Luo et al., 2009). It must also be noted that other compounds, such as hexa-peri-hexabenzocoronene linked to fatty chains (**11**), which are known to give columnar liquid crystals, can afford micrometer-long fibers (Pisula et al., 2004) (Fig. 4).

Amphiphilic compounds that self-organize into fluorescent nanofibers can be obtained by branching, for example, three poly(ether) segments to a pyrene core (**12**) (Kimura et al., 2009). In the T-shaped aromatic amphiphiles based on oligo(ethylene oxide) dendrons (**13**), the aromatic segments are stacked with dimeric association to maximize  $\pi$ - $\pi$  interactions. Curiously, these molecules lead to a reversible phase transition from a fluid state to a gel with increasing temperature (Moon et al., 2007). The presence of an ionized group in the compound also bestows amphiphilic properties, and so water is allowed to be used as a solvent for thin film deposition. For instance, nanofibers were formed from aqueous solutions of a bola-amphiphile containing two carboxylic terminal groups and a central aromatic moiety (**14**) (Song et al., 2007). This is also the case for a cationic perylene diimide incorporating a hydrophobic ether tail (**15**) (Everett et al., 2006) (Fig. 5).

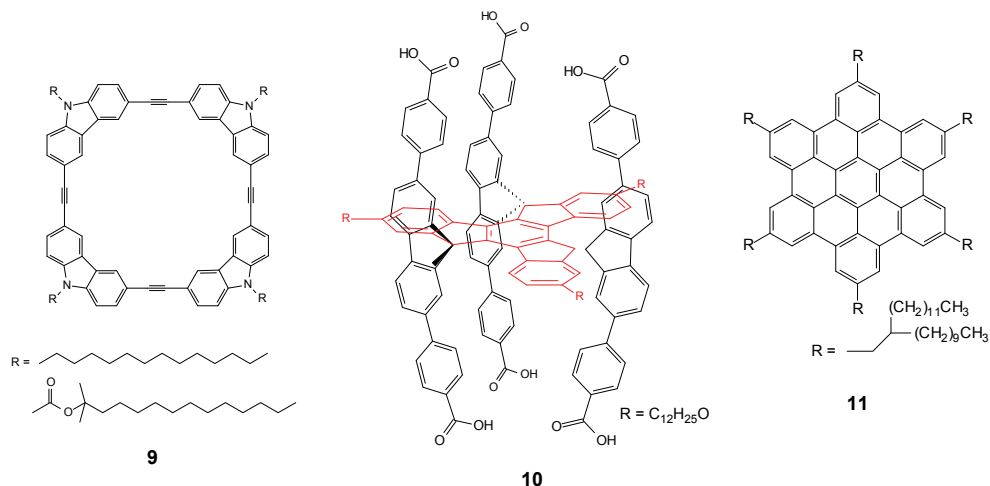


Fig. 4. Chemical structure of compounds 9 to 11

These fibers could lead to interesting future applications. Some of them show chemical sensing (Naddo et al., 2007) and thermosensing ability (Moon et al., 2007), as well as light-harvesting properties (Desvergne et al., 2006). Their use has been proposed as semiconducting wires in organic electronics and photovoltaics (Everett et al., 2006; Luo et al., 2009). It is noteworthy that the fibers made of **12** were subsequently wrapped with an ultrathin silica wall, using a sol-gel process. The resulting fibers can then be considered as electronic cables that are composed of a conductive organic core and an insulating inorganic layer (Kimura et al., 2009).

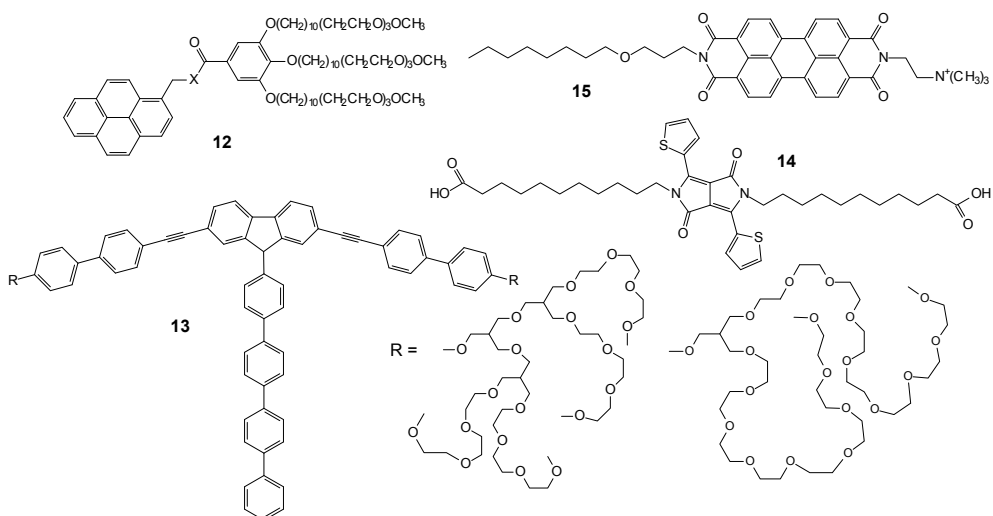


Fig. 5. Chemical structure of compounds 12 to 15



### 3.5 Nanofibers made of low-molecular-weight molecules without appended fatty moieties

Most of the fibers made of molecules that contain a bulky fatty moiety are not crystallized. If the aim is to prepare crystallized materials, it is better to work with small molecules deprived of long alkyl chains. Many of them can give needle-like crystals that can be seen like nanofibers. But, the formation of these fibers is not easy and sometimes requires elaborated preparation methods. The fibers may be grown by either vapor or solution processes. The vapor growth process is usually carried out in a quartz tube by sublimating the compounds in a high temperature zone, and transporting the vapor with an inert gas till a low-temperature zone where it can crystallize again. This approach is widely used for oligomers and low-molecular-weight organic semiconductors, for example phthalocyanines (Tang et al., 2008). A variant is to sublimate the compound into a hot-wall tube loaded with a mineral substrate in a vacuum chamber, so that the molecules grow epitaxially on the substrate under conditions close to thermodynamic equilibrium (Yanagi et al., 2001 and refs cited). This method has been used independently by many teams (Balzer et al., 2003; Balzer & Rubahn, 2005; 1999; Hernandez-Sosa et al., 2009; Yanagi et al., 2001; Yanagi & Morikawa) to fabricate nanofibers of *p*-hexaphenyl (**16**) (Fig. 6). The structures obtained are morphologically well-defined and can be individually transferred by micromanipulation to be integrated in various devices (Kjelstrup-Hansen et al., 2006). They emit intense blue light upon electrical or UV-light stimulation. Light is polarized because of the crystallinity of the fibers. Interestingly, waveguiding and coherent random laser action have been observed in single and bundled nanofibers (Quochi et al., 2006; Yanagi & Morikawa, 1999; Yanagi et al., 2001). Functionalizing *p*-hexaphenyl would allow the morphology and the luminescence of the fibers to be modified. Unfortunately, the compound does not lend itself easily to chemical modifications, because of its low solubility. Functionalization has thus been achieved on quaterphenyl (**17**) (Brewer et al., 2006; Schiek et al, 2006; Schiek et al, 2007). Another strategy is to dope the nanofibers *p*-hexaphenyl with  $\alpha$ -hexathiophene (**18**). Since the two materials are combined in a crystalline arrangement, their transition dipoles are highly aligned and the energy transfer efficiency is maximized. This results in a significant modification of the emission properties (Hernandez-Sosa et al., 2009). Fluorescent pyrene (**19**) and POPOP (**20**) nanowires with a diameter of about 70 nm were also obtained by classical vapor-deposition method, by introducing the organic fluorophore into a porous anodic aluminium oxide membrane and then dissolving the matrix (Lee et al., 2002). These examples show that single-crystalline nanofibers can indeed be obtained from small molecules. Their optical properties are extremely interesting for subsequent use in optoelectronic devices. It can also be noted that nanofibers of *p*-hexaphenyl have recently been coupled to bovine serum albumin, which could lead to a new type of protein sensors (Madsen et al., 2007).

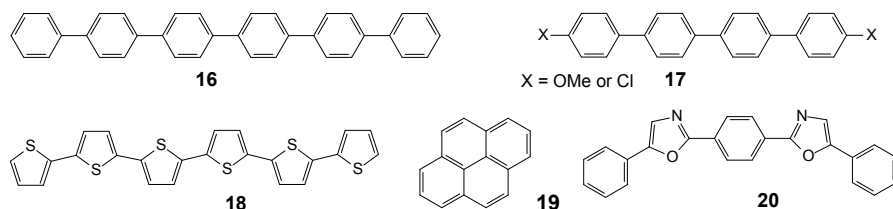


Fig. 6. Chemical structure of compounds 16 to 20

However, the vapor-deposition method is only suitable for a small number of organic molecules, because many of them decompose upon heating. Therefore, a convenient alternative to generate nanofibers is to use a very simple and soft method based on solvent exchange. For instance, the perylene derivative **21** (Fig. 7) gives entangled fibers when a small volume of a concentrated solution of this compound is injected into a large volume of hexane (Che et al., 2008; Che & Zang, 2009). More often, the hydrophobic dye is dissolved in an organic solvent and water is used as a non-solvent. The dye very quickly precipitates and may crystallize. A very nice example of the use of the “reprecipitation” method has been given by Park’s team for the cyanostilbene derivative **22**. Interestingly, these nanofibers are highly fluorescent while the isolated molecule itself is inherently nonfluorescent. This is a rare example of aggregation-induced emission enhancement (AIEE), which has been attributed here to the planarization and rigidification of the aromatic system in the solid state (An et al., 2004). Using analogues deprived of cyano and fluorinated groups, it was shown that a synergistic effect from these groups was necessary to induce the formation of fluorescent fibers. A strong  $\pi$ - $\pi$  stacking interaction arises from the rigid rod-like aromatic segments, while additional intermolecular interactions are induced by  $\text{CF}_3$  groups and the cyano group induces the head-to-tail type molecular arrangement. (An et al., 2009). Keeping these essential features, substituted molecules (**23-25**) were synthesized, all giving nanofibers that emit in different spectral range. It can be noted that the nanofibers actually display a hierarchical organization, since they consist of the assembly of nanofibril-like structural entities with particular orientation.

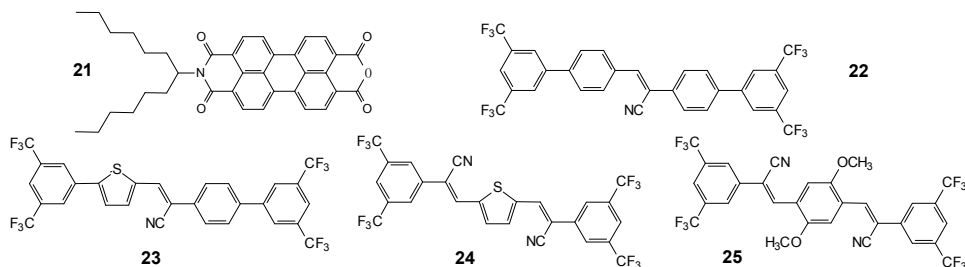


Fig. 7. Chemical structure of compounds **21** to **25**

The interest of the “reprecipitation” method is that many parameters such as dye concentration, temperature, aging time and the presence of additives, can be varied, thus inducing significant differences in the morphology of the particles obtained. This method has been used successfully in the literature to generate nanofibers from different molecules. For instance, the formation of nanowire crystals has been reported for 1,3-diphenyl-2-pyrazoline (**26**) (Fu et al., 2003) (Fig. 8). It is interesting to note that the morphology of the particles obtained strongly depends on the concentration of a surfactant, cetyltrimethylammonium bromide (CTAB), used as additive. It was proposed that the surfactant plays the role of both surface-active stabilizer and template, rod micelles directing the growth of cylindrical dye nanofibers. Similarly, sodiumdodecylsulfate (SDS) micelles induce the formation of pyrene (**19**) nanofibers (Zhang et al., 2005). In these cases, no 1D self-assembly is formed in the absence of micelles. In contrast, nanofibers of Sudan II (**27**) are formed in the presence of an amphiphilic triblock copolymer (F127) at concentrations below the critical micelle concentration. Curiously, the shape of the particles passes from

nanofibers to microrods with increasing the copolymer concentration (Yu & Qin 2009). For a phenylenediamine derivative (**28**) (Li et al., 2004) and triphenylimidazole **29** (Zhao, Peng et al., 2008), the key factor is the aging time. Actually, nanoparticles convert spontaneously from spherical to rod-like aggregates, and then to nanofibers as time elapses. In some cases, many parameters must be optimized together, as for the polydiacetylene derivative (**30**) studied by the team of Nakanishi, a pioneer of the reprecipitation method (Onodera et al., 2001). This compound gives microcrystals after reprecipitation at 298 K in the absence of additive. Adding sodiumdodecylsulfate (SDS) and rising the temperature to 333 K induces the formation of nanowires, the diameter of which is about 50 nm. It must be added that fibers and rod-shaped microcrystals have also been obtained by this method from compounds such as fullerene (Masuhara et al., 2008; Tan et al., 2008), which are potentially fluorescent but whose optical properties have not been reported.

These few examples show that the formation of fluorescent nanofibers using the reprecipitation method has just begun to be investigated. The method has proved to be very efficient. It leads to the formation of homogeneously-sized nanofibers that are obtained as a suspension in an aqueous medium. They can be subsequently filtered and dried before being micromanipulated. It can just be noted that particular experimental conditions can be required to obtain such structures.

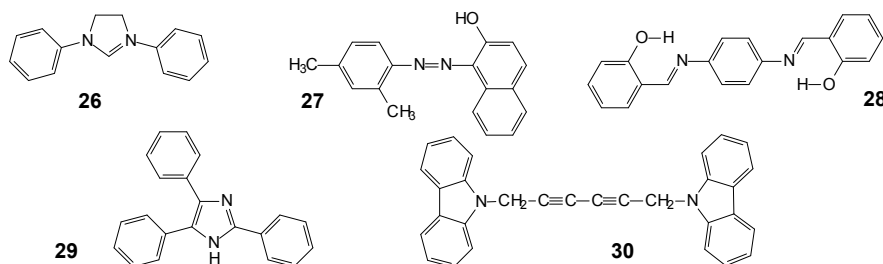


Fig. 8. Chemical structure of compounds **26** to **30**

It appears that the spontaneous formation of fluorescent nanofibers from small dyes without any fatty chains is rather uncommon. Some molecules, such as dye **26**, readily self-assemble into fluorescent nanofibers, whatever the preparation method used. Besides reprecipitation, different fabrication methods have been investigated, including drop casting, recrystallization and vacuum evaporation. All lead to nanofibers, although in different yield, diameter and aspect. However, this is far from being the case for the majority of molecules, for which appropriate fabrication methods must be implemented. And it is very difficult to predict that a molecule will give crystallized fibers or any other type of nano- or microparticle, and whether the fluorescence properties will be interesting or not. As an illustration, we report below a summary of the work that has been performed in our team using the reprecipitation method to prepare fibers from three different families of dyes.

#### 4. Nanofibers in the coumarin series

The first study (Fery-Forgues et al., 2008; Mille et al, 2008) deals with four dyes of the coumarin series. This type of dyes is currently used for applications in fields as varied as the coloring of textile fibers, medical imaging, lasers, photonic devices and organic light-emitting diodes and their spectroscopic behavior in solution is well known. The selected

compounds were made of the same chromophores with very little chemical modifications (Fig. 9). Since they are hydrophobic and very fluorescent in the solid state, the molecules appeared as good candidates to give fluorescent particles by the reprecipitation method.

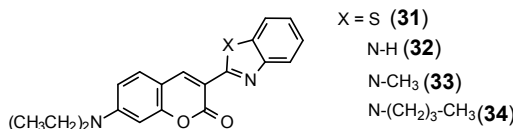


Fig. 9. Chemical structure of the coumarin derivatives **31-34**.

The reprecipitation process took between 4 and 40 min depending on the dye. When observed by fluorescence microscopy, all samples showed strongly emissive particles. It appeared that Coumarin 6 (**31**) lead to small rod-shaped microcrystals that were about 1-2  $\mu\text{m}$  long. Coumarin 7 (**32**) gave significantly longer microcrystals (Fig. 10a). Coumarin 30 (**33**) gave straight individual nanofibers (Fig. 10b) and the butyl derivative **34** gave bundles of fibers.

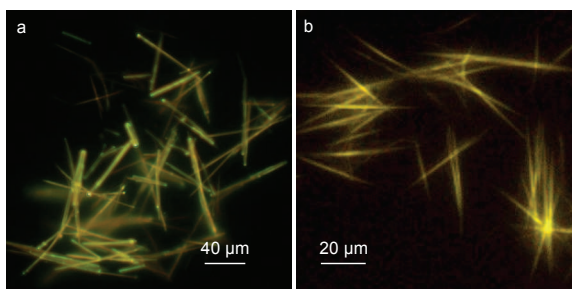


Fig. 10. Fluorescence microscopy images of compounds **32** (a) and **33** (b) after reprecipitation in water containing 2% ethanol. Dye concentration:  $2 \times 10^{-5}$  M.

The size of the particles was measured precisely by transmission (TEM) and scanning (SEM) electron microscopy. In particular, the straight fibers of Coumarin 30 were between 5 and 10  $\mu\text{m}$  long, and less than 500 nm wide (Fig. 11a). For the butyl coumarin **34**, the fibers were about 1  $\mu\text{m}$  long and 25 nm wide, but closely entangled (Fig. 11b). It was clear from the SEM images that all fibers were solid.

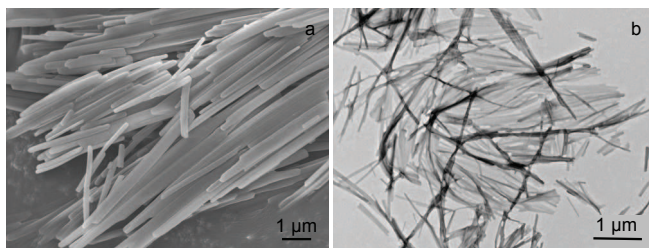


Fig. 11. a) Scanning electron microscopy image of the nanofibers formed in the aqueous suspensions of compound **33** after reprecipitation. b) Transmission electron microscopy image of the nanofibers formed by **34**.

Concerning the molecular arrangement, the crystal structures of Coumarin 6 and 7 has been published (Jasinski & Paight, 1995; Chinnakali et al. 1990). The molecules are almost planar and centrosymmetrically arranged in the crystal unit. The dipole moments are thus stabilized and this configuration is compatible with fluorescence. The crystal structure of the two other compounds was unknown, but for **33**, a clear powder diffraction spectrum ascertained the crystallinity of the nanofibers, which actually can be seen as a modification of the crystal. For **34**, close spectroscopic similarities suggested that the molecular arrangement was quite close from that encountered in **33**, and the anisotropic growth indicates a preferred direction of assembly and thus some degree of order.

The spectroscopic properties of the particles were investigated directly on the suspensions when reprecipitation was complete. The most striking feature was that the fluorescence lifetimes were shorter for the suspensions than for the dissolved dyes, and the quantum yields, all in the  $10^{-2}$  range, were much lower. This can result from crystallization, but also from fluorescence quenching by water molecules, around or within the particles.

It was interesting to see through these examples that Coumarin 6 and 7 that tend to crystallize anisotropically, with a preferred growth axis, giving macroscopic rod-shape crystals, lead to microrods by the reprecipitation method. When tiny modifications were introduced in the chemical structure of Coumarin 7 by increasing the length of the alkyl chain, resulting in compounds **33** and **34**, the major crystallization trend was retained. Actually, the ultimate fate of these molecules appears to be mostly solid nanofibers. The presence of a small alkyl group that bring additional Van der Waals interactions between the molecules is thus enough to induce the formation of elongated crystals. Increasing the size of this alkyl chain by two carbon atoms favors the formation of fiber bundles. It must be underlined that the spontaneous formation of nanofibers was rather unexpected considering the chemical structure of the dye molecules.

## 5. Nanofibers in the 2-phenylbenzoxazole series

To avoid the problem of fluorescence quenching by water, attention was paid to another series of dyes, which were expected to be much less sensitive to hydrogen bonds. The derivatives of 2-phenyl-benzoxazole are rod-shaped molecules, with excellent fluorescence properties. They are used as textile whitening agents, electroluminescent materials in OLEDs, etc. They display very good chemical and photochemical stability and they are quite easy to synthesize. So, a series of compounds differently substituted on the phenyl group was prepared, as well as a naphthoxazole derivative (Fig. 12).

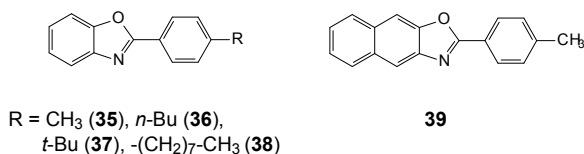


Fig. 12. Chemical structure of the benzoxazole derivatives **35-39**

The particles obtained by reprecipitation were observed by fluorescence microscopy. It is very interesting to see that, among the compounds investigated, only the methyl derivative **35** gave long beautiful nanofibers. Compounds **36** to **38** gave platelets and shapeless microcrystals, agglomerated or not. The naphthoxazole derivative **39** gave microrods. If

comparing the particles obtained by the reprecipitation method with the crystals obtained by recrystallization in methanol, it was obvious that the reprecipitation method did not just reduce the size of the crystals, but also changed the shape. This is reminiscent of a former work done by our team on fluorescent microcrystals made of a nitrobenzoxadiazole (NBD) derivative. We showed that the shape of the microcrystals was strongly affected by the reprecipitation conditions, although the crystal packing mode seemed to be unchanged (Abyan et al., 2009). So, it not easy to predict which type of particles will be obtained by reprecipitation.

The X-ray analysis of a single crystal of the methyl derivative was obtained. In the unit cell the molecules are displayed by pairs, parallel to each others. They are arranged head-to-tail and the one is shifted with regard to the other one. A second pair of molecules is displayed perpendicularly to first one. This molecular arrangement may favor fluorescence. Actually, the spectroscopic study of the suspensions showed that particles are indeed very fluorescent. The emission spectra, in the ultra-violet range, were almost the same for the four benzoxazole derivatives. It was shifted to the visible for the naphthoxazole derivative, which emitted blue light as could be expected. The lifetimes were in the nanosecond range and the quantum yields were quite high. These properties indicate the interest of such molecules for subsequent use (D'Altério et al., to be published).

## 6. Nanofibers based on berberine ion pairs

The last series of dyes that was investigated is based on the berberine cation. This cation is an alkaloid, derived from several families of plants. It displays wide biological activity and has been used for long in traditional medicines. This aromatic heterocycle is also known for its interesting spectroscopic properties. In the bibliography, it appears that this cation has been associated to different inorganic anions, thus giving a crystallized, water-soluble salt. So, the idea was to associate this cation to organic anions such as palmitate, dodecylsulfate or laurate (Fig. 13), in order to promote aggregation in water, with the hope to keep crystallinity.

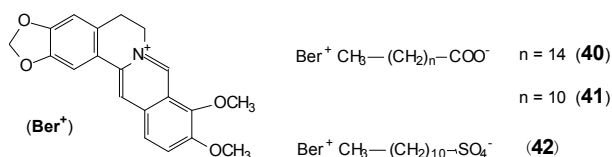


Fig. 13. Chemical structure of the berberine derivatives 40-42

Reprecipitation of the three dyes was thus performed, the process being achieved in less than 8 min. The three suspensions contained microfibers that were visible with the fluorescence microscope, as well as nanofibers that were detected with TEM. Examples are given in Figure 14. Regarding the spectroscopic properties, it must be stressed that the berberine cation is very poorly fluorescent in water. We showed that this is due to a dynamic fluorescence quenching by water molecules. However, all the suspensions obtained by reprecipitation were very fluorescent. It was easy to show that fluorescence arises from the crystallized salt. This is a very nice example of aggregation induced emission enhancement.

The explanation must be found in the very unusual packing mode of these compounds. Actually, the berberine cations form a layer that is sandwiched between two layers of fatty chains. So, the fatty chains prevent fluorophore stacking. Meanwhile, the berberine cations are protected from the access of water molecules and this explains why the fibers are so strongly fluorescent (Chahine et al., to be published).

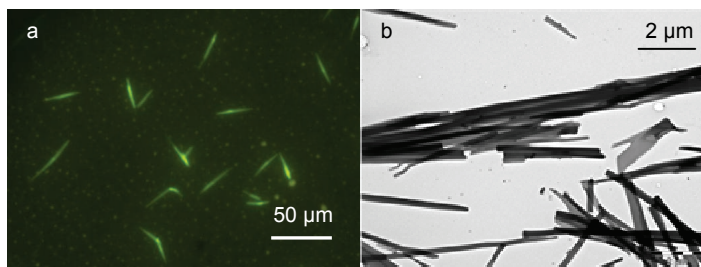


Fig. 14. Fluorescence (a) and transmission electron microscopy image (b) of the micro- and nanofibers formed in the aqueous suspensions of berberine laurate (**41**) after reprecipitation (dye concentration:  $6.17 \times 10^{-5}$  M in water containing 1.2% ethanol).

This fluorescent ion-pair concept is extremely interesting because of its large versatility and ease of implementation. Actually, a large combination of ion pairs can be investigated to modulate both the photophysical properties and the morphology of the particles obtained, in view of a desired application. There is no doubt that this strategy can be of high interest for the design of new molecular materials.

## 7. Conclusion

A cursory glance at the bibliography is enough to see that the interest for fluorescent nanofibers has very recently emerged. This field is still in its infancy, but rapidly expanding. Various preparation methods are available depending on the type of fibers that must be obtained. Progress can be expected in improving the physical properties of the fibers, which must be of homogeneous size and if possible deprived of surface defects. Concerning the photophysical properties, the limitations are now well understood, and there are numerous possibilities to cope with them. For example, encapsulation of dyes to produce fluorescent nanofibers is particularly promising and still poorly developed. Consequently, systems that display efficient light emission can be expected for a near future.

With slight improvements, luminescent nanofibers have potential for becoming important key elements for nanoscaled optoelectronic devices. These novel materials may also enable a number of new technologies. Their story is only beginning.

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## **Nanofibers**

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“There’s Plenty of Room at the Bottom” this was the title of the lecture Prof. Richard Feynman delivered at California Institute of Technology on December 29, 1959 at the American Physical Society meeting. He considered the possibility to manipulate matter on an atomic scale. Indeed, the design and controllable synthesis of nanomaterials have attracted much attention because of their distinctive geometries and novel physical and chemical properties. For the last two decades nano-scaled materials in the form of nanofibers, nanoparticles, nanotubes, nanoclays, nanorods, nanodisks, nanoribbons, nanowhiskers etc. have been investigated with increased interest due to their enormous advantages, such as large surface area and active surface sites. Among all nanostructures, nanofibers have attracted tremendous interest in nanotechnology and biomedical engineering owing to the ease of controllable production processes, low pore size and superior mechanical properties for a range of applications in diverse areas such as catalysis, sensors, medicine, pharmacy, drug delivery, tissue engineering, filtration, textile, adhesive, aerospace, capacitors, transistors, battery separators, energy storage, fuel cells, information technology, photonic structures and flat panel displays, just to mention a few. Nanofibers are continuous filaments of generally less than about 1000 nm diameters. Nanofibers of a variety of cellulose and non-cellulose based materials can be produced by a variety of techniques such as phase separation, self assembly, drawing, melt fibrillation, template synthesis, electro-spinning, and solution spinning. They reduce the handling problems mostly associated with the nanoparticles. Nanoparticles can agglomerate and form clusters, whereas nanofibers form a mesh that stays intact even after regeneration. The present book is a result of contributions of experts from international scientific community working in different areas and types of nanofibers. The book thoroughly covers latest topics on different varieties of nanofibers. It provides an up-to-date insightful coverage to the synthesis, characterization, functional properties and potential device applications of nanofibers in specialized areas. We hope that this book will prove to be timely and thought provoking and will serve as a valuable reference for researchers working in different areas of nanofibers. Special thanks goes to the authors for their valuable contributions.

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