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*Contact: John Toon (404-894-6986)  
E-mail: (john.toon@edi.gatech.edu)  
or Jane Sanders (404-894-2214)*

## **GOLD QUANTUM DOTS: FLUORESCING “ARTIFICIAL ATOMS” COULD HAVE APPLICATIONS IN BIOLOGICAL LABELING, NANOSCALE OPTOELECTRONICS**

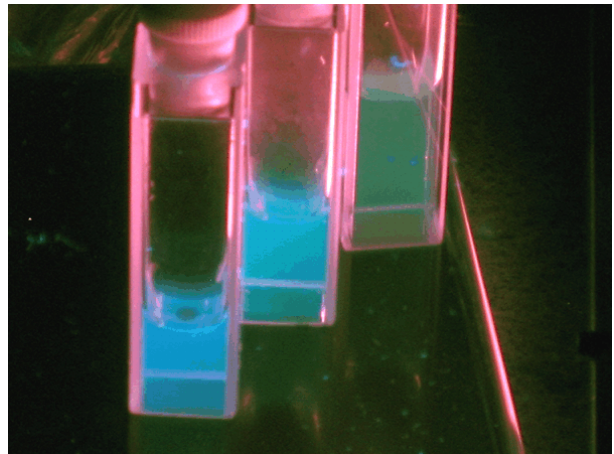
A new class of water-soluble quantum dots made from small numbers of gold atoms could be the basis for a new biological labeling system with narrower excitation spectra, smaller particle size and fluorescence comparable to systems based on semiconductor quantum dots.

Providing the “missing link” between atomic and nanoparticle behavior in noble metals, these multi-electron “artificial atoms” could also serve as light-emitting sources in nanoscale optoelectronics and in energy transfer pairs.

“We have discovered a new class of quantum dots that are water soluble, strongly fluorescent, and display discrete excitation and emission spectra that make them potentially very useful for biological labeling,” said Robert Dickson, associate professor in the School of Chemistry and Biochemistry at the Georgia Institute of Technology. “Their potential applications are really complementary to those of semiconductor quantum dots.”

The gold nanodots are made up of 5, 8, 13, 23 or 31 atoms, each size fluorescing at a different wavelength to produce ultraviolet, blue, green, red and infrared emissions, respectively. The fluorescence energy varies according to the radius of the quantum dot, with the smallest structures the most efficient at light emission.

In contrast, quantum dots made from semiconductors such as cadmium selenide are much larger, containing hundreds or thousands of atoms.



Fluorescence is shown from solutions of small gold nanoclusters dissolved in water. These nanoclusters behave like multi-electron artificial atoms, emitting at discrete wavelengths in the visible and infrared with the wavelength increasing with the size of the cluster. Shown from left to right are emissions from gold nanoclusters containing 5, 8 and 13 atoms.

Semiconductor quantum dots obey different size scaling under confinement, producing weaker emissions.

The gold quantum dots were reported August 13 in the journal *Physical Review Letters*, and highlighted on the journal cover. Additional information on the work was presented August 23<sup>rd</sup> at the 228th national meeting of the American Chemical Society in Philadelphia, PA. The work was sponsored by the National Science Foundation, National Institutes of Health, Sloan and Dreyfus

Foundations, Blanchard and Vassar Woolley Endowments and the Georgia Tech Center for Advanced Research in Optical Microscopy.

In addition to Dickson, the research team includes Professor Yih Ling Tzeng of Emory University; Jie Zheng, Lynn Capadona and Caiwei Zhang of Georgia Tech, and Jeffrey Petty of Furman University.

Because of their narrow excitation spectra and small physical size, the gold quantum dots could be particularly useful in fluorescence resonance energy transfer (FRET) systems, in which emission from one nanodot would be used to excite another as a means of measuring proximity.

The broad excitation spectra of semiconductor quantum dots and their larger size make them more difficult to use in FRET-based research, Dickson noted.

By using poly-amidoamine (PAMAM) dendrimers to encapsulate their gold clusters, the researchers produced quantum dots with very clean mass spectra. The 8-atom cluster, for instance, produces bright blue emission and fluorescence quantum yields of 42 percent in an aqueous solution.

The researchers produce the nearly spectrally pure, size-tunable gold nanodots through a slow reduction of gold salts ( $\text{HAuCl}_4$  or  $\text{AuBr}_3$ ) within aqueous PAMAM solutions, followed by centrifugation to remove large nanoparticles. By controlling the relative concentration of gold to PAMAM and the generation of the dendrimers, the researchers can control nanocluster size – and therefore the emission wavelengths.

“Nanodots encapsulated through PAMAM exhibit higher fluorescence quantum yields than do clusters encapsulated by other matrices, suggesting an important role for amines in gold nanodot creation,” Dickson noted.

The nanodot solutions are stable, lasting for months either in solution or as dried powders. Solutions from re-dissolved nanodot powders have the same properties as when they were originally created.

Dickson’s research group has been working with fluorescent and electroluminescent silver nanoclusters for several years, evaluating their use in optical computing and other applications. While silver quantum dots offer promise because of their strong emission, their narrower size range (2-8 atoms) makes them difficult to separate to create solutions with distinct emission spectra.

“Silver fluoresces very strongly and it has awesome optical properties, even better than gold because it has very short lifetimes and high quantum

yields,” Dickson said. “But it is more difficult for us to separate them to get high concentrations of pure samples. Right now the scalings are much clearer and more easily understood in gold, so we will take what we’ve learned there and ultimately apply it to silver.”

Before these gold quantum dots can be useful in biological labeling, however, the researchers must develop a mechanism for attaching them to proteins that scientists wish to track in cells.

“We are continuing to investigate these quantum dots, to probe their fundamental photophysical and spectroscopic properties, and to develop different chemistries for functionalizing the scaffolding that encapsulates the nanoclusters so we can attach them to other molecules,” Dickson noted.

Much of that work will be done with newly obtained support from the National Institutes of Health, which has funded a Roadmap Initiative Center in High Resolution Cellular Imaging to a team of Georgia Tech chemists and Prof. Tzeng at Emory University.

“We will need to determine ways to functionalize these quantum dots so they will get across cell membranes, seek out specific proteins inside a cell and label those proteins,” explained Dickson. “We are basically developing the tools for in-vivo, single-molecule sensitivity and labeling in living systems in the presence of very high backgrounds. We expect to produce a new set of probes that will be size-tunable, non-toxic and very bright.”

Beyond the potential applications, studying the gold clusters provides basic information about the properties of small clusters of noble metals, how they share conduction electrons, and how they fluoresce under quantum confinement.

“They can help us understand the very small size scale that is really not well understood for noble metals,” Dickson added. “They can provide the ‘missing link’ between atomic and nanoparticle behavior in these metals.”

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**Technical contact:** Robert Dickson (404-894-4007);  
E-mail: (robert.dickson@chemistry.gatech.edu).

**URL for release on Web:**  
([gtresearchnews.gatech.edu/newsrelease/quantumdot.htm](http://gtresearchnews.gatech.edu/newsrelease/quantumdot.htm))