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Information encryption with a high information-carrying capacity based on a stimulus-responsive hydrogen-bonded organic framework and a smartphone

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ABSTRACT

Information-carrying capacity has become an important factor in the development of encryption and anti-counterfeiting. Herein, a hydrogen-bonded organic framework (HOF-PyTTA) was developed as novel anti-counterfeiting ink without rare metals and a smartphone-based APP was written for encryption and anti-counterfeiting. We found that the fluorescence of HOF-PyTTA can be quenched by Fe^{3+} ions and recovered by the addition of ascorbic acid. And the fluorescence of HOF-PyTTA can be enhanced by the increasing concentrations of ethanol. Based on these stimulus-response properties, four anti-counterfeiting models with gradually increased security were studied. Mode one was printed by HOFs ink and decrypted by UV light. Mode two was based on HOF-PyTTA and CsPbBr_3 inks (or HOF-PyTTA- Fe^{3+}) which are used to separately print the genuine and pirated information. A decryption reagent was applied to get the genuine information. Furthermore, we successfully construct a dynamic information encryption anti-counterfeiting model using a fluorescence array in combination with an information encryption anti-counterfeiting APP. The circular array is printed by several concentrations of HOF-PyTTA ink and different RGB thresholds are set with the help of the information encryption anti-counterfeiting APP, to obtain distinct encrypted anti-counterfeiting information, thus accomplishing a high information-carrying capacity.

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Counterfeiting in books, luxury goods, food [1–3], etc., has caused huge economic losses in modern society. To reduce the losses, various anti-counterfeiting technologies have been developed, including radiofrequency identification [4], watermarks [5], holograms [6], molecular tag [7], structural colors [8], smart polymeric gel [9], and luminescence techniques [10,11]. Among them, fluorescence-based optical anti-counterfeiting technology shows its superiority due to its high confidentiality, excellent fluorescence intensity, and tunable coded patterns.

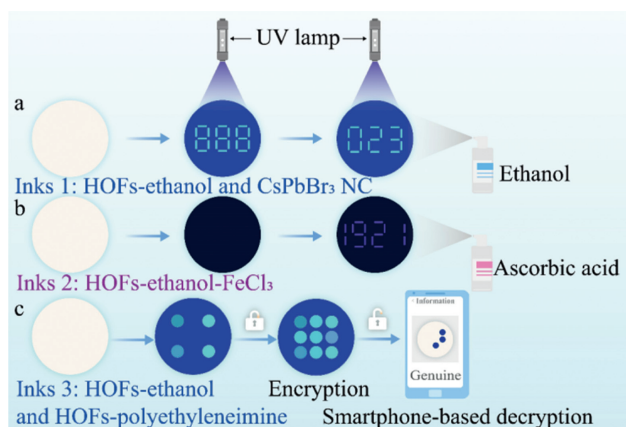
A variety of fluorescent materials have been developed as anti-counterfeiting inks [12], such as CsPbBr_3 [13,14], upconversion nanoparticles [15], fluorescent hydrogel [16–19], erbium-doped silicon thin films [20], graphitic carbon nitride [21], carbon dots [22] and persistent luminescent materials [23]. By using these stimulus-response fluorescent materials as signal producers, these works can achieve double-mode and multi-mode encryption. However, most of the previous reports usually only give a genuine or pirated pattern which is easy to be inferred. Thus, the information-

carrying capacity still needs to be improved by providing more patterns to make it not easy to be inferred. In recent years, hydrogen-bonded organic frameworks (HOFs), formed by highly rigid and aromatic molecular blocks held together by strong non-covalent interactions [24], have attracted increased attention because of their outstanding luminescence properties. They have been used for gas storage and separation [25,26], sensing [27], antibacterial [28], and drug delivery [29] applications, but limited incidences of use [30,31] in information encryption and anti-counterfeiting have been reported. Besides, most of the applications of HOFs in anti-counterfeiting still need the doping of rare metal elements to achieve a genuine or pirated fluorescence pattern. Hence, it is still a challenge to develop an eco-friendly and user-friendly method for encryption and anticounterfeiting with high information-carrying capacity.

In this study, we selected 4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl) tetraaniline (PyTTA) as the organic monomer for self-assembling into a hydrogen-bonded organic framework (HOF-PyTTA) [24]. The fluorescence properties of HOF-PyTTA were investigated and it showed stimulus-responsive fluorescent properties with the addition of Fe^{3+} ions and ethanol. In recent years, the smartphone-

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Scheme 1. Schematic illustration of (a, b) double-mode and (c) multi-mode encryption and decryption based on a smartphone.

based device and analysis for food safety [32], healthcare [33], and environmental monitoring [34] have attracted wide attention because the smartphone has some advantages such as high-resolution imaging, ease of use, portability, image storage, and programmability. Thus, a novel strategy with high information-carrying capacity was obtained based on the stimulus-responsive fluorescence properties of HOF-PyTTA and a self-written smartphone APP. We prepared HOFs-polyethyleneimine, CsPbBr₃ NC-*n*-hexane, HOFs-ethanol-FeCl₃ inks, and HOFs-ethanol ink for anti-counterfeiting printing. We use HOFs-polyethyleneimine as an anti-counterfeiting ink for printing anti-counterfeiting messages on filter paper, which is both colorless and invisible under ambient light (Fig. S1a in Supporting information). Therefore, it is only possible to obtain the genuine information under UV light, thus achieving single-mode encryption (Fig. S1b and c in Supporting information). We also have successfully printed other patterns by using this ink on other materials such as sticky note, book, and counting coupons (Fig. S2 in Supporting information). To improve the information security level, we prepared CsPbBr₃ NC-*n*-hexane and HOFs-ethanol inks. A double-mode encryption method was designed by using the fluorescence properties of the two inks under UV light (Scheme 1a and Fig. S3 in Supporting information). We used two inks to print a mixture of encrypted anti-counterfeit information on filter paper and then used the decryption reagent (ethanol) to burst the CsPbBr₃ NC-*n*-hexane ink fluorescence, thus achieving a double conversion of the encryption information. To further enhance the concealment of the encrypted information, we introduced HOFs-ethanol-FeCl₃ (Scheme 1b and Fig. S4 in Supporting information) as an anti-counterfeiting encryption ink, which was printed on yellow oil paper. By introducing Fe³⁺, the fluorescence of the HOF-PyTTA ink broke out, making it invisible in both ambient light conditions and UV light conditions. A decrypting agent (ascorbic acid solution) is then used to restore the HOFs ink fluorescence, completing the dynamic fluorescence burst-recovery process to enhance the concealment of encrypted anti-counterfeit information. Finally, we selected HOFs-ethanol ink and HOFs-polyethyleneimine ink to print 3 × 3 encryption array with different concentration gradients. An array of different fluorescence intensities under UV light was observed. We introduced our self-developed intelligent encryption and anti-counterfeiting APP, which can decrypt the information of the encryption array with a correct 'RGB' (red, green, blue) threshold (Scheme 1c and Fig. S5 in Supporting information). Due to the different combinations of the thresholds, dynamic encryption and anti-counterfeiting are achieved with a high information-carrying capacity.

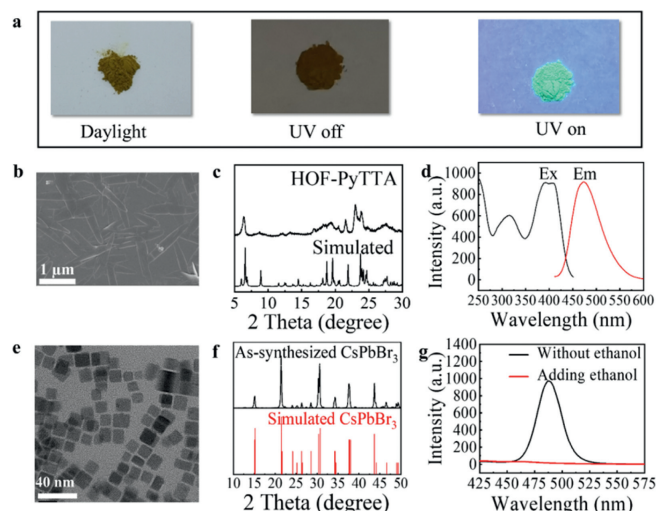


Fig. 1. (a) Image of the HOF-PyTTA with daylight, UV off, or UV on. (b) TEM image of HOF-PyTTA. (c) XRD pattern for HOF-PyTTA and simulated XRD pattern for HOF-PyTTA. (d) Excitation and emission fluorescence spectrum of HOF-PyTTA. (e) TEM image of CsPbBr₃. (f) XRD pattern of CsPbBr₃ and simulated XRD pattern of CsPbBr₃. (g) Fluorescence spectra of CsPbBr₃ without and with the addition of ethanol.

To study the fluorescence properties of HOF-PyTTA, we observed the luminescence of HOF-PyTTA under daylight, 'UV Off', and 'UV on' conditions (Fig. 1a). Bright fluorescence was observed under UV light. TEM image of HOF-PyTTA showed filamentous shape (Fig. 1b) with a width of about 200 nm and length of 1000 nm. The XRD pattern of the synthesized HOF-PyTTA (Fig. 1c) is consistent with the simulated XRD pattern [24]. Fig. 1d shows the excitation/emission spectrum of the HOF-PyTTA. It shows strong fluorescence with excitation/emission peaks at 400/500 nm. The solid-state fluorescence emission spectrum and excitation spectrum (Fig. S1a) were also carried out and the fluorescent emission was corresponding to the color changes (Fig. S6a in Supporting information). In the FTIR spectrum (Fig. S6b in Supporting information), the peak at 2923 cm⁻¹ can be attributed to the O-H stretching vibration of N-H-O, while the peaks at 3216 cm⁻¹ and 3034 cm⁻¹ were attributed to the N-H stretching vibration of N-H-N. The fluorescence lifetime (Fig. S6c in Supporting information) was determined as 3.1 ns. In addition, XPS spectra (Figs. S6d, e and f in Supporting information) showed that HOF-PyTTA consisted of three main elements (C, N, and O). The above results suggested that HOF-PyTTA had been successfully synthesized and showed a good fluorescent property.

The TEM image (Fig. 1e) of the CsPbBr₃ NC showed a homogeneous material arrangement with a regular morphology of square flakes with a particle size of approximately 14 nm. The XRD of the CsPbBr₃ NC (Fig. 1f) were generally in agreement with the simulated peaks, demonstrating a successful synthesis of the CsPbBr₃ NC. The fluorescence emission spectra of CsPbBr₃ NC showed a strong fluorescence intensity at 488 nm (Fig. 1g). After the addition of ethanol, a significant fluorescence bursting effect emerged on CsPbBr₃ NC-*n*-hexane ink. Based on the different fluorescent responses of the CsPbBr₃ NC and HOF-PyTTA when encountered with ethanol, it can realize double-mode information encryption and anti-counterfeiting.

The stimulus-responsive performances of HOF-PyTTA were investigated in Fig. 2. With the increase of Fe³⁺ concentration, the fluorescence intensity of HOF-PyTTA solution gradually decreased (Fig. 2a). After the addition of ascorbic acid (AA) solution, the fluorescence intensity is increased (Fig. 2b). Similar results were observed by increasing the ethanol concentration of HOF-PyTTA solution (Fig. 2c). These performances inspired us to design a double-

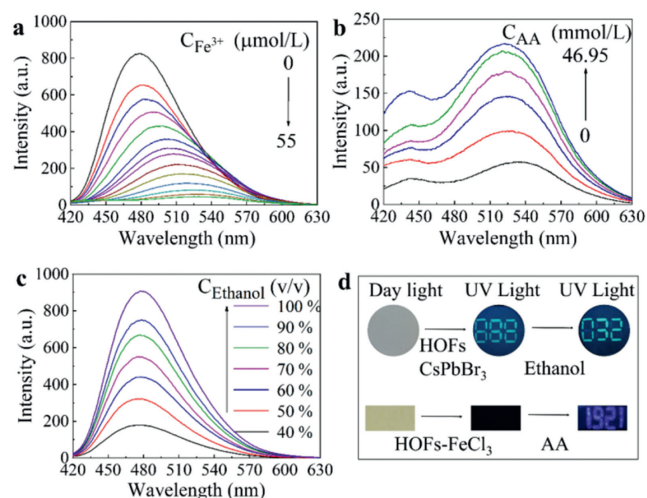


Fig. 2. Stimulus-responsive performances of HOF-PyTTA. (a) Fluorescence spectra of HOF-PyTTA solution with the addition of different concentrations of Fe^{3+} . (b) Fluorescence spectra of HOF-PyTTA- Fe^{3+} solution with the addition of different concentrations of AA. (c) Fluorescence spectra of HOF-PyTTA solution with different concentrations of ethanol. (d) A series of patterns using different inks and decryption by ethanol and AA, respectively.

mode encryption strategy by combining HOF-PyTTA with some decryption reagents. Thus, we chose HOFs-ethanol ink and CsPbBr_3 NC-*n*-hexane ink for double-mode encryption, where the two inks were used to print the graphic information, respectively. Under daylight conditions, no graphical information is visible (Fig. 2d). Under UV light irradiation, the graphical information of '888' is visible. After spraying the decryption reagent (ethanol), the fluorescent information of the CsPbBr_3 NC-*n*-hexane ink is burnt out, revealing another graphic message '032'. The combination of the two types of information encryption inks and the decrypting agent effectively increases the graphic information security during transmission. Besides, the decryption method is easy to be used by the recipient to obtain the genuine information.

In order to further strengthen the invisibility of anti-counterfeiting information, we prepared the HOFs-ethanol- FeCl_3 ink as the invisible anti-counterfeiting ink. The graphics were invisible under daylight conditions (Fig. 2d). However, when sprayed with a decryption reagent (0.1 mol/L ascorbic acid (AA) solution), a clear and bright fluorescent message of '1921' was instantly visible (Fig. 2d). The encryption method is very easy to operate, meaning it can be set up and used quickly, and effectively enhances the invisibility of information encryption and anti-counterfeiting in daily life.

Finally, to enhance the concealment and security of our encryption method, we have designed a self-made smartphone APP and an encrypted array using different concentrations of HOFs ink (Fig. 3). The smartphone APP was tested for information encryption by using a haphazard color array (Fig. S7 in Supporting information). No valuable information can be obtained from the array by naked eyes. Firstly, the user opens the APP (Fig. S7a) and logs in with a password (Fig. S7b). Secondly, the user imports the graphics (Fig. S7c) and sets the identified range (Fig. S7d). Finally, with a threshold 1 (Fig. S7e), APP will output information 1 (Fig. S7f). With a threshold 2 (Fig. S7g), APP will output information 2 (Fig. S7h) to obtain the numerical information '1932' and '2022'. This verifies that we have successfully created a smartphone-based APP for information encryption and decryption.

Subsequently, as an example, a 3×3 encrypted array was printed on paper by using different concentrations of HOF-PyTTA ink and HOFs-ethanol ink (Fig. S8 in Supporting information and Fig. 3). The encrypted paper was blank under daylight conditions,

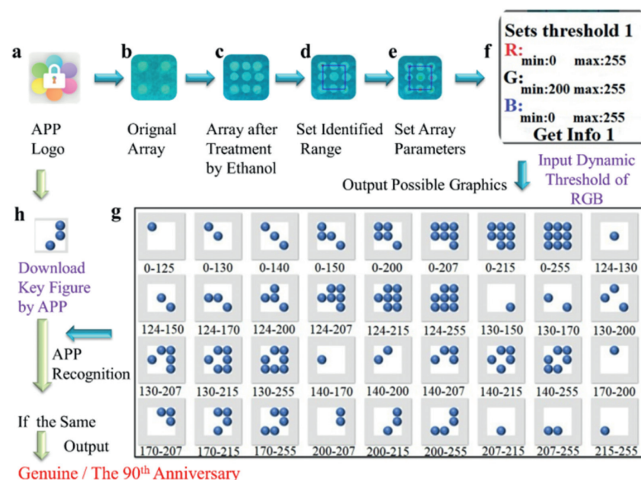


Fig. 3. Smartphone APP based on RGB analysis for identifying encrypted fluorescence array. (a) APP logo in the mobile interface. (b) The fluorescence array under UV light. (c) The fluorescence array after the treatment by ethanol. (d) Set identified range. (e) Set array parameters. (f) Input threshold range of RGB. (g) Identify graphic information corresponding to the different threshold ranges. (h) The key figure.

while a fluorescence array with four circles was presented under UV light (Fig. S8). By introducing ethanol as a decryption reagent, another five invisible circles became visible and a fluorescence array with nine circles was present. It is worth noting that the information security was improved because no information will be divulged even if someone sees the array.

The APP was then used to decrypt the fluorescence array through the RGB analysis. The array pattern after the addition of ethanol was imported into the phone (Figs. 3a–c). We set the identified range (Fig. 3d) and array parameters (Fig. 3e), and the corresponding graphics can be obtained by continuously changing the RGB threshold value (Fig. 3f) according to the encryption and anti-counterfeiting requirements. Detail reading process of the APP is shown in Figs. S9 and S10 (Supporting information). By changing the RGB threshold combinations, 36 types of graphics are obtained accordingly (Fig. 3g). Only the right RGB thresholds can get the genuine information of 'Genuine/The 90th Anniversary' (Fig. 3h). This strategy can be considered as a three-lock management system, and only an information receiver who knows the APP password, the true decryption reagent, and the RGB thresholds can open the safe door. This strategy has exhibited good comprehensive performance in various points including (1) large information storage capacity; (2) low equipment requirements; (3) easy to obtain information; (4) difficult to be reproduced; and (5) low cost without any rare or noble metal elements. Furthermore, the information-carrying capacity of the array can be increased with the array order which will bring a higher level of information-carrying capacity and security.

In summary, we successfully developed a new strategy by using HOF-PyTTA as an eco-friendly encryption ink and a smartphone-based APP for decryption. We prepared HOFs-polyethyleneimine ink, CsPbBr_3 NC-*n*-hexane ink, HOFs-ethanol- FeCl_3 ink, and HOFs-ethanol ink. Using a combination of the four inks and decryption reagents for printing encrypted information, it can realize the construction of an intelligent encryption system from single, concealed, double, and dynamic multi-mode. By introducing decryption reagents and an intelligent smartphone-based APP, the security level of encrypted anti-counterfeiting information is gradually improved. Compared to current methods for encryption and anti-counterfeiting, this method has the advantages of a high information-carrying capacity, high-security level, strong conceal-

ment, low cost, eco-friendly, and user-friendly. This work provides a new strategy for information encryption and anti-counterfeiting, and it also expands the application of HOFs.

Declaration of competing interest

There are no conflicts to declare.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ccl.2022.107864.

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