Substituted naphthoquinones as novel amino acid sensitive reagents for the detection of latent fingermarks on paper surfaces

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Abstract

In this paper, we present our preliminary studies into naphthoquinones as novel reagents for the detection of latent fingermarks on paper. Latent fingermarks deposited on paper substrates were treated with solutions of selected naphthoquinones in ethyl acetate/HFE-7100, with subsequent heating. The selected compounds were 1,4-dihydroxy-2-naphthoic acid, 1,2-naphthoquinone-4-sulfonate, 2-methoxy-1,4-naphthoquinone and 2-methyl-1,4-naphthoquinone. All of the tested compounds yielded purple-brown visible fingermarks, which also exhibited photoluminescence when illuminated with a high intensity filtered light source at 555 nm and viewed through red goggles. Indirect heat using an oven at 150 °C for 1 hour was found to be superior to direct heat with an iron, which while providing faster development lead to increased levels of background colouration. Luminescence spectrophotometry revealed differences in photoluminescence characteristics for fingermarks developed with the different naphthoquinones, with excitation over the range 530-590 nm. Luminescence spectrophotometry of developed lysine, glycine and serine spots on paper was used to confirm that the naphthoquinones were reacting with amino acids in the latent fingermark.

Keywords: naphthoquinones, latent fingermarks, fingerprints, amino acids, paper surfaces, forensic science

Introduction

The ability to establish links between persons, objects and locales is extremely important in the course of criminal investigations. The impressions left by the palmar surfaces of the hands, commonly known as fingermarks, are important in this context as they not only demonstrate contact but are also considered sufficiently unique to allow identification of a person [1-3]. The most commonly encountered are latent fingermarks, which are formed by the transfer of natural skin secretions and contaminants from the skin to the substrate. Successful recovery and subsequent analysis of latent fingermarks on a particular substrate relies upon their detection, and a range of physical and chemical methods are available to enable this [1-3]. Fingermark detection chemistry shares with other areas of analytical chemistry the constant search for improved selectivity and sensitivity [4-13].

The substrate is highly influential in determining the most suitable methods for visualisation of latent fingermarks. Paper items such as documents, wrappings and containers are common forms of physical evidence, and establishing who has handled them can be extremely important [1-3]. For paper items, the visualisation of latent fingermarks has predominantly been based on the use of amino acid sensitive reagents [14]. Amino acids are present in the aqueous (eccrine) component of a fingermark deposit and, when transferred onto a paper surface, will adhere with minimal migration as long as the surface is not wet or exposed to high humidity. These amino acid impressions can be very long-lived, and can remain on the substrate for an extended period of time [3].

Ninhydrin (2,2-dihydroxy-1,3-indanedione) was the first amino acid sensitive reagent for developing fingermarks on porous surfaces and is still the most widely used. Ninhydrin reacts with amino acids to form a dark purple coloured compound known as Ruhemann's purple (Scheme 1) [2].

Scheme 1: Reaction mechanism of ninhydrin with amino acids to form Ruhemann's purple [2]**.**

Developed impressions may be further enhanced by treatment with zinc and cadmium salts to produce complexes that exhibit photoluminescence when cooled with liquid nitrogen and excited with a high intensity filtered light source (often referred to as a 'forensic light source') [15].

Since the early 1980s, a range of ninhydrin analogues have been synthesized and tested for their suitability as reagents for the detection of latent fingermarks. Only two of the studied compounds have found widespread operational use; 1,8-diazafluoren-9-one and, more recently, 1,2-indanedione [1, 15] (Figure 1). These reagents produce developed fingermarks that are photoluminescent at room temperature without further treatment.

Figure 1: Structures of 1,2-indanedione, 1,8-diazafluoren-9-one and genipin.

The visualisation of latent fingermarks on porous surfaces using these reagents can be considered to be the trace detection of amino acids where their spatial distribution needs to be retained for subsequent fingerprint analysis [14]. Prior to 2004, the main focus of

research in this area was the further development of compounds related to ninhydrin. An alternative research path has been suggested by Almog and co-workers, with the use of genipin (Figure 1) as a latent fingermark detection reagent [16, 17].

Genipin, which is a natural product, is obtained from a number of plants including *Gardenia jasminoides* and *Genipa americana L.* Extracts from these plants have been used as traditional medicines, food and fabric colorants, and as skin dyes [16, 17]. When evaluated for use as a stain for amino acids on TLC plates, the genipin products were found to have higher molar absorptivities than Ruhemann's purple and were also more stable [16, 17]. These observations lead Almog and co-workers to investigate genipin as a fingermark reagent, and it was found that it could develop prints that were both coloured and luminescent [16, 17]. Genipin reacts with latent fingermarks on paper to produce blue impressions, with photoluminescence emission occurring at longer wavelengths than for existing treatments. This provides a potential operational advantage by improving the signal-to-noise ratio by shifting the luminescence emission away from any background interference from the paper substrate itself [16, 17]. In addition, considering its long past history of human usage, and low cytotoxicity, occupational hazards associated with using genipin are significantly reduced compared to other fingermark development reagents [16, 17].

Henna, a natural product sourced from the leaves of *Lawsonia inermis* [18], has been used as a skin and hair dye for millennia, with reports of its use dating back to 1,400 BC [18]. The compound thought to be responsible for the staining properties of henna is lawsone (2-hydroxy-1,4-naphthoquinone) (Figure 2). Prompted by Almog's studies into genipin, we

recently investigated lawsone as a potential fingermark reagent for porous surfaces [4]. Latent fingermarks on filter paper surfaces were dipped in lawsone solutions and then heated for 1 hr at 140 – 170 ºC. The fingermarks developed as purple/brown prints that were luminescent without further treatment [4]. Further luminescence studies confirmed that the amino acids present in the fingermark deposit were responsible for the developed marks.

Figure 2: Structures of lawsone and selected naphthoquinones.

In addition to lawsone, other naphthoquinones have been reported to give coloured products on reaction with amino acids. 1,2-Naphthoquinone has been reported as yielding brown/purple pigments with cysteine and proteins. Spectroscopic evidence indicates that the reaction of 1,2-naphthoquinone is with the amino group of the amino acids [19]. 1,2-Naphthoquinone-4-sulfonate has been applied to the determination of amino acids through the formation of highly coloured compounds [20-24]. Substituted naphthoquinones therefore represent a class of compounds of significant interest as potential fingermark detection reagents.

On this basis, we have commenced an investigation into selected substituted naphthoquinones as potential amino acid sensitive reagents for the detection of latent fingermarks on porous surfaces (Figure 2), the preliminary results of which are presented here. Selection was based upon availability, safety, cost and structural similarity to lawsone, with the intention that any variation in performance could provide an insight into the mechanism associated with lawsone and amino acids.

Materials and Methods

Reagents

The following naphthoquinones and related compounds were obtained from Sigma Aldrich (Australia) and were used as supplied without any further purification: 1,4-dihydroxy-2-naphthoic acid; 1,2-naphthoquinone-4-sulfonic acid, sodium salt (1,2-naphthoquinone-4-sulfonate); 2-methoxy-1,4-naphthoquinone; 2-methyl-1,4-naphthoquinone; and 2-hydroxy-1,4-naphthoquinone (lawsone).

Solutions of amino acids in water – lysine (Sigma, Australia), glycine (Chem-Supply, Australia), serine (Sigma, Australia) and proline (Sigma, Australia) – with a concentration of 0.1M unless otherwise specified, were dispensed (5 μL) onto filter paper and allowed to air dry before subsequent naphthoquinone treatment.

Zinc chloride solution was prepared by dissolving 0.4 g anhydrous zinc chloride (analytical grade, BDH, Australia) in 10 mL of absolute ethanol (analytical grade, CSR Chemicals, Australia). Dichloromethane (Mallingkrodt Chemicals, Australia), ethyl acetate (Univar Analytical, Australia), glacial acetic acid (CSR Chemicals, Australia), HFE-7100™ (3M Novec, Australia) and petroleum spirit 60-80 °C (Univar, Australia) were all analytical grade unless stated otherwise and were used as supplied, without further purification.

Preparation of samples

Latent fingermarks were collected on filter paper (Whatman No 1, England) or cellulose thin-layer chromatography plates (Merck, Germany) from a number of different donors. These substrates were selected for their inherently low photoluminescent properties. Donors were requested not to wash their hands immediately before collecting impressions and the fingers were not "charged" with additional secretions (for example, by rubbing against the forehead). However, the donors were asked to rub their hands together just prior to touching the paper surface (to ensure a uniform coating of natural secretions across the fingertip surfaces). Samples were developed shortly after deposition (within two days).

Naphthoquinone working solution

Preliminary investigations into a naphthoquinone working solution formulation were carried out using lawsone as a representative compound. Four different formulations were prepared according to Table 1. Formulations A to C are based upon formulations used for existing amino acid reagents [15].

Table 1: Preparation of naphthoquinone working solutions.

Treatment of latent fingermarks

Fresh fingermark deposits on filter paper and cellulose TLC plates were dipped in the naphthoquinone working solution and allowed to air dry. Subsequently, the samples were

heated for colour and luminescence development. The heating procedure for fingermark visualisation was via two methods: (i) direct heat from a commercial steam iron (Mistral, Australia); and (ii) heating in an oven (All-lab Scientific, Australia) at 150 °C for 1 hour. When developing using the iron, a high heat setting of around 170 °C (without steam) was applied for 30-60 s, with a paper towel placed between the hot plate of the iron and the sample. Treated fingermarks were allowed to cool before observation or photographic recording.

Photography

Samples were photographed in both the absorbance (white-light) mode and the photoluminescence mode using a Nikon D300 digital camera mounted on a Firenze Mini Repro camera stand. The camera settings for all photographs were as shown in Table 2, unless otherwise stated. Illumination in the absorbance mode was achieved using incandescent light bulbs with no camera filter attachments. Illumination in the luminescence mode was achieved using a Rofin Polilight PL500 (Rofin Australia), with an excitation wavelength of 530, 555 or 590 nm as required. Images were captured to a desktop computer using Nikon Camera Control Pro Version 2.0.0 and adjusted for brightness and contrast using Adobe Photoshop CS4 Version 9.0.

Table 2. Photographic conditions for absorbance and luminescence mode photographs, unless otherwise stated.

Developed fingermarks were also recorded in the photoluminescence mode using a Poliview image capture and enhancement system (Rofin, Australia), with excitation at 590 nm and observation through a 650 nm interference filter (with a 1 s exposure time unless otherwise stated).

Luminescence spectra

Luminescence spectra were obtained using a Cary Eclipse Fluorescence Spectrophotometer with a fibre optic probe attachment (Varian, Mulgrave, Australia). Luminescence spectra for the treated fingermarks were collected using excitation at 530 and 590 nm, with data being recorded as an average of 10 scans and with excitation and emission slit widths of 5 nm.

Results and Discussion

Based on our initial studies with lawsone [4], a number of structurally related compounds were selected for investigation as to their ability to develop latent fingermarks on paper surfaces (Figure 2). This approach is very similar to that taken in relation to ninhydrin and its analogues, with the advantage that naphthoquinones are commercially available, thus removing the necessity for synthesis which was the case with the ninhydrin analogues [2, 25]. There is a wide range of naphthoquinones available and the compounds to be tested in this study were selected on the basis of their availability and the low hazard they represent to health.

Method Development

The development of latent fingermarks on paper requires treatment with a solution of the reagent, either by immersion or by spraying [1-3]. This is often followed by heating either directly using a laundry press or clothes iron, or indirectly through the use of an oven [1-3]. A wide range of formulations for amino acid sensitive reagents have been proposed, with the carrier solvent being a key component. The ideal solvent should evaporate rapidly, be non-toxic, non-flammable and non-polar so as to avoid any running of ink on treated documents [2, 3]. The last requirement is a significant issue with the selected naphthoquinones as they are not readily soluble in non-polar solvents such as HFE-7100 (1-methoxynonafluorobutane). This is a non-flammable, non-toxic CFC replacement that is widely used as a carrier solvent for fingermark reagents [2, 3].

In our initial study into lawsone, we used ethyl acetate as a co-solvent to dissolve the lawsone prior to mixing with HFE-7100 (Table 2; formulation D). We did not use any additional components such as acetic acid and zinc salts, which have been shown to provide improved development with other reagents [26-28]. As a preliminary step in the current study, a number of lawsone formulations were investigated for their performance in developing latent fingermarks. The formulations selected, as outlined in Table 2, were based on existing formulations used with ninhydrin, DFO and 1,2-IND [15]. Formulations A to C were compared directly against formulation D by using the "split print" approach. This involves cutting each fingermark sample in half, and treating each half separately with the treatments to be compared [14].

It was found that formulations C and D consistently performed better than formulations A and B in terms of both colour and luminescence. In addition, formulations A and B were extremely unstable, with lawsone precipitating from solution almost immediately. It is important to note that decisions concerning the most appropriate formulation must not rely just upon the intensity of the colour/luminescence produced, but also the clarity of the enhanced fingermark. While formulations C and D were similar in terms of colour and luminescence, closer examination of the developed fingermarks showed a slight loss of fine ridge detail for formulation C (Figure 3). The reasons for this, at this stage, are unclear; however, the inclusion of ethanol could have resulted in the apparent diffusion of the resulting product. Based on simplicity and performance, subsequent working solutions of the naphthoquinones tested were prepared by dissolution of the reagent in ethyl acetate and subsequent dilution with HFE-7100 (ie. formulation D).

Figure 3: Effect of different naphthoquinone formulations using the "split print" approach: (a) Formulation C (left half) vs. Formulation D (right half) under white light; and (b) Formulation C (left half) vs. Formulation D (right half) captured under photoluminescence conditions. A larger version of figure 3 (b) is available as supplementary material.

In our previous study into lawsone, we investigated the use of an oven to heat the treated fingermarks. This lead to development times of up to an hour when heated at 150 °C. Attempts to use a laundry press led to inconsistent development due to the short heating time, with a safety switch preventing direct heat for longer than 10 s. To overcome this, a clothes iron was substituted as the direct heat option. This was found to successfully

develop fingermarks in a much shorter period of time compared to the oven (30 – 60 s). In addition, the developed marks exhibited a deeper colour. However, along with development of the print, there was an increase in background colouration of the paper substrate (Figure 3). This is disadvantageous for subsequent fingerprint analysis due to reduced contrast. Therefore, despite the longer development time required, the oven (150 °C for 1 hour) was used for all subsequent treatments.

Figure 4: Effect of heating process on development of latent fingermarks with lawsone: (i) and (iii) oven; (ii) and (iv) iron heated lawsone treated fingermarks. Images (i) and (ii) taken under white light, (iii) and (iv) taken under photoluminescence conditions.

Development of latent fingermarks by selected naphthoquinones

Four compounds with naphthoquinone structures were tested for their ability to visualise latent fingermarks on filter paper: 1,4-dihydroxy-2-naphthoic acid; 1,2-naphthoquinone-4-sulfonate; 2-methoxy-1,4-naphthoquinone; and 2-methyl-1,4-naphthoquinone (Figure 2). Each of the naphthoquinones was prepared at the concentration of 0.1% (w/v). A non-treated fingermark was also heated in order to ensure that any results were not due to the development of the print by heat alone [29]. All of the tested naphthoquinones gave visible, brown coloured, impressions that exhibited photoluminescence when illuminated at 555 nm using the high intensity filtered light source and viewed through red goggles, or when illuminated at 590 nm and viewed using the Poliview system (Figure 4). A latent fingermark on filter paper, which was heated but not treated with naphthoquinone, showed

no significant development under the heating conditions used in this experiment. Initial observations revealed some variation in intensity of colour and luminescence for the naphthoquinone treated fingermarks. Latent fingermarks developed with 1,4-dihydroxy-2-naphthoic acid consistently showed stronger colour but weaker luminescence intensity, while those developed with 2-naphthoquinone-4-sulfonate were less coloured but exhibited stronger photoluminescence.

Figure 5: Latent fingermarks developed with naphthoquinones (a) (i) lawsone and (ii) 1,4-dihydroxy-2-naphthoic acid under white light (iii) lawsone and 1,4-dihydroxy-2-naphthoic acid in the photoluminescence mode. Images were taken with a Nikon D300 SLR, 60 mm focal length, ISO 200, white light shutter speed 1/40 s, aperture f10, and photoluminescence mode, excitation with a Polilight PL 500 at 590 nm and viewed through a Wratten NA29 filter, shutter speed 15 s, aperture f10. (b) Photoluminescence from naphthoquinone treated latent fingermarks, acquired using a Poliview digital imaging system (Rofin, Australia) with excitation at 590 nm, viewed through a 650 nm interference filter with a 1 s exposure time: (i) lawsone (ii) 1,4-dihydroxy-2-naphthoic acid iii) 2-methoxy-1,4-naphthoquinone (iv) 2-methyl-1,4-naphthoquinone (v) 1,2-naphthoquinone-4-sulfonate.

Marked differences in photoluminescence characteristics for fingermarks developed with the different naphthoquinones were visually observed when examined under different wavelength bands from the Polilight over the range λ_{ex} 530-590 nm. To examine this in more detail, luminescence spectra from the developed fingermarks were obtained using a luminescence spectrophotometer fitted with a fibre optic probe. Excitation was carried out

at 530, 555 and 590 nm. These wavelengths were chosen as they correspond to wavelengths available on the Polilight high intensity filtered light source. Examination of the spectra revealed variations between lawsone and the related naphthoquinones selected (Figure 6a). The optimal response for the substituted naphthoquinones occurred at λ_{ex} 530 nm, in comparison to lawsone at λ_{ex} 590 nm. Additionally, different luminescence emission characteristics for some of the individual naphthoquinones became apparent once the spectra had been normalised for comparison. 1,4-Dihydroxy-2-naphthoic acid showed weaker luminescence emission characteristics, with slightly noisy spectra; however, it appears to have a slight shift in emission maximum towards the red. In comparison, 1,2-naphthoquinone-4-sulfonate, although producing similar spectra to 2-methoxy-,4-naphthoquinone and 2-methyl-1,4-naphthoquinone, showed greater luminescence emission, which corresponded to our visual observations (Figure 6b). Operationally, these variations in wavelength would not be a major issue as all of the developed prints were visible using the combination of excitation at 555 nm and observation through red goggles (corresponding to a red long-pass filter), although they may be some impact on sensitivity. Emission spectra for latent fingermarks developed with each individual naphthoquinone, with excitation at the optimum wavelength based on emission intensity, are presented in Figure 6.

Figure 6: Luminescence emission spectra for fingermarks developed with naphthoquinones. Spectra have been normalised and offset to illustrate similarities and differences in shape and maxima. (a) (i) Lawsone (λ_{ex} 590 nm) and (ii) 1,2-naphthoquinone-4-sulfonate (λ_{ex} 530 nm); b) Selected naphthoquinones (λ_{ex} 530 nm); (i) 1,2-naphthoquinone-4-sulfonate (ii) 2-methoxy-1,4-naphthoquinone (iii) 2-methyl-1,4-naphthoquinone (iv) 1,4-dihydroxy-2-naphoic acid.

In our previous lawsone study, we confirmed that it was reacting with amino acids in the latent fingermark by treating dried amino acid spots on paper [4]. A similar approach was taken with the other naphthoquinone compounds in this current study. Initially, lysine was selected for this investigation due to an enhanced response with lawsone in comparison to other amino acids (Figure 7a). For each compound, solutions of lysine in water (900 μg/mL) were dispensed (5 μL) onto filter paper and allowed to air dry before development. In a similar fashion to the developed latent fingermarks, the treated amino acid spots were visible as brown stains which were also photoluminescent. Luminescence spectra of the developed amino acid spots were measured at the optimum excitation wavelengths for each naphthoquinone as described above. The signal obtained was found to be quite weak, indicating that the level of sensitivity of these selected naphthoquinones was reduced in contrast to lawsone. Along with this, the potential role of the additional amino group present in lysine could influence the resulting product in a way that does not correlate with the characteristics observed with fingermarks. Therefore, this investigation was replicated with the use of glycine and serine. These amino acids were selected based on simplicity and their relatively high concentration in latent fingermark residues [30]. Amino acid concentrations were increased to 0.1 M (around 9000 μg/mL) to ensure enough signal

intensity. As seen in Figure 7b, different luminescence characteristics were observed between the two amino acids. This may be due to the presence of the side chain in the resulting luminescent species altering the observed luminescence characteristics. The spectra obtained from the serine product correlated closely with that obtained from treated fingermarks, in contrast to the product formed from the glycine reaction. Although difficult to ascertain due to the complex matrix of fingermark residue, it could be speculated that this similarity may be a result of higher levels of serine in fingermark deposits compared to glycine [30]. As was observed in our earlier paper, the luminescence spectra are very similar between the developed latent fingermarks and the amino acids, thus indicating that the reagents are targeting the amino acids in the latent fingermark deposit [4]. Attempts were made to collect excitation spectra, however due to the low emission intensities encountered this was only successful with lawsone (Figure 7 c).

Figure 7: Luminescence characteristics of naphthoquinone treated amino acids. Spectra have been normalised and offset to illustrate similarities and differences in shape and maxima. (a) Lawsone treated amino acid spots (λ_{ex} 590 nm) (i) lysine (ii) glycine (iii) serine (iv) fingermark (b) glycine and serine amino acid spots treated with naphthoquinones (λ_{ex} 530 nm), for both acids (i) 2-methoxy-1,4-naphthoquinone (ii) methyl-1,4-naphthoquinone (iii) 1,2-naphthoquinone-4-sulfonate. (c) excitation spectra for lawsone treated glycine spot (λ_{em} 645 nm) compared with emission spectra for same spot (λ_{ex} 590 nm)

This study has shown the potential of naphthoquinones as effective reagents for the detection of latent fingermarks on paper and other porous surfaces. Lawsone shows the

most promise as a potential fingermark visualisation reagent in comparison to the other naphthoquinones tested. However, this investigation may be favouring lawsone due to the replication of its established formulation and procedural conditions. Further research into optimised development conditions for the other members of this new class of amino acid targeting fingermark visualisation reagents is required. 1,4-dihydroxy-2-naphthoic acid and 1,2-naphthoquinone-4-sulfonate are the most likely candidates for further in-depth method development on an individual basis to evaluate their potential as fingermark reagents. In order to establish their significance and suitability for application in an operational context, comparison against current benchmark reagents is essential in order to determine what advantages naphthoquinones may have to complement current reagents. Furthermore, studies into factors such as reagent stability and shelf life, position in fingermark detection protocols (sequence), and effect of substrate are required. In particular, issues with performance and solubility of the naphthoquinones in the carrier solvent are of concern. It has been noted that lawsone and other naphthoquinones have a tendency, within a relatively short period of time, to precipitate from solution and it appears that the rate is influenced by environmental factors such as ambient temperature. In addition, the performance of lawsone and related naphthoquinones appears to degrade over time. Results have been extremely promising with solutions prepared with freshly purchased lawsone to a point where, even before heating the sample, an orange outline of the fingermark becomes visible. However, after the initial opening of the container and storage under normal laboratory conditions, subsequent performance diminishes over a period of 12 to 18 months. Investigations are currently underway into the cause of these effects and the best approach which to address them.

The variations observed in terms of colour and luminescence may indicate the formation of alternative products resulting from the reaction with amino acids. This may provide some insight into reaction mechanisms and the effects of the differences in structure associated with each naphthoquinone. Consequently, this information may play an important role in predicting other naphthoquinones that may surpass the current performance of these naphthoquinones. If the electronic properties of a conjugated system are altered in a manner that allows for optimal visualisation characteristics, then we can achieve the best possible outcome with respect to the use of naphthoquinones as fingermark detection reagents.

We are currently undertaking studies using synchrotron-infrared microscopy to examine developed latent fingermarks and amino acid spots on paper and cellulose TLC plates. We are also conducting synthetic studies to provide an insight into the potential reaction pathways. It is important to note that characterisation of the reaction product(s) formed in solution may not necessarily represent what occurs in the constrictive in-situ environment in which these reactions proceed when fingermarks on paper are developed. However the continued studies as proposed here will provide greater insight into the fingermark/detection reagent chemistry, with the knowledge gained providing a platform for further development of these novel fingermark reagents.

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Scheme 1:

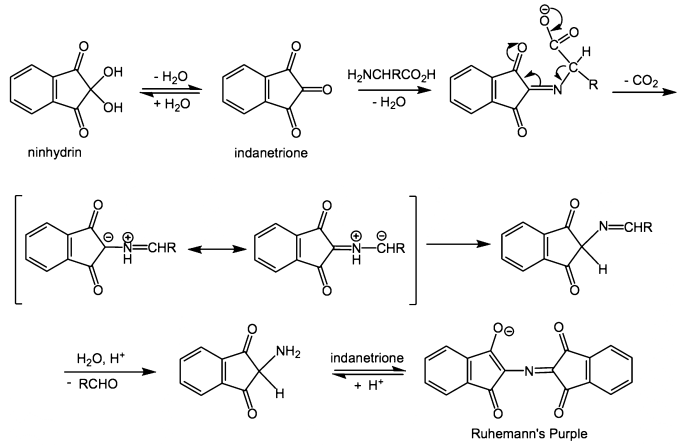

Figure 1:

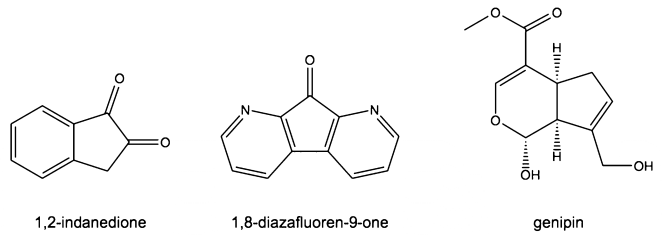

Figure 2:

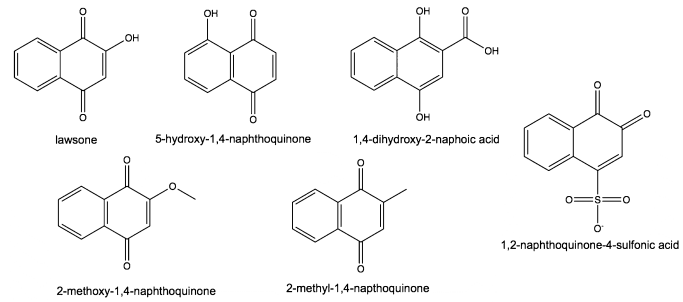

Figure 3:

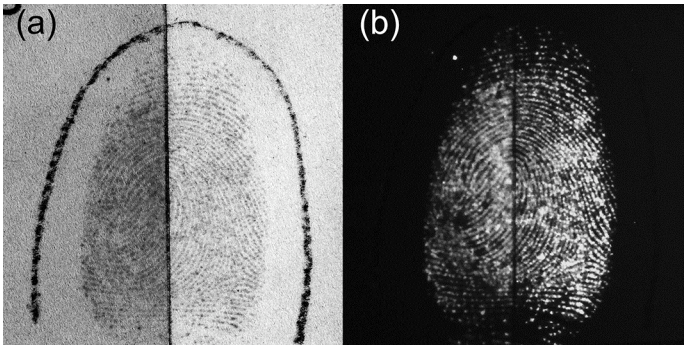

Figure 4:

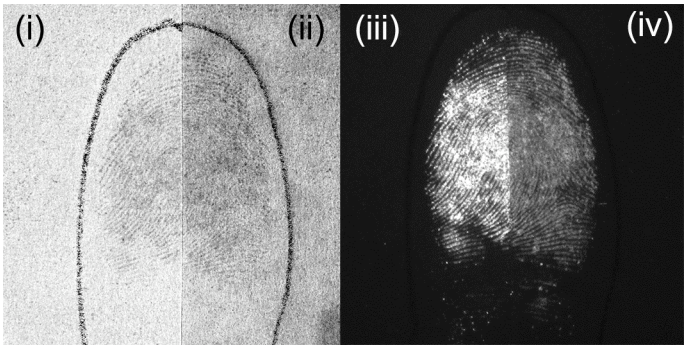

Figure 5:

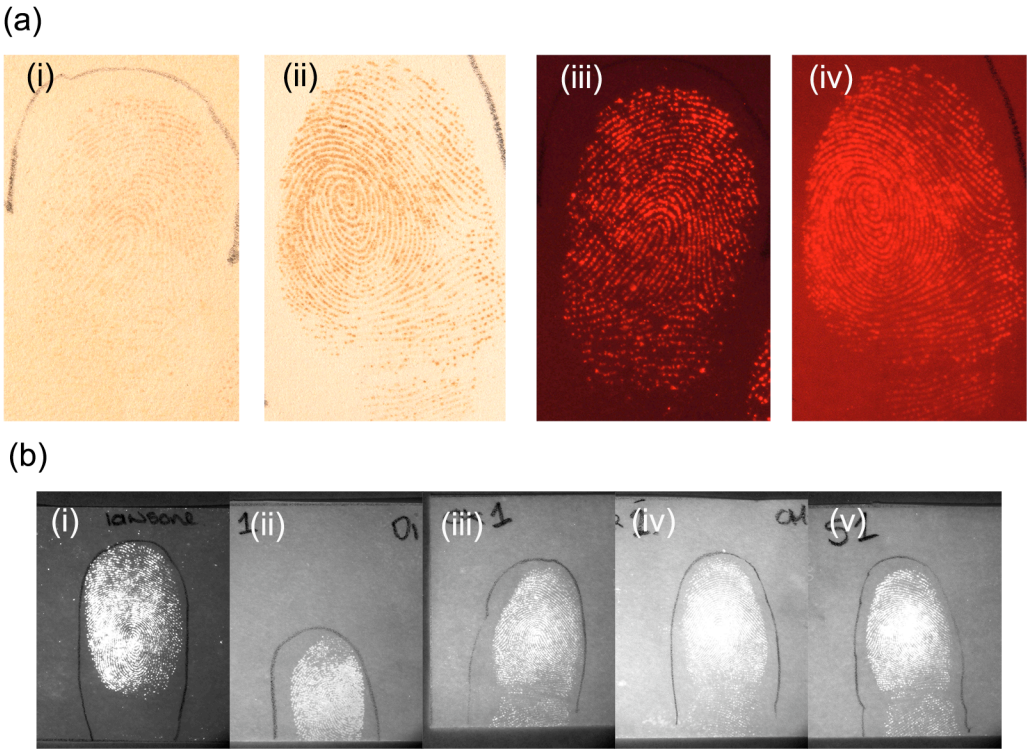

Figure 6a:

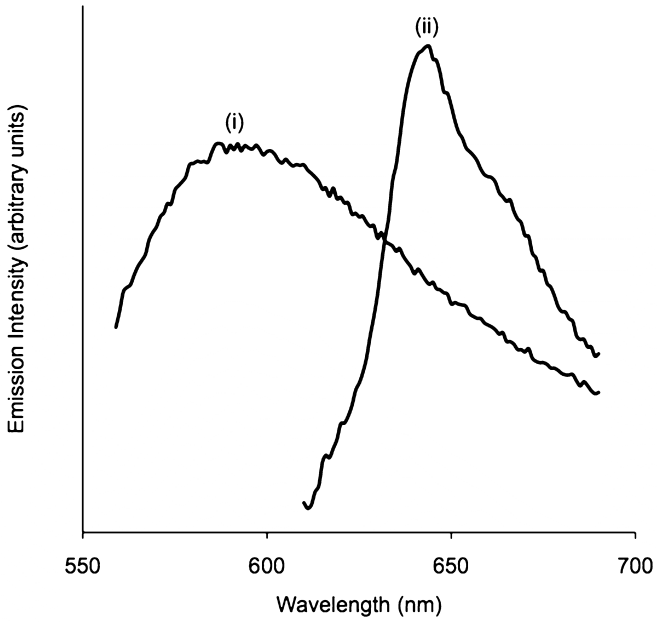

Figure 6b:

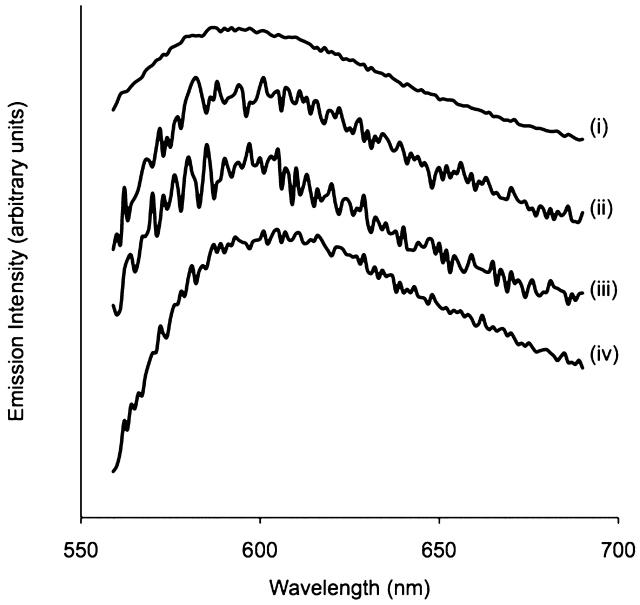

Figure 7a

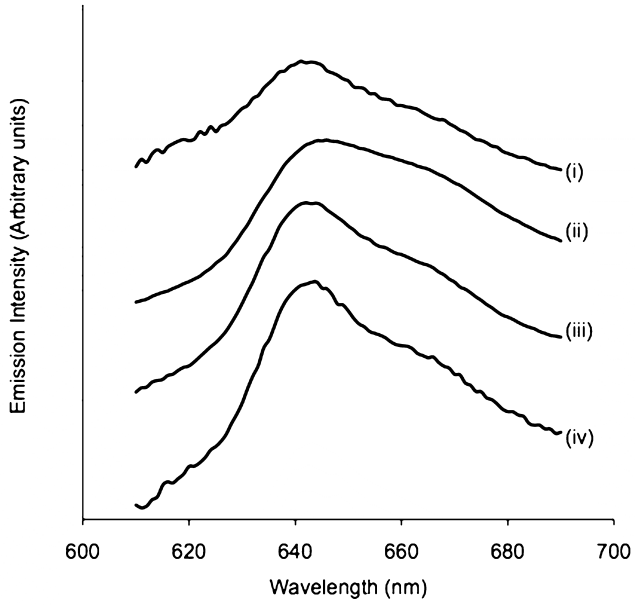

Figure 7b

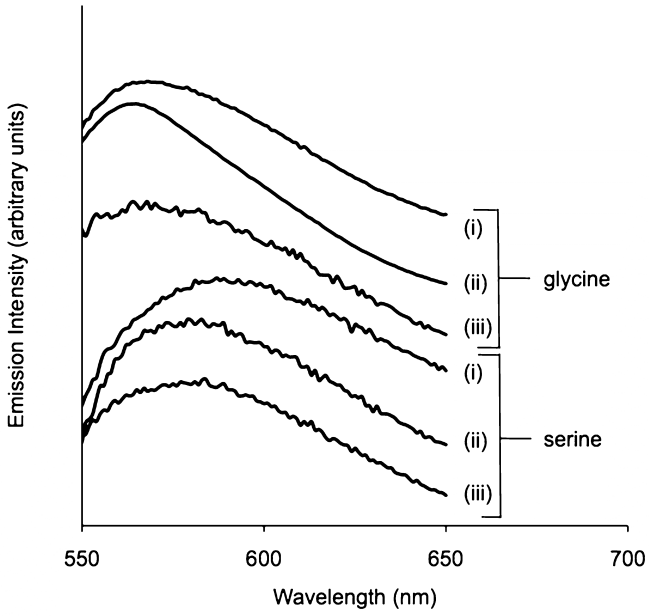

Figure 7c

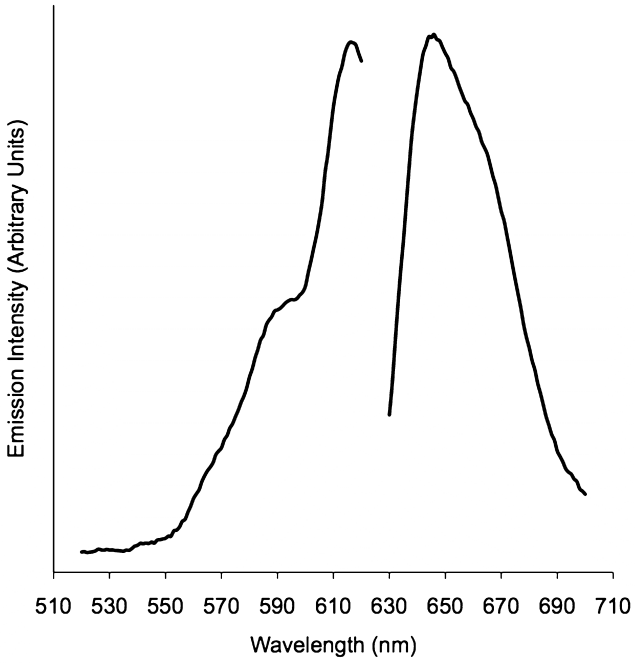
Emission Intensity (Arbitrary Units)
510 530 550 570 590 610 630 650 670 690 710
Wavelength (nm)

Table 1: Preparation of naphthoquinone working solutions

Formulation A	**Formulation B**	**Formulation C**	**Formulation D**
0.1 g naphthoquinone 3 mL dichloromethane 6.4 mL ethanol 0.6 mL acetic acid 90 mL HFE-7100	0.1 g naphthoquinone 3 mL dichloromethane 6 mL ethyl acetate 1 mL acetic acid 0.1 mL zinc chloride solution 90 mL HFE-7100	0.1 g naphthoquinone 8.5 mL ethanol 0.7 mL ethyl acetate 0.8 mL acetic acid 90 mL HFE-7100	0.1 g naphthoquinone 20 mL ethyl acetate 80 mL HFE-7100

Table 2. Photographic conditions for absorbance and luminescence mode photographs, unless otherwise stated.

	Absorbance mode	Luminescence mode
Focal Length (mm)	60	60
Exposure Mode	Manual	Manual
Shutter Speed (s)	1/30	15
Aperture	f/11	f/11
Sensitivity	ISO 200	ISO 200
Filter	none	Wratten NA29 filter*

* equivalent to long-pass barrier filter with 50% transmission at 620 nm.