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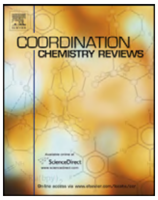

Review

Metal-containing nanofibers via coordination chemistry

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Contents

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ABSTRACT

One-dimensional fibrous nanostructures may exhibit unique mechanical, optical, magnetic, and electronic properties as a result of their nanoscale dimensions. Various approaches have been used to prepare nanofibers (e.g., electrospinning, vapor deposition), but this review focuses on the research and development of self-assembled nanofibers formed through coordination chemistry. By employing metal–ligand interactions that extend along the backbone of the aggregates, nanofibrous, often gel-forming, materials with appealing properties have been formed. Other fibers formed through electrostatic interactions between charged coordination complexes are also discussed. The optical, electronic, and magnetic properties conferred upon the materials by the embedded coordination complexes render the nanofibers useful for applications in the fields of catalysis, sensors, and gas storage, and potentially for developing nanosized devices.

1. Introduction

The field of nanochemistry is rapidly expanding, and will lead to facile routes to construct sophisticated nanoscale materials [1]. This "bottom-up" approach has many benefits over traditional "top-down" approaches (e.g., lithography) as it enables more control of the molecular architecture and assembly of more sophisticated structures. Over the past several decades, supramolecular self-assembly has emerged as a powerful technique for the construction of complicated, often hierarchical materials with significant functions and properties. The utility of supramolecular chemistry in the construction of nanomaterials and devices is well-exemplified by recent work in the literature, including the one-pot, 18-component assembly of diformylpyridine, 2,2′-bipyridine-containing diamine and zinc ions into three macrocycles that interlock into the shape of a Borromean ring [2], the self-assembly of tris-2,2′-bipyridine and iron(II) chloride into a circular double helicate [3], conjugated polyrotaxanes composed of cyclodextrin with threads based on poly(*para*-phenylene), polyfluorene, and poly(diphenylenevinylene) and stoppered with naphthalene groups [4], and the family of metal–organic frameworks with metal–oxygen polyhedra linked by bridging ligands [5].

The applications of nanostructured supramolecular assemblies depend on the shapes and their functionalities, which can be imparted by selection of molecular precursors. For instance, bowl-shaped complexes can self-organize into nanocapsules for host–guest chemistry [6] and structures shaped like badminton shuttlecocks can organize into one-dimensional columnar structures [7]. By choosing precursors with specific geometries,

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nanostructures with particular forms may be anticipated. However, it is often by chance that new nanomaterials are discovered, and their shapes may not be obvious extensions of the molecular geometry.

Nanofibers are an exciting class of materials with excellent potential for real applications, fundamental investigations, and for understanding biological systems. They are long-range-ordered, one-dimensional, nanosized supramolecular aggregates that can be linear or helical [8]. Nanofibers have been investigated in nanosized electronic [9], mechanical [10] and medical fields [11]. One-dimensional nanostructures are also ubiquitous in biological systems, exemplified by collagen, axons, and keratin. There has been a rapid growth of interest in generating biomimetic fibrous structures with medical applications in terms of compatibility, degradability and cell–matrix interactions [12].

One interesting property that is frequently observed for nanofibers is gelation. The fibers form network structures, often through weak interfiber interactions, that can trap and immobilize solvent molecules, resulting in the formation of a gel [13]. Gels are interesting materials and already have a wide range of applications including biomedical applications [14], drug delivery [15], and catalysis [16], depending on the nature of the materials forming the nanofibrils. They are also being explored for environmental sensors and have been used to template sol–gel polycondensation of metal alkoxides such as tetraethyl orthosilicate (TEOS) and tetra-*n*-butyl titanate [17]. Given their interesting applications and properties, the synthesis and investigation of nanofibers with unique properties has become an attractive topic for researchers [18].

Numerous methods have been employed to manufacture nanofibers that span diverse size ranges. One way to produce fibrous nanostructures artificially is through the electrospinning technique. This process involves applying a high voltage between a metal collector plate (generally rotating) and the tip of a tiny needle that is ejecting a viscous polymer solution [19]. The polymer solution becomes charged in the electrical field, inducing electrostatic repulsion that creates a charged jet of solution erupting from the tip of the needle. While the jet is in air, the solution evaporates and the nanofibers deposit on the metal collector [20]. This method has many advantages – it allows good control over the morphology and porosity of the fibers, and it can be applied to diverse polymers and mixtures, permitting good control over composition [21]. The diameters of the electrospun fibers are in the range of nanometers to micrometers, but their lengths can extend to the kilometer scale [22]. These synthetic polymeric fibers possess good physical properties, including high specific surface area, flexibility in surface functionalities, and superior mechanical properties, which impart the nanofibers with excellent properties for use in biomedical engineering [21]. Long hollow nanofibers can also be fabricated by electrospinning [23], thus enhancing the specific surface area. Complementary to electrospinning, supramolecular self-assembly has also received a great deal of attention for making nanofibers. Appropriately designed molecules and macromolecules act as the building units of the fibrillar aggregates, which then assemble into one-dimensional nanostructures through non-covalent interactions, such as hydrogen-bonding, intermolecular π–π stacking, electrostatic interaction/coordination chemistry, or the hydrophobic effect [24]. These molecule-based construction approaches to nanofibers provide a way to diversify the properties of the aggregates by tuning the functionalities of the building units. In recent years, fabrication of one-dimensional nanostructures has predominately involved intermolecular hydrogen-bonding and π–π stacking, or a combination of both non-covalent interactions, but significantly fewer with metal–ligand coordination interactions. Nevertheless, coordination chemistry offers a large and fascinating assortment of complexes with different geometries, and electronic and magnetic properties that can be incorporated into nanomaterials. Indeed, many elegant inorganic nanostructures with well-defined shapes, such as helicates, nanoboxes, catenanes and nanocages [25], have been built using coordination chemistry, often relying on the bonding angles and geometry at the metal centers to dictate the final structure. Nanofibers constructed from extensive one-dimensional metal–ligand coordination interactions are an appealing class of materials because of their potential applications including catalysis, sensing, and gas storage. Their interesting electronic and magnetic properties also make them good candidates for nanoscale devices [26]. One can imagine using changes at the metal center (e.g., changes in coordination number, oxidation state, or electronic configuration) as a means to change the properties of the material.

In this review, we describe the use of coordination chemistry to obtain nanofibers. In some cases, the assembly is formed through electrostatic interactions rather than extended metal–ligand interactions, but all contain metals and the metal is important to the assembly. We have restricted the review to examples where the fiber morphology has been imaged by a technique such as transmission electron microscopy (TEM), scanning electron microscopy (SEM), or atomic force microscopy (AFM). We also do not include the vast number of rigid nanocrystallites that can resemble fibers. We have primarily covered recent exciting developments in the field, and there are undoubtedly other reported examples of nanofibers from coordination complexes (some of these are described in Section 4).

2. Nanofibers constructed from macrocyclic units

Numerous types of macrocycles have been synthesized and studied, and they have played an important role in the development of the field of supramolecular chemistry. Some well-known groups of macrocycles, including crown ethers, aza-crowns, cryptands and cyclodextrins, are capable of coordinating to metal ions within their cavities [27], which provide insight into supramolecular interactions and molecular recognition. The metal-containing macrocycles can exhibit intriguing magnetic, catalytic, or supramolecular behavior [28]. There are several reports of using intermolecular hydrogen-bonding and π–π stacking as the driving forces of aggregation to form self-assembled fibrous superstructures from macrocycles [29]. Another approach to fabricate one-dimensional nanofibers is by using the metal–ligand coordination or electrostatic interactions. With macrocycle-based examples, most of these use the latter, where the charge of the metal complex is central to the assembly.

2.1. Metalloporphyrins and metallophthalocyanines

Porphyrins are shape-persistent and conjugated macrocycles comprised of four pyrrole subunits that are interconnected by methine bridges. These heterocycles can be used as proligands to coordinate various metals in their central cavities; metallated porphyrins play important roles in nature, such as in heme and chlorophyll. The π-conjugated backbone, the metal center and the functional groups appended on the periphery render the metalloporphyrins the ability to self-assemble into a variety of supramolecular structures through non-covalent interactions [30]. Extensive efforts have been devoted to the research of multiporphyrin arrays due to their promising applications in molecular switching, electronic and photonic devices [31]. Intermolecular π–π stacking and hydrogen-bonding are commonly used to induce nanofiber structures [32]; these interactions can also combine with coordination chemistry and electrostatic interactions to construct beautiful fibrous networks and to prepare excellent gelators [33]. One-dimensional polymeric metalloporphyrins synthesized solely