Invisible inks could help foil counterfeiters of all kinds

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Real or counterfeit? Northwestern University scientists have invented sophisticated fluorescent inks that one day could be used as multicolored barcodes for consumers to authenticate products that are often counterfeited. Snap a photo with your smartphone, and it will tell you if the item is real and worth your money.

Counterfeiting is very big business worldwide, with $650 billion per year lost globally, according to the International Chamber of Commerce. The new fluorescent inks give manufacturers and consumers an authentication tool that would be very difficult for counterfeiters to mimic.

These inks, which can be printed using an inkjet printer, are invisible under normal light but visible under ultraviolet light. The inks could be stamped as barcodes or QR codes on anything from banknotes and bottles of whisky to luxury handbags and expensive cosmetics, providing proof of authenticity.

A key advantage is the control one has over the color of the ink; the inks can be made in single colors or as multicolor gradients. An ink's color depends on the amounts and interaction of three different "ingredient" molecules, providing a built-in "molecular encryption" tool. (One of the ingredients is a sugar.) Even a tiny tweak to the ink's composition results in a significant color change.

"We have introduced a level of complexity not seen before in tools to combat counterfeiters," said Sir Fraser Stoddart, the senior author of the study. "Our inks are similar to the proprietary formulations of soft drinks. One could approximate their flavor using other ingredients, but it would be impossible to match the flavor exactly without a precise knowledge of the recipe."

Sir Fraser is the Board of Trustees Professor of Chemistry in the Weinberg College of Arts and Sciences.

"The rather unusual relationship between the composition of the inks and their color makes them ideal for security applications where it's desirable to keep certain information encrypted or to have brand items with unique labels that can be authenticated easily," Stoddart said.

With a manufacturer controlling the ink's "recipe," or chemical composition, counterfeiters would find it virtually impossible to reverse engineer the color information encoded in the printed barcodes, QR codes or trademarks. Even the inks' inventors would not be able to reverse engineer the process without a detailed knowledge of the encryption settings.

Details of the fluorescent inks, which are prepared from simple and inexpensive commodity chemicals, will be published April 22 by the journal *Nature Communications*.

Stoddart's research team, led by Xisen Hou and Chenfeng Ke, stumbled across the water-based ink composite serendipitously. A series of rigorous follow-up investigations unraveled the mechanism of the unique behavior of the inks and led the scientists to propose an encryption theory for security printing.

Hou, a third-year graduate student, and Ke, a postdoctoral fellow, are co-first authors of the paper.

The researchers developed an encryption and authentication security system combined with inkjet-printing technology. In the study, they demonstrated both a monochromic barcode and QR code printed on paper from an inkjet printer. The information, invisible under natural light, can be read on a smartphone under UV light.

As another demonstration of the technology, the research team loaded the three chemical components into an inkjet cartridge and printed Vincent Van Gogh's "Sunflowers" painting with good color resolution. Like the barcodes and QR codes, the printed image is only visible under UV light.

The inks are formulated by mixing a simple sugar (cyclodextrin) and a competitive binding agent together with an active ingredient (a molecule known as heterorotaxane) whose fluorescent color changes along a spectrum of red to yellow to green, depending upon the way the components come together. An infinite number of combinations can be defined easily.

Although the sugar itself is colorless, it interacts with the other components of the ink, encapsulating some parts selectively, thus preventing the molecules from sticking to one another and causing a change in color that is difficult to predict. This characteristic presents a formidable challenge to counterfeiters.

Hou and Ke were trying to prevent fluorophore aggregation by encircling a fluorescent molecule with other ring-shaped molecules, one being cyclodextrin. Unexpectedly, they isolated the compound that is the active ingredient of the inks. They found that the compound's unusual arrangement of three rings trapped around the fluorescent component affords the unique aggregation behavior that is behind the color-changing inks.

"You never know what Mother Nature will give you," Hou said. "It was a real surprise when we first isolated the main component of the inks as an unexpected byproduct. The compound shows a beautiful dark-red fluorescence under UV light, yet when we dissolve it in large amounts of water, the fluorescent color turns green. At that moment, we realized we had discovered something that is quite unique."

The fluorescent colors can be tuned easily by adding the sugar dissolved in water. As more cyclodextrin is added, the fluorescent color changes from red to yellow and then green, giving a wide range of beautiful colors. The fluorescent color can be reversed, by adding another compound that mops up the cyclodextrin.

The researchers also discovered that the fluorescent ink is sensitive to the surface to which it is applied. For example, an ink blend that appears as orange on standard copy paper appears as green on newsprint. This observation means that this type of fluorescent ink can be used to identify different papers.

"This is a smart technology that allows people to create their own security code by manually setting all the critical parameters," Hou said. "One can imagine that it would be virtually impossible for someone to reproduce the information unless they knew exactly all the parameters."

The researchers also have developed an authentication mechanism to verify the protected information produced by the fluorescent security inks. Simply by wiping some wet authentication wipes on top of the fluorescent image causes its colors to change under UV light.

"Since the color changing process is dynamic, even if counterfeiters can mimic the initial fluorescent color, they will find it impossible to reproduce the color-changing process," Ke emphasized.

More information: "Tunable Solid-State Fluorescent Materials for Supramolecular Encryption" *Nature Communications*, 2015.

Provided by Northwestern University