Tuning the wavelength of fluorescent carbon tubes

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Carbon is not just the most important element for life, it also has fascinating properties of its own. Graphene—a pure carbon sheet just one atom thick—is one of the strongest materials. Roll graphene into a cylinder and you get carbon nanotubes (CNTs), the key to many emerging technologies.

Now, in a study reported in *Chemical Communications*, researchers at Japan's Kyushu University learned to control the fluorescence of CNTs, potentially allowing new applications.

CNTs are naturally fluorescent—when placed under light, they respond by releasing light of their own, a process called photoluminescence. The wavelength (color) of fluorescence depends on the tubes' structure, such as the angle at which they are rolled. Fluorescent CNTs have been studied for use in LED lighting and medical imaging.

The Kyushu team aimed to gain finer control over the emission wavelength. "Fluorescence occurs when electrons use energy from light to jump into higher orbitals around atoms," the lead authors explain. "They sink back to a lower orbital, then release excess energy in the form of light. The wavelength of emitted light differs from the input light, depending on the energy of the emitting orbital." Although fluorescence is often associated with yellow materials, the fluorescence of these CNTs is infrared, which is invisible to the eye but can be detected by sensors.

The researchers used chemistry to tether organic molecules—hexagons of carbon atoms—onto the CNTs. This pushed the orbitals up or down, thus tuning the fluorescence. One of the six atoms in each hexagon was bonded to a CNT, anchoring the molecule to the tube. Another was bonded to an extra group of atoms (a substituent). Because of the hexagonal shape, the two bonded carbons could be adjacent (denoted "o"), or separated by one carbon ("m"), or by two ("p"). Most studies use the "p" arrangement, where the substituent points away from the CNT, but the Kyushu team compared all three.

The "o" pattern produced very different fluorescence from "m" and "p"—instead of one infrared wavelength, the CNTs now emitted two. This resulted from distortion of the tubes by the substituents, which were squeezed against the tube walls. Meanwhile, for the "m" and "p" arrangements, the energies depended on which elements were in the substituent. For example, NO2 produced bigger gaps between orbitals than bromine. This was no surprise, as NO2 is better at attracting electrons, creating an electric field (dipole). However, the size of the effect differed between "m" and "p."

"The variation in orbital energies with different substituents gives us fine control of the emission wavelength of CNTs over a broad range," the authors say. "The most important outcome is to understand how dipoles influence fluorescence, so we can rationally design CNTs with the very precise wavelengths needed by biomedical devices. This could be very important for the development of bioimaging in the near future."

The article, "Near infrared photoluminescence modulation by defect site design using aryl isomers in locally functionalized single-walled carbon nanotubes," was published in *Chemical Communications*.

More information: Tomohiro Shiraki et al, Near infrared photoluminescence modulation by defect site design using aryl isomers

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