New Approach for Securing and Dating Valuable Printed Documents

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This work deals with using a novel approach for securing and dating printed documents, which will detect any forging crime present. In this respect, the coded dots matrices (machine identification code (MIC)) for the used printers are extracted via a binary system of base 2 (0, 1). The UV ink used in the printing process is prepared from novel fluorescence compounds together with polyvinyl alcohol. Different Xerox models of color laser printers are used for printing the document designs. The data obtained reveal that the investigated approach is succeeded in specifying the date of the printing process together with translating the embedded data of the printer to visible information, which can be tracked under a UV lamp. This innovative approach will assist workers in examining the questioned document by specifying the authorized date and position of printed documents from the MIC.

1. Introduction

In recent years, attention has been focused on developing and enhancing the quality and safety performance of valuable paper documents (checks, receipts, etc.). Many investigators studied the role of paper sheet compositions (type cellulosic fibers and sizing agent), metal complexes, fire retardant additives, coating by biopolymers, as well as surrounding environment on the quality and durability of paper.[1–8] While, for forging purposes, safety paper must be durable and include safety marker resistance to forgery and counterfeiting.[9–12]

Fluorescence active compounds are important materials succeeded to gain the paper document safety property. In this subject, we synthesized 2-alkoxy-3-pyridinecarbonitrile derivatives as well as heterocyclic compounds gathering the whole functional moieties responsible for fluorescence properties. In the synthesis we used variety of pyridine derivatives possessing both amino and alkoxy group oriented o- and o′-positions of the pyridine nucleus and neighboring to nitrile functions. The behavior of these compounds in nanoparticles form as security marker for production of unfalsifiable documents by erasure technique (chemical and mechanical) was also studied.[9,10,12]

On the other hand, the determination of the document date is a very necessary query in the field of the questioned document examination. It is also one of the most challenging and dialectical issues. Numerous approaches have been developed to address this issue. The first approach is “time tags”, which relates the concomitant properties of the ink and the paper via the introduction date of paper substrate, or market ink. The second approach is used to investigate the aging of documents, but unfortunately it is not influenced only by the passage time but also by the storage conditions and the document components. Finally, the third approach is focused on the relative age of the documents and aims at reconstructing their chronology.[13] In general, the application of these approaches is complex and accompanied with many drawbacks. In digital forensic labs, there is a serious dilemma that is concerned with determining the date of the documents. In the recent decade via developing the technology of color laser printing, we could do a little bit to achieve efficient results in determining the date of the questioned documents, using the special types of color laser printing.

The work of the active technique aims for tracking the extrinsic features embedded in the colored machines, on the contrary with the passive technique that focused on using the imperfection raised from optical, electrical, or mechanical defects in the machines.[14] The form of active technique appears as yellow dots, which are called machine identification codes (MIC) and counterfeit protection system (CPS) codes.[15–17] The tracking dots sizes are very small and cannot be seen via the naked eye.[18–20] So, the tracking of these yellow dots will guide to information about the color laser machines such as serial number, model, as well as, in special cases, the time and date of the printing process. From this point of view and for enhancing the application of fluorescence heterocyclic compounds, in this present work we evaluate the role of fluorescence active fluorinated pyrazolines as active compounds for extracting the MIC and securing together with dating the valuable printed documents.

Recently, the authors succeeded in synthesizing a variety of fluorescence-active fluorinated pyrazolines (21 compounds) in

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2. Results and Discussion

2.1. UV–Vis Absorption and Fluorescence Spectra

The UV–vis spectra of the synthesized pyrazolines 7–10 were estimated in chloroform with constant concentration (4 mg L\(^{-1}\)). The maximum absorption wavelength (\(\lambda_{\text{max}}\)) and molar extinction coefficient (\(\epsilon_{\text{max}}\)) are recorded in Table 1. It is clear that all investigated pyrazolines have two prominent peaks around 238 and 358 nm, which are related to the \(\pi-\pi^*\) and \(n-\pi^*\) transitions, respectively. The effect of introducing different electron-donating (EDG) and withdrawing groups (EWG) in R, R\('\), and R\('\) have a remarkable effect on the differences in both the position and intensity of absorption peaks, whereas, the presence of the 2-naphthyl group in compound 9 provided an additional absorption peak together with a higher absorption peak relative to the other synthesized analogues.

With regard to the fluorescence spectra of synthesized pyrazolines, this test is also undertaken in chloroform with constant concentration (1 \(\times\) 10\(^{-3}\) mol L\(^{-1}\)) (Table 1). Table 1 shows that the synthesized pyrazolines are excited at 360–370 nm (corresponding to the high wavelength absorption band), affording fluorescence emission in the blue to green regions (emission peak wavelengths 438–471 nm). It has also been noticed that the quantum yield (\(\Phi_{\text{sample}}\)) value is greatly affected by the substitution-type synthesized pyrazolines. The fluorescence quantum yields were measured relative to quinine sulfate using the following equation:

\[
\Phi_{\text{sample}} = \frac{F_{\text{sample}} A_{\text{sample}} \eta_{\text{sample}}}{F_{\text{ref}} A_{\text{ref}} \eta_{\text{ref}}} 
\]

(1)

On applying these fluorescence compounds to treat the Bible paper sheets, Table 2 shows that the treated paper sheets are excited at the range of 360–370 nm that corresponding to the absorption band in the solutions. It is noticed that the presence of the 4-chlorophenyl group at pyrazoline moiety for compounds 7 and 9 provides higher intensity; however the lower intensity is illustrated in case of treated paper with compounds including 4-methylphenyl, as the case of compounds 8 and 10.

2.2. Fluorescence Compounds as Secure and Dating Markers

To evaluate the role of the investigated approach for translating the machine identification codes to date the printed valuable documents, four fluorescence compounds (7, 8, 9, and 10) with different fluorescence quantum yield \(\Phi_s\) (0.55–0.86) were used to prepare UV inks. We designed two forms of check and receipt by using Microsoft Office 2016. Then we printed the designed forms on the paper sheets using different color laser printers of Xerox brand. The safety performance of the valuable documents is achieved by the following stages.

2.2.1. Extracting the Authorized Data from Printer

The investigated approach is applied for extracting the authorized data printed from five color laser printers (Xerox Phaser 6500 DN, Xerox WorkCentre 7675, Xerox WorkCentre 7556, Xerox DocuColor 250, and Xerox WorkCenter 7132). This

Table 1. Absorption, excitation, and emission spectral properties of active fluorescence pyrazoline compounds (7–10) in chloroform.

| Fluorescence measurements of active pyrazolines | Absorption
| \(\lambda_{\text{max}}\) [nm] | \(\epsilon_{\text{max}}\) | Excitation \(\lambda_{\text{max}}\) [nm] | Emission \(\lambda_{\text{max}}\) [nm] | \(\Phi_s\) |
|---|---|---|---|---|---|
| 7 | 241 | 117 001.805 | 267 | 455.8 | 0.819 |
| | 367 | 67 096.2375 | 369.3 | | |
| 8 | 242 | 45 313.75 | 265 | 443.7 | 0.858 |
| | 358 | 37 171.125 | 363.2 | | |
| 9 | 243 | 189 520.7475 | 294 | 453.7 | 0.553 |
| | 277 | 116 558.7675 | | | |
| 10 | 242 | 104 819.485 | 300 | 471.6 | 0.844 |

Table 2. Fluorescence spectra of treated paper sheets.

| Sample no. | Excitation maxima \(\lambda_{\text{max}}\) [nm] | Emission maxima \(\lambda_{\text{max}}\) [nm] | Fluorescence intensity |
|---|---|---|---|
| Untreated Paper | – | – | – |
| Treated with Cpd. 7 | 279.5, 399.9 | 467.7 | 3077.900 |
| Treated with Cpd. 8 | 279.7, 380 | 453.2 | 1688.620 |
| Treated with Cpd. 9 | 281371 | 458.3 | 4755.480 |
| Treated with Cpd. 10 | 280, 376 | 467.6 | 1360.270 |
approach includes scanning of the printed paper sheets at 1200 dots per inch (DPI). Adobe Photoshop CC 2015 was used as an image processing technique for the extraction step. Finally, we extracted all the machine identification codes that are printed on paper sheets. Figure 1a–d illustrates the distributions of MIC for each type of printer used. It is clear that the authorized data printed on papers are presented in a form of binary system dots that are machine known. Based on this the authorized data are calculated and converted from binary system state to decimal numbers.

From Figure 1a–c, it is observed that all the coded dots matrices (MIC) for the used color lasers consist of a regular grid of dots spread in fifteen columns and eight rows in a defined pattern, and then the area that exhibited the date of the printing is specified. There are three columns numbered 6, 7, and 8 that express the day, month, and year of the printing process, respectively. The date of the printing could simply be calculated from the binary system for base 2 (0, 1), and the calculation direction from down to up. The extraction and the calculation of the date of the printing process are as follows:

![Figure 1](https://example.com/image1.png)

**Figure 1.** a) Exhibiting the machine identification code (MIC) of different Xerox laser printers, with the date of the printing process. b) Exhibiting the machine identification code (MIC) of different Xerox laser printers, with the date of the printing process. c) Exhibiting the simulated machine identification code related of Xerox WorkCenter 7132.
* For the unit of the year as present in Figure 1a–c, in row number one and column number eight, one point is found that is calculated as $2^0$ and equals one. At the same column but at row number five, it contains another dot that calculated as $2^4$, which is equivalent to sixteen. The specified year 2017 is a result of summation.

* From Figure 1b, which is corresponds to the Xerox DocuColor 250 printer, at column seven and row number four, one point only is observed, which is calculated as $2^3$ and is equivalent eight. This is the month of printing.

* For Xerox WorkCenter 7132 (Figure 1c), from column number six, it contains two dots at rows number three and four that calculated as $2^2$ and $2^3$. The summation represents the day of the printing.

2.2.2. Illustrating the Extracted Date on Printed Paper Documents

The extracted and calculated dates are clear on the valuable document by using the prepared UV via print dater, numerator, and stamp print, using Sirdas print dater S810, numerator, and stamp print design, respectively. The used UV inks from four selected novel compounds (7, 8, 9, and 10) are colorless. The final images of the designed checks and receipt, under UV light at 365 nm are given in Figures 2a–d and 3.

With regard to designed check model and for improving the safety performance of paper documents, we have created the printed number of the check and micro text in two positions adjacent to two sentences “SIGNATORY NAME” and “AUTHORIZED SIGNATURE.” By magnifying at 20× it is

![Figure 2](a) Designed check printed with fluorescence compound 7-based UV ink (i) and under UV light at 365 nm (ii). b) Designed check printed with fluorescence compound 8-based UV ink (i), and under UV light at 365 nm (ii). c) Designed check printed with fluorescence compound 9-based UV ink (i), and under UV light at 365 nm (ii). d) Designed check printed with fluorescence compound 10-based UV ink (i) and under the UV light at 365 nm (ii).
possible to read the micro text sentence “THE INNOVATIVE BANK,” as given in Figure 4. Moreover, a new feature added at the upper right corner of the check and down left of receipt is quick respond barcode (QR). This added barcode is a static one, and it is just scanned with any barcode reader to benefit the worker in a bank or in the field of the questioned document.

Figure 3. a) Live image of the designed receipt printed with the four UV-ink-containing compounds 7, 8, 9, and 10, as indicated in yellow circles. b) UV images of the four receipt printed from UV inks made from fluorescence compounds 7–10.
examination, through the text messages appeared for both check and receipt as clear in Figure 5.  
With regard to check design (Figure 2a–d), the number of the check is printed adjacent to the text “Check No.” It is printed with two hidden numbers, using colorless synthesized UV inks, while, the date of the printing process or the creation date of the document is printed in three different positions in both check and receipt with the invisible UV inks. The Eiffel Tower of Paris is also printed as a latent image. Finally, we printed six stars to complete the design for both checks and receipts in different positions with the invisible UV inks to promote the document security and difficulty to forgery. These printed stars indicate

* Presence of secured star  
* Presence of micro print  
* Presence of fluorescent number of novel check  
* Presence of fluorescent date of novel check  
* Presence of static quick barcode

Because these security features have not been designed into any check before we believe this work is new in providing a safety measure, and will be provided to help with advanced levels of security, which will help workers in the field of the questioned document examination for detecting the forging crime through specifying the authorized date and position of printed documents from MIC.

3. Conclusion

In this study, we investigated a new methodology to date the valuable documents (checks and receipt). The approach used was focused on extracting the coded dots matrices (MIC) from color laser printers. For dating the print process, in a binary system for base 2 (0, 1) was used, while novel invisible UV inks based on a pyrazoline derivative were used for printing the date and security information. This approach was succeeded in presenting a new application of fluorescence-active compounds for dating and securing valuable documents with an advanced level of security.

4. Experimental Section

Materials—Paper Sample

Durable paper sheets known as Bible paper (45 g m⁻²) were used as substrate for printing the valuable documents. This type was made from 25% cotton and linen in combination with chemical wood pulp.

Materials—Polyvinyl Alcohol

PVA (Mowiol grade 28–99) is a product of Hoechst Co. (Germany), with the following specifications: degree of saponification: 99.4%, viscosity of 4% aqueous solution: 28 cP, ester no.: 8 mg KOM per g, residual acetyl: 0.5, and ash: 0.5%.

Materials—Fluorescence Active Compounds

Four pyrazoline derivatives were synthesized[21] and applied in UV ink to print the paper substrate. The methods of synthesizing these fluorescence compounds were summarized in the following scheme. These fluorescence compounds were selected from 21 compounds previously synthesized and have different fluorescence quantum yield (Φs). The choice of these fluorescence compounds, numbered 7–10, was based on their quantum yield values (Φs), fluorescence intensity of treated paper sheets and it mostly had positive effect on quality number of paper sheets.[22] The general method for synthesizing 4,5-dihydro-1H-pyrazoles (general procedure) is as follows

1,3,5-Triaryl-4,5-dihydro-1H-pyrazoles compounds 7–10, were synthesized through a cyclocondensation reaction of equimolar amounts of 1,3-diaryl-2-propen-1-ones 1–3 with aryl hydrazines 4–6 in refluxing ethanol. The solid separated upon storing the reaction mixture at room temperature overnight and was collected and crystallized from a suitable solvent, affording the corresponding pyrazolines 7–10. The obtained yields are in the range of 69% to 89% and are given in Scheme 1.

Melting points were recorded on a Stuart SMP3 melting point apparatus. IR spectra (KBr) were recorded on a Shimadzu FT-IR 8400S spectrophotometer. 1H-NMR spectra were recorded on a Varian MERCURY 300 (300 MHz) and Bruker Ascend 400/R (400 MHz) spectrometers. 13C-NMR spectra were recorded on a Bruker Ascend 400/R (100 MHz) spectrometer. Compounds 7–10 were prepared according to the reported procedures. UV spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Emission spectra were determined on LUMINA fluorescence spectrometer.

* 3-(4-Chlorophenyl)-5-(4-fluorophenyl)-1-phenyl-4,5-dihydro-1H-pyrazole (7)

This compound was obtained from the reaction of 1 and 4 over 6 h. The almost colorless microcrystals were obtained from n-butanol, mp 156–158 °C, yield 89%. IR ν (cm⁻¹): 1589, 1558, 1504, and 1493. 1H-NMR δ (ppm): (300 MHz) 3.08 (dd, J = 7.5, 17.1 Hz, 1H, upfield H of pyrazolinyl H₂C₄), 3.81 (dd, J = 12.5, 17.0 Hz, 1H, downfield H 8400S spectrophotometer. 1H-NMR spectra were recorded on a Varian apparatus. IR spectra (KBr) were recorded on a Shimadzu FT-IR spectrophotometer. Emission spectra were determined on LUMINA fluorescence spectrometer.

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Figure 4. Indication of the micro test created in the designed check model and magnified inside red two ovals.

Figure 5. Exhibiting two static QR and their included text after scan: A) for check and B) for honest rest.
of pyrazolinyl H$_2$C-4), 5.28 (dd, $J = 7.2, 12.3$ Hz, 1H, pyrazolinyl HC-5), 6.78–6.85 (m, 1H, arom. H), 7.01–7.43 (m, 10H, arom. H). 13C-NMR δ (ppm): (100 MHz) 34.3 (pyrazolinyl H$_2$C-4), 64.0 (pyrazolinyl HC-5), 113.5, 116.0, 116.2, 119.5, 125.3, 126.9, 127.1, 127.5, 128.8, 129.8, 129.9, 129.1, 131.2, 134.4, 138.0, 138.1, 144.5, 145.6, 161.0, and 163.4 (arom. C). Elemental analysis: C$_{21}$H$_{16}$ClFN$_2$ required C, 71.90; H, 4.60; N, 7.99, found C, 72.09; H, 4.71; N, 8.07.

4. R$''$ = Ph
5. R$''$ = 4-ClC$_6$H$_4$
6. R$''$ = 4-H$_2$CC$_6$H$_4$

Scheme 1. Synthetic route of pyrazoline fluorescence active compounds (7–10).

Table 3. Exhibiting the printers’ models with the authorized date printed.

| No. | Printer model       | Authorized coded date | UV printed date |
|-----|---------------------|-----------------------|-----------------|
| 1   | Xerox Phaser 6500   | 15 JAN 2017           | 15 JAN 2017     |
| 2   | Xerox WorkCentre 7665 | 05 JUN 2017         | 05 JUN 2017     |
| 3   | Xerox WorkCentre 7675 | 07 JUN 2017         | 07 JUN 2017     |
| 4   | Xerox WorkCentre 7132 | 12 JUN 2017         | 12 JUN 2017     |
| 5   | Xerox DocuColor 250 | 22 AUG 2017          | 22 AUG 2017     |

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Conflict of Interest
The authors declare no conflict of interest.
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