

# Synthesis of Nanoscale Materials Using Organogels

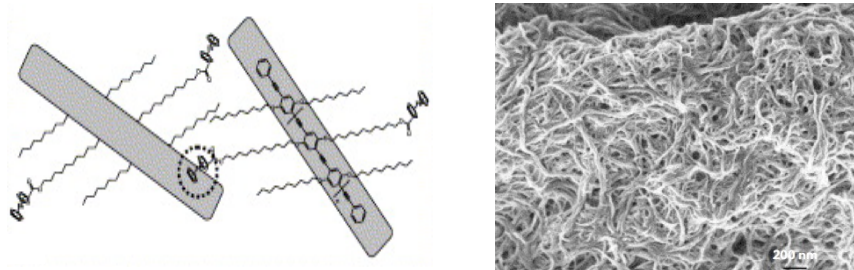
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A variety of materials for emerging technologies have been developed both comprising organogels and employing them in a synthetic procedure. An organogel is a three-dimensional network of non-covalently interacting molecules with interstitial spaces filled by organic liquid.<sup>1</sup> Motivation for their development includes the potential for new pharmaceuticals and materials which cannot be produced in aqueous solvent as they may with hydrogels.<sup>2</sup> Once generated, organogels can be used in many of the same ways that hydrogels are applied. Properties of organogels have been extensively reviewed, and new applications are continually developing.<sup>3-6</sup> These applications range from gelation of carbon nanotubes for composite materials to the fabrication of photoactive materials in organic phase.

Carbon nanotubes have been shown by Chen and co-workers<sup>1,7</sup> to form an organogel when cross-linked by the gelator poly(*p*-phenyleneethynylene) functionalized with ferrocene, as shown in Figure 1. The three-dimensional nanotube network had not been formed using organic solvent; in fact, little work has been reported on other nanotube gel networks.<sup>8-11</sup>



**Figure 1.** Ferrocene cross-linker and the resulting nanotube organogel film.<sup>1</sup>

The potential of *in vivo* supramolecular devices for therapeutics and molecule scale reactions motivated Ray and co-workers to develop an organogel which incorporates gold and silver nanoparticles *in situ*.<sup>12</sup> Tyrosine, an amino acid rendered redox-active upon deprotonation, is incorporated into the gelator backbone. The one-pot synthesis developed here comprises gel formation in organic solvent with the simultaneous reduction of gold or silver cations when triethylamine base is added. This simple technique sparks considerable interest for commercial application as a therapeutic delivery agent.

The transcription of molecular structure is useful for mimicking the function of other molecules in new materials. Chirality is of particular interest for its specific selectivity in reactions. Transcription of chirality was serendipitously discovered by Ono and Shinkai during the preparation of silica fibers from an organogel framework.<sup>13</sup> A cholesterol-based gelator was used to generate a three-dimensional network in which tetraethoxysilane would polymerize through a sol-gel mechanism. A neutral gelator

framework promoted the formation of granular silica, but a cationic gelator attracted the silicate intermediate to the framework during polymerization, which produced hollow fibers grown along the organogel. Microscopy showed a right-handed, helical conformation to the fibers matching that of the pure organogel fibers, suggesting that the chirality in the cholesterol gelator is transcribed in the silica product.

One technologically applicable property of these materials is photoactivity. Organogels which can switch their structure by light excitation may be employed in coatings and other “intelligent” materials. An example of this is the two-component organogel was very recently developed by Zhou and co-workers.<sup>14</sup> This material was fabricated by gelating a  $C_3$ -symmetrical trisamide molecule. Another trisamide molecule containing a photoactive azobenzene moiety fits into the organogel by hydrogen bonding. The inserted molecule freely switches its azobenzene moieties reversibly from *trans*- to *cis*- conformation upon light excitation.

In addition to switching the structure of a material using light, the morphology of a material may be tuned through reaction conditions. The material that one reaction can produce at a certain pH may be quite distinct from the product of that same reaction at a higher pH. This result was shown recently by Roy and co-workers.<sup>15</sup> Among other results, their work indicated that morphological characteristics of organogels such as thickness and entanglement of a fibrous product corresponds to acidic conditions. Understanding appropriate reaction conditions will aid materials chemists in the optimization of these organogel-based reactions.

The study of various reactions utilizing organogels as both synthetic matrix and target material is burgeoning and will continue to do so as more practical applications of organogels are realized. Already the materials are being used in topical pharmaceuticals<sup>16</sup> and are being targeted for use as molecular scaffolds and drug delivery systems in which the organogel will have amphiphilic character.<sup>17</sup> For reactions which necessitate an organic phase, the organogel matrix is a well-suited alternative to hydrogels.

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