

Metallic molecules to nanotubes: Spread out!

February 23 2011



A photo of the research team

(PhysOrg.com) -- A lab at Rice University has stepped forward with an efficient method to disperse nanotubes in a way that preserves their unique properties -- and adds more.

The new technique allows inorganic [metal complexes](#) with different functionalities to remain in close contact with single-walled carbon nanotubes while keeping them separated in a solution.

That separation is critical to manufacturers who want to spin fiber from nanotubes, or mix them into composite materials for strength or to take advantage of their [electrical properties](#). For starters, the ability to functionalize the nanotubes at the same time may advance imaging sensors, catalysis and solar-activated [hydrogen fuel cells](#).

Better yet, a batch of nanotubes can apparently stay dispersed in water for weeks on end.

Keeping carbon nanotubes from clumping in aqueous solutions and combining them with molecules that add novel abilities have been flies in the ointment for scientists exploring the use of these highly versatile materials.

They've tried attaching organic molecules to the nanotubes' surfaces to add functionality as well as solubility. But while these techniques can separate nanotubes from one another, they take a toll on the nanotubes' electronic, thermal and mechanical properties.

Angel Marti, a Rice assistant professor of chemistry and bioengineering and a Norman Hackerman-Welch Young Investigator, and his students reported this month in the Royal Society of Chemistry journal [Chemical Communications](#) that ruthenium polypyridyl complexes are highly effective at dispersing nanotubes in water efficiently and for long periods. Ruthenium is a rare metallic element.

One key is having just the right molecule for the job. Marti and his team created ruthenium complexes by combining the element with ligands, stable molecules that bind to [metal ions](#). The resulting molecular complex is part hydrophobic (the ligands) and part hydrophilic (the ruthenium). The ligands strongly bind to nanotubes while the attached ruthenium molecules interact with water to maintain the tubes in solution and keep them apart from one another.

Another key turned out to be moderation.

Originally, Marti said, he and co-authors Disha Jain and Avishek Saha weren't out to solve a problem that has boggled chemists for decades, but their willingness to "do something crazy" paid off big-time. Jain is a

former postdoctoral researcher in Marti's lab, and Saha is a graduate student.

The researchers were eyeing ruthenium complexes as part of a study to track amyloid deposits associated with Alzheimer's disease. "We started to wonder what would happen if we modified the metal complex so it could bind to a nanotube," Marti said. "That would provide solubility, individualization, dispersion and functionality."

It did, but not at first. "Avishek put this together with purified single-walled carbon nanotubes (created via Rice's HiPco process) and sonicated. Absolutely nothing happened. The nanotubes didn't get into solution -- they just clumped at the bottom.

"That was very weird, but that's how science works -- some things you think are good ideas never work."

Saha removed the liquid and left the clumped nanotubes at the bottom of the centrifuge tube. "So I said, 'Well, why don't you do something crazy. Just add water to that, and with the little bit of ruthenium that might remain there, try to do the reaction.' He did that, and the solution turned black."

A low concentration of ruthenium did the trick. "We found out that 0.05 percent of the ruthenium complex is the optimum concentration to dissolve nanotubes," Marti said. Further experimentation showed that simple ruthenium complexes alone did not work. The molecule requires its hydrophobic ligand tail, which seeks to minimize its exposure to water by binding with nanotubes. "That's the same thing nanotubes want to do, so it's a favorable relationship," he said.

Marti also found the nanotubes' natural fluorescence unaffected by the ruthenium complexes. "Even though they've been purified, which can

introduce defects, they still exhibit very good fluorescence," he said.

He said that certain ruthenium complexes have the ability to stay in an excited state for a long time -- about 600 nanoseconds, or 100 times longer than normal [organic molecules](#). "It means the probability that it will transfer an electron is high. That's convenient for energy transfer applications, which are important for imaging," he said.

That [nanotubes](#) stay suspended for a long time should catch the eye of manufacturers who use them in bulk. "They should stay separated for weeks without problems," Marti said. "We have solutions that have been sitting for months without any signs of crashing."

Provided by Rice University

Citation: Metallic molecules to nanotubes: Spread out! (2011, February 23) retrieved 3 May 2024 from <https://phys.org/news/2011-02-metallic-molecules-nanotubes.html>

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