Nanofibers and Gels

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Supramolecular Assembly of Zinc Salphen Complexes: Access to Metal-Containing Gels and Nanofibers**

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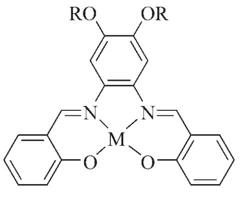
The supramolecular self-assembly of molecules into 1D nanostructures is an important goal for developing future nanoscale technologies, such as molecular circuitry and machines.[1–5] Nanowires and nanotubes can be assembled using noncovalent interactions, including hydrogen-bonding and intermolecular π–π stacking.[6–10] The formation of nanofibrils is also relevant to biological systems and diseases (for example, Alzheimer's).[11] Moreover, there has been much recent interest in the gelation of fiber-forming assemblies.[12]

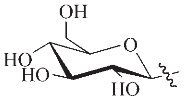
Herein we report the first examples of nanofiber formation promoted by Zn···O interactions between Schiff-base complexes. Such interactions between zinc and a phenolic oxygen have been reported as the basis of the reversible dimerization of [Zn(salen)]-type complexes (salen = *N*,*N'*-bis(salicylidene)ethylenediamine dianion).[13,14] In these complexes, the metal is unable to adopt a tetrahedral geometry and therefore dimerizes to give a five-coordinate metal center. We have ascribed the aggregation of large, zinc-containing macrocycles in solution to Zn···O interactions.[15] Batley and Graddon proposed in 1967 that [Zn(salen)] complexes could form polymeric structures,[16] but definitive evidence for aggregation has not been reported. We present a new family of Schiff-base complexes that organize into gels and 1D nanofibrils. Furthermore, we demonstrate the ability to control the nanofibril widths by modification of the substituents.

We prepared a series of salphen complexes **1**–**5** (salphen = *N*,*N'*-bis(salicylidene)-*o*-phenylenediamine dianion) with peripheral linear and branched alkoxy groups. We were surprised to discover that zinc compound **4a** forms luminescent gels in methanol (ca. 3 mg mL^{-1}), Figure 1. Gel formation was also observed in toluene, but not in DMF or chloroform. In gel-forming solvents, formation was thermoreversible, and could be readily disrupted with addition of pyridine (< 2%), which coordinates to the zinc center. Table 1 shows the gel-forming abilities of compounds **1a**–**5a** in various solvents. Notably, the complexes form gels best in aromatic solvents, such as benzene, toluene, and *o*-xylene.

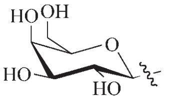


1a (M = Zn, R = CH_3)
1b (M = Ni, R = CH_3)
2a (M = Zn, R = C_6H_{13})
3a (M = Zn, R = 2-ethylhexyl)
4a (M = Zn, R = $C_{14}H_{29}$)
4b (M = Ni, R = $C_{14}H_{29}$)
5a (M = Zn, R = $C_{16}H_{33}$)

6a M = Zn
6b M = Ni
R =



7a M = Zn
7b M = Ni
R =



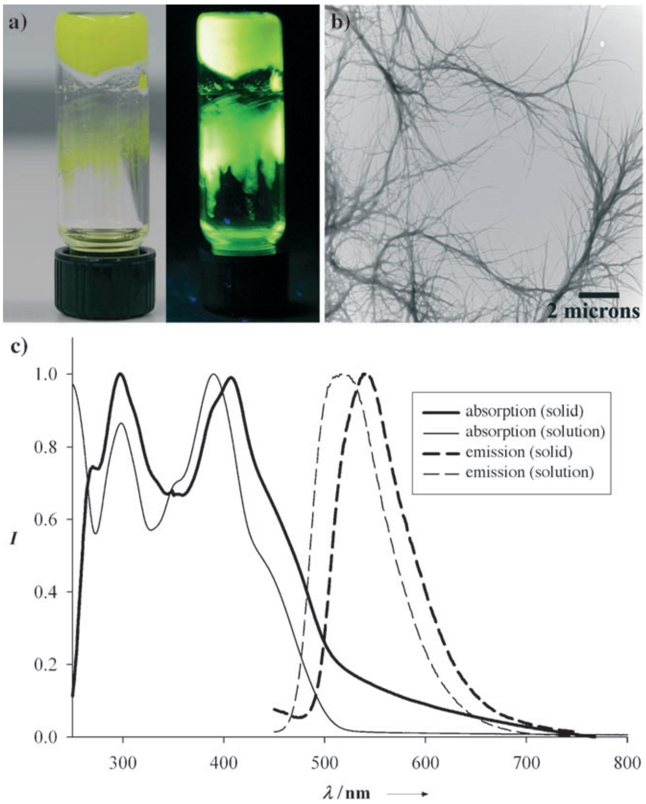


Figure 1. a) Photograph of gel **4a** in methanol under visible light (left) and when irradiated with UV light (right). b) Fiber morphology of **4a** cast from methanol, as observed by TEM. c) UV/Vis and fluorescence spectroscopy of **4a** in methylene chloride and in the solid state (gel).

Transmission electron microscopy (TEM) revealed that complexes **1a**–**5a** all form fibers when cast from methanol (Figure 2). In each case, the fibers are only tens of nanometers

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Table 1: Gel-forming abilities of **1a**–**5a** in various solvents.[a]

	1a	**2a**	**3a**	**4a**	**5a**
MeOH	–	–	–	Y	–
EtOH	–	–	–	–	–
Toluene	–	Y	Y	Y	Y
MeCN	–	–	–	–	–
EtOAc	–	–	–	–	–
Benzene	–	Y	Y	Y	Y
Pyridine	–	–	–	–	–
o-Xylene	–	Y	Y	Y	Y
DMF	–	–	–	–	–

[a] Concentration 3 mg mL^{-1}. Y gel observed; – no gel observed. OAc = acetate.

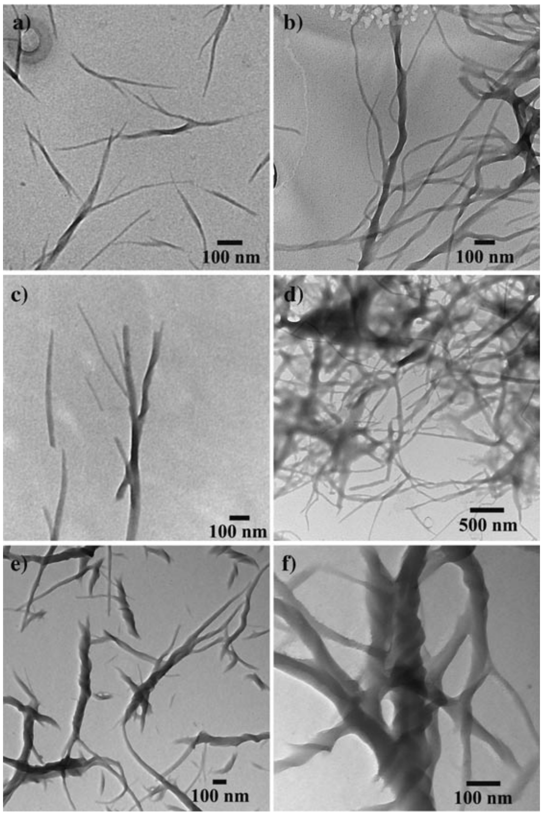


Figure 2. TEM images of a) complex **1a**, b) complex **2a**, c) complex **4a**, d) complex **5a**, and e),f) complex **3a** deposited from methanol.

in diameter but extend several microns in length. The relatively large diameters and rope morphology of the fibers suggest that they are not one molecule thick, but instead are formed from the assembly of 1D fibers into bundles. Fiber formation was observed for chain lengths ranging from methoxy to hexadecyloxy.

The fibers on the TEM grids do not exhibit electron diffraction and were too small to study by X-ray diffraction (XRD). Powder XRD studies of dried films of the zinc complexes cast from methanol do show some crystallinity. In the case of complex **2a**, the peaks fit to a tetragonal unit cell with $a = b = 14.90$ Å, $c = 20.49$ Å and $\alpha = \beta = \gamma = 90°$. For the other complexes, an insufficient number of peaks were observed to determine the unit cell with confidence. We initially thought that the fiber morphology observed in the [Zn(salphen)] complexes may be a consequence of the hydrophobic alkoxy substituents on the salphen complexes, which lead the complexes to aggregate in methanol. We hypothesized that replacing the alkoxy substituents of **1**–**5** with hydrophilic substituents, such as monosaccharides, may disrupt the organization or may favor the formation of single-strand nanofibrils from methanol. To test this hypothesis, compounds **6** and **7**, functionalized with glucose and galactose, respectively, were prepared. Drop-casting of Zn^{2+} complexes **6a** and **7a** from methanol, in which they are very soluble, mostly led to the formation of nanofibrils on the TEM grid (Figure 3). For both complexes, very narrow structures with diameters of about 5–7 nm, but with lengths that extend over micrometers, are formed. The fibers are all of similar width, and are much narrower than those from **1a**–**5a**.

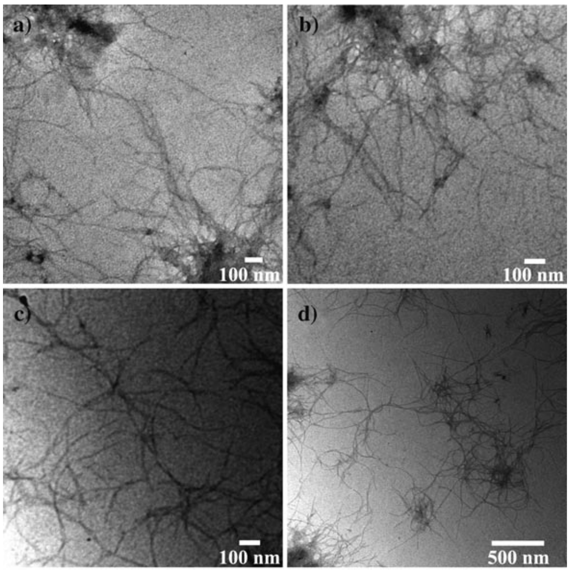
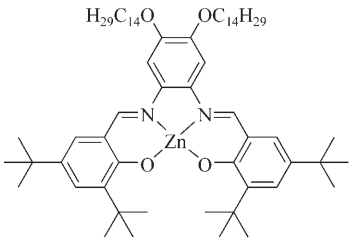


Figure 3. TEM images of a),b) complex **6a** and c),d) complex **7a** deposited from methanol.

We believe the 1D assembly observed for **1a**–**7a** involves Zn···O interactions rather than hydrogen-bonding or π–π interactions between the salphen complexes. Although we cannot directly observe Zn···O interactions, we have made several model compounds (**1b**, **4b**, **6b**, **7b**, **8**, **9**) and have carried out control experiments that support this assignment.[17] We rule out π–π interactions, which are frequently



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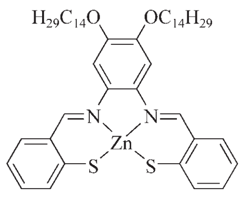

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seen in polycyclic aromatics, as the exclusive interaction, as square-planar Ni^{2+} complexes **1b**, **4b**, **6b**, and **7b** do not show similar organization to the Zn^{2+} complexes. TEM images of the nickel complexes show only ill-defined morphologies when cast from methanol or solvent mixtures. Complexes **6** and **7** with copper or vanadyl in the place of zinc also show no fiber assembly.

Complex **8** has bulky *tert*-butyl groups that should inhibit aggregation of the zinc complexes. Indeed complex **8** does not form a gel in methanol or in toluene, and TEM images of this complex cast from methanol showed no fibrillar texture. Complex **9**, which is the thiol analogue to complex **4a**, does not self-assemble into fibers in methanol. In this case, the aggregation is most likely inhibited by the bulky sulfur atoms at the zinc center that prevent expansion of the coordination sphere of the metal center. Additionally, the softer sulfur atom would be expected to interact less strongly with zinc than oxygen. These control compounds further support that the aggregation is mediated at the metal center.

The UV/Vis spectra for films of Zn^{2+} complexes **1a**–**7a** exhibit small red-shifts and broadening relative to the solution-phase spectra. Moreover, they are all luminescent, emitting at 525–540 nm, red-shifted by 20 nm from the solution phase. The similarity of the absorption and emission spectra for solutions and films of **1a**–**7a** indicates that a similar aggregation mechanism is involved in both the assembly of alkoxy- and carbohydrate-substituted complexes.

Further evidence for aggregation was obtained from electrospray ionization mass spectra (ESI-MS) of the complexes. All the spectra of the zinc complexes showed the molecular ion, but also showed peaks corresponding to aggregates. In fact, when the instrument was optimized for measurements on **2a**, we were able to observe singly and doubly charged species up to nine monomers (Figure 4). Although quantifying the individual species by ESI-MS is not feasible, the technique is known to give a snapshot of species present in solution. Thus, large aggregates of **2a** are formed in solution, supporting the strong tendency of these complexes to aggregate.

Semi-empirical (PM3) calculations were performed to better understand the supramolecular organization in these structures. Assuming the Zn^{2+} center is five-coordinate in the fibers as observed in dimers of [Zn(salphen)]-type complexes, an oligomer containing seven unsubstituted [Zn(salphen)] was constructed and its energy minimized, starting from several different conformations. Figure 5 shows an energy-minimized structure for the 1D heptamer with five-coordinate zinc ions. Calculated Zn–O and Zn–N distances are in agreement with crystallographic studies of dimers. The polymeric backbone contains a $(ZnO)_n$ polymer as illustrated in Figure 5, with an insulating organic sheath.

An interesting revelation from the modeling is that the complexes assembled in the 1D structures will likely assume a helical conformation. We have observed regions of fibers of the zinc complexes **1a**–**5a** that appear to have helical structure, and it is possible this motif derives from the helical conformation of the polymer strand. Figures 2e,f show regions of fibers formed from compound **3a**. In these images, there are segments that appear to have helical organization that may arise from the stacking of the salphen moieties.

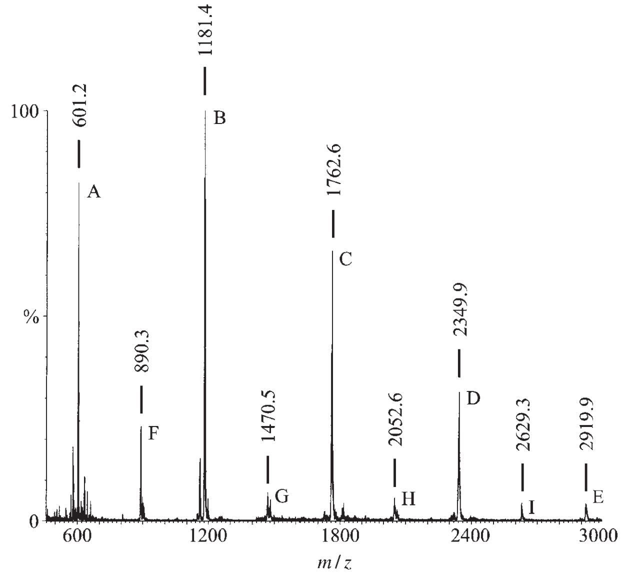

Figure 4. ESI-MS spectrum of complex **2a** exhibits singly (A–E) and doubly (F–I) charged species. A: $[\mathbf{2a}+Na]^+$, B: $[(\mathbf{2a})_2+Na]^+$, C: $[(\mathbf{2a})_3+Na]^+$, D: $[(\mathbf{2a})_4+Na]^+$, E: $[(\mathbf{2a})_5+Na]^+$, F: $[(\mathbf{2a})_3+Na_2]^{2+}$, G: $[(\mathbf{2a})_5+Na_2]^{2+}$, H: $[(\mathbf{2a})_7+Na_2]^{2+}$, I: $[(\mathbf{2a})_9+Na_2]^{2+}$.

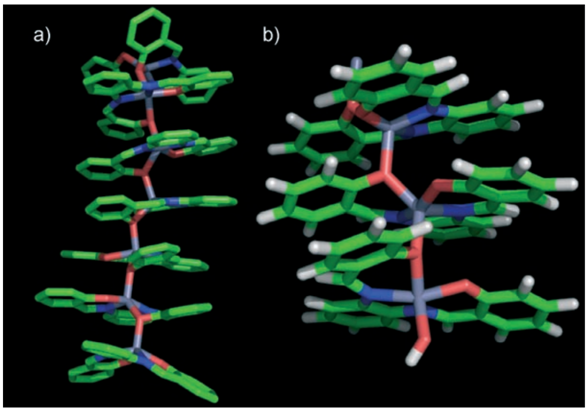

Figure 5. Energy-minimized (PM3) calculated structure for a heptamer of [Zn(salphen)]. a) The entire oligomer containing seven [Zn(salphen)] molecules connected into a 1D structure. b) An expanded view of three [Zn(salphen)] units from the middle of the heptamer. (Zn gray, O red, N blue, C green).

It is noteworthy that the aggregation behavior we have observed for metal salphen complexes is distinct from that of porphyrins.[10,18] Whereas porphyrins (and phthalocyanines) are known to aggregate, their assembly is dominated by π–π stacking or interactions of substituents, and the metal dependence is generally less pronounced. As an example, Shinkai and co-workers have observed improved gelation properties of a copper-containing porphyrin over the analogous zinc-containing porphyrin and have attributed this improvement to the stabilization of H-aggregates.[18] The coordination environment of salphen complexes is much more flexible than that of porphyrin complexes, offering new possibilities for self-assembly.

In conclusion, we have demonstrated the first supramolecular assembly of [Zn(salphen)] complexes into luminescent metal–organic gels and 1D nanofibers. This work demonstrates the potential of reversible Zn···O interactions for self-assembly of nanostructures. Structural changes to the side groups enable control over the morphology and dimensions of the nanofibers. Supramolecular assembly of salphen complexes may be used for the controlled organization of nanoscale patterns and wires, and the carbohydrate shell may ultimately prove beneficial for biological integration. We are now studying the scope of this fiber assembly.

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[17] We cannot rule out the possibility that the zinc salphen complexes dimerize then further assemble through π–π interactions. However, MALDI-TOF mass spectrometry studies of the fibers show the monomeric zinc complex rather than the dimer as the prevalent species.

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