Graphical Abstract

To create your abstract, type over the instructions in the template box below.
Fonts or abstract dimensions should not be changed or altered.

Novel Design and Approach to Latent Fingerprint Detection on Paper Using a 1,2-Indanedione-Based Bi-functional Reagent

Jisun Lee and Madeleine M. Joullié

Leave this area blank for abstract info.

Novel Design and Approach to Latent Fingerprint Detection on Paper Using a 1,2-Indanedione-Based Bi-functional Reagent

Jisun Lee and Madeleine M. Joullie *

Department of Chemistry, University of Pennsylvania, 231 S. 34th Street, Philadelphia, PA 19104, USA

ARTICLE INFO

Article history:

Received
Received in revised form
Accepted
Available online

Keywords:

Forensic science
Fingerprint detection
1,2-Indanedione
Multi-metal deposition

ABSTRACT

A novel 1,2-indanedione-based bi-functional reagent was designed for the development of latent fingerprints on paper substrates. The reagent was synthesized using a concise five-step protocol and applied using a modified multi-metal deposition (MMD) process. Positive images of latent fingerprints were developed showing preferential binding to the fingerprint ridges. Fingerprints that contain both amino acids as well as oily substances were successfully detected supporting the reagent's efficiency.

2014 Elsevier Ltd. All rights reserved.

1. Introduction

Fingerprint detection is a crucial area in forensic science. Detection of latent (hidden) fingerprints by chemical methods is amongst the most sensitive techniques available today, and may be applied on porous or non-porous surfaces and on a large variety of materials, such as paper, plastic, wood, etc.¹ Of considerable importance are chemical techniques used for latent fingerprint detection on paper and related cellulosic materials, since our society relies heavily on such materials for official documents, currency printing, and packaging. More specifically, these chemical methods are based on the detection of amino acids present in natural skin secretions. When a fingerprint is deposited on paper substrates, the amino acids are believed to bind to the cellulose of the paper preserving either a visible or latent (invisible) impression of the friction ridge patterns.¹ Latent fingerprints are the most common type of evidence found at crime scenes, and the most problematic, since they require methods to develop fingerprints that can be visualized and recorded. For latent fingerprint detection, eccrine and sebaceous glands are the most important glands that are responsible for skin secretions within the dermis.¹ Eccrine (sweat) glands are found on the palms of the hands, and various amino acids are present in secretions from these glands, where the exact composition depends upon the individual and a variety of other factors including general health, diet, gender, and age.² The palms also contain sebaceous secretions as a contaminant due to interactions with the face and hair. Upon interaction with cellulosic material,

these secretions are readily transferred to the surface of the paper substrate and may be stable over a prolonged period of time.¹

Over the years, a wide array of chemical reagents was identified for latent fingerprint detection on paper (Figure 1).³ Since the amino acid composition of a fingerprint could vary depending on the individual, non-specific amino acid sensitive reagents were developed. The first of its kind was ninhydrin,⁴ which upon stoichiometric reaction with an amino acid⁵ of a fingerprint residue produces a purple print known as Ruhemann's purple. 1,8-Diazafluoren-9-one (DFO)⁶ and 1,2-indanedione⁷ (Figure 1) followed a similar reaction pathway in which the latent fingerprint could be visualized as red or pink (also known as Joullie's pink⁸) prints on paper respectively.

Figure 1. Some chemical reagents for fingerprint detection.

However, despite the plethora of available chemical reagents, considerable portions of latent fingerprints still escape detection.^{1,2} The main limitation of the existing methods is their stoichiometric nature, which sets an upper limit to sensitivity. Since latent fingerprints often do not contain adequate quantities of amino acids (or other relevant components such as lipids), even the most sensitive chemical reagents do not produce a

*Corresponding author. Tel.: +1-215-898-3158; fax: +1-215-573-9711; e-mail: mjoullie@sas.upenn.edu (M. M. Joullie).

sufficiently meaningful image.² Furthermore, most amino acid sensitive reagents rely on luminescence⁹ for visualization of latent fingerprints, which significantly limits the general accessibility.

There are alternative methods of latent fingerprint detection. One notable method is the use of silver physical developer (Ag-PD), which is a process that utilizes metastable silver colloid to develop latent prints on wet, porous surfaces, such as paper and cardboard.¹⁰ The developer deposits a black silver precipitate along the fingerprint ridges by associating or reacting with the lipid (or water insoluble) material present in the fingerprint residue. Prints developed using Ag-PD appear as dark ridges on lighter/white background, creating enough contrast that allows visualization under white light (or ambient light). Although the process eliminates the use of expensive, specialized light sources for visualization, it suffers from instability of the developing solution and poor reproducibility.¹⁰ Multi-metal deposition (MMD)¹¹ is a variation of the process that allows latent fingerprint enhancement based on gold nanoparticle (AuNP) deposition followed by reinforcement with silver (Ag-PD). Advantages of using MMD are based on its sensitivity, specifically with aged fingerprints, and its efficiency on porous as well as non-porous surfaces. Such techniques that require use of nanomaterials have been rapidly evolving, but in all cases the adherence of nanoparticles to the fingerprint material is the main premise.¹²

Research in our group has been focused on the precise mechanism¹³ and application of 1,2-indanedione in detection of latent fingerprints since our first discovery in 1997.^{7,8} In the present work, we wish to extend the utility of 1,2-indanediones in a novel approach using 1,2-indanedione functionalized AuNPs as bi-functional reagent towards detection of latent fingerprints on paper substrates.

2. Design and synthesis of a novel 1,2-indanedione reagent

2.1 Proposed methodology and reagent design

Due to limitations set by the stoichiometric nature of using amino acid-detecting chemical reagents, the variability in the sweat content on a given fingerprint residue, and the cumbersome requirement of using specialized equipment (light sources such as lasers) to visualize fingerprints, the focus of recent efforts in the area of fingerprint development has been shifted to utilization of nanotechnology (i.e. MMD) as a promising alternative. In this context, development of a new highly sensitive, non-stoichiometric AuNP-based technology following the basic principle of MMD was envisioned. In particular, a bi-functional reagent containing a 1,2-indanedione moiety, which would react with amino acids of the fingerprint ridge *via* conventional methods^{7,8} and a long alkylthiol chain that would act as stabilizing ligand on AuNPs was envisaged (Figure 2).

Figure 2. General scheme for the proposed latent fingerprint development.

Since the bi-functional reagent would act as a ligand on the AuNP, in theory, each AuNP could have many of these ligands appended on it, thereby increasing the likelihood of reaction between fingerprint residue and the ligand. The resulting ternary complex could then catalyze silver deposition from the Ag-PD, generating a high-contrast fingerprint image that could be visualized without the use of specialized light source. Unlike existing methods¹⁴ that target either amino acids (eccrine secretions)⁸ or hydrophobic lipids (sebaceous secretions)^{14a}, this reagent could detect both eccrine-rich and sebum-rich fingerprint residues, increasing the overall efficiency of latent fingerprint detection on paper substrates.

2.2 Synthesis of novel bifunctional reagent

In accordance with previous studies by Almog et al.¹⁴ in employing bi-functional reagents that contain long alkyl chains as stabilizing ligands on AuNPs, a chain length of ten carbons was determined to be a reasonable starting point to test the viability of the proposed approach. A concise, four-step synthesis was designed to afford the desired 1,2-indanedione derivative (**1**) (Scheme 1). Commercially available 5-chloro-1-indanone was treated with a 10-carbon chain potassium alkyltrifluoroborate salt **2** using the Suzuki-Miyaura cross-coupling reaction to afford **3** in acceptable yield.¹⁵ Subsequent displacement of the tosylate moiety with potassium thioacetate generated intermediate **4** in good yield. Formation of the oxime (**5**), followed by conversion to the desired 1,2-indanedione **1** was accomplished with a variation of previously developed methods^{7,13} in nearly quantitative yields without requiring the use of silica gel chromatography purification steps. Not surprisingly, a minor amount of deprotected thiol **6** was observed under the acidic aqueous conditions employed in the last step (Scheme 1). The mixture of major and minor products **1** and **6** were carried onto the next step of AuNP functionalization, since *in situ* removal of the thioacetate protecting group occurs during the ligand exchange.^{14b,16}

Scheme 1. Synthesis of 1,2-indanedione derivative **1**.

AuNPs stabilized by dodecyldimethylammonium bromide (DDAB) was synthesized¹⁷ and subsequently functionalized *via* ligand exchange with **1** to afford the desired bi-functional reagent.

3. Development of latent fingerprints on paper

To test the efficiency in detecting amino acids on latent fingerprint residue, eccrine-rich fingerprints were deposited on a paper substrate (Whatman® filter paper). The paper substrate was left to age for 1-2 days and then immersed in a solution of the 1,2-indanedione bi-functional AuNP reagent (0.01% w/v in dimethyl sulfoxide) for about 3-5 min. Subsequent water rinse followed by post-treatment with standard Ag-PD solution^{14b} for <50 sec gave rise to visible fingerprint ridges (Figure 3). A positive fingerprint image was obtained, in which the silver

deposition was more apparent on the fingerprint ridges in comparison to the background. This result strongly suggests the preferential interaction of the novel bi-functional reagent with the fingerprint residue. Next, sebum-rich latent fingerprints were developed using the same process (Figure 3). Similar to the outcome of the eccrine-rich fingerprint, a positive fingerprint image was obtained (Figure 3), further supporting the hypothesis of preferential interaction of the bi-functional reagent to the fingerprint residue than the cellulose material of the paper. However, this reaction could be attributed to hydrophobic interactions between the sebum-rich, oily residue and the long alkyl chain on the bi-functional reagent.^{14a} Finally, fingerprint that was not intentionally charged with eccrine or sebaceous secretions was deposited on a paper substrate (standard copy paper). The paper containing latent fingerprint was then soaked in an aqueous solution of maleic acid (2.5% w/v) for about 5 min. This pre-wash step decreases the likelihood of undesired spontaneous silver deposition during the Ag-PD step by removing the calcium carbonate deposits on standard copy paper, which is a remnant of the paper manufacturing process.^{2,10} Spontaneous silver deposition would lead to total blackening of the paper substrate, which reduces contrast. The paper substrate treated with the pre-wash step was air-dried, and then immersed in a solution of the bi-functional AuNP reagent (0.04% w/v) for about 5 min. Subsequent water rinse followed by post-treatment with standard Ag-PD solution^{14b} for <1 min gave rise to positive, visible fingerprint ridges (Figure 3).

Figure 3. Latent fingerprints developed on paper substrates using the 1,2-indanedione bi-functional reagent.¹⁸ Left: eccrine-rich fingerprint sample. Middle: sebum-rich fingerprint sample. Right: uncharged fingerprint sample.

Taken together, this data strongly suggest that the novel bi-functional reagent could react with both amino acid and oily (hydrophobic) fingerprint residues, which increases the overall likelihood of fingerprint detection on paper. The sensitivity of this bi-functional reagent was especially highlighted in the fact that even uncharged fingerprint residues were readily developed. Interestingly, this data is contrary to Almog *et al.*'s result obtained using a bi-functional reagent that contains an acyl pyridazine moiety (**7**)^{14b} or mercaptocarboxylic acid (**8**) (Figure 4).^{14c} The acyl pyridazine and mercaptocarboxylic acid based bi-functional reagents showed preferential binding to cellulose rather than the fingerprint residue, which resulted in negative images.^{14b,14c}

Figure 4. Structural comparison of existing bi-functional reagents **7** and **8** to **1**.

The difference in this preferential binding mode could be attributed to the relative increase in polarity of acyl pyridazines as well as mercaptocarboxylic acid moieties in comparison to 1,2-indanedione, which allows more extensive hydrogen bonding interactions with cellulose material of the paper substrate. These results suggest the ability to tune the reactivity of such bi-functional reagents to obtain either positive or negative images.

However, in terms of sensitivity of detection, unlike reagents **7** and **8** which were used to detect sebum-rich latent fingerprints (fingerprints charged with oily sebaceous secretions), the novel 1,2-indanedione based bi-functional reagent showed great potential in detecting eccrine-based as well as sebum-rich fingerprint residues.

4. Conclusion

A novel 1,2-indanedione-based bi-functional reagent was designed and successfully synthesized by a high yielding, concise, 5-step protocol. Eccrine-rich, sebum-rich, and uncharged (fingerprints that were not intentionally coated) latent fingerprints were all developed with this reagent in a modified MMD protocol. In all cases, positive images on paper substrates were obtained, strongly suggesting the novel bi-functional reagent's efficiency in detecting fingerprint residues that contain both sweat (eccrine gland secretions or amino acids) and oily substances (sebaceous secretions). This reagent could be used as an alternative or in conjugation with other bi-functional reagents in cases where sensitivity poses an issue. Further studies regarding the effect of the side chain length, AuNP dispersity, and optimization of the formulation protocol are currently in progress.

Acknowledgments

This paper is dedicated to Professor Harry Wasserman for his many contributions to various areas of Chemistry and mentorship. Financial support for this research was provided by the University of Pennsylvania, the National Science Foundation (NSF-CHE-0951394), National Institute of Justice graduate research fellowship (2012-IJ-CX-0019 to J.L.), and Novartis graduate research fellowship in organic chemistry for minorities and women (to J.L.). We thank Robert Ramotowski (FSD) and Antonio Cantu for helpful discussions regarding fingerprint development. Dr. Simon Berritt (University of Pennsylvania) is gratefully acknowledged for aiding the imaging process. We also thank Dr. George Furst and Dr. Rakesh Kohli (University of Pennsylvania) for NMR and MS assistance, respectively.

References

- Jelly, R.; Patton, E. L. T.; Lennard, C.; Lewis, S. W.; Lim, K. F. *Anal. Chim. Acta* **2009**, 652, 128-142.
- Ramotowski, R. In *Advances in Fingerprint Technology Second Edition*; Lee, H. C., Gaensslen, R. E. Eds.; CRC Press: Boca Raton, 2001; pp 63-104.
- Hansen, D. B.; Joullié, M. M. *Chem. Soc. Rev.* **2005**, 34, 408-417.
- a) Ruhemann, S. *Trans. Chem. Soc.* **1910**, 97, 1438-1449. b) Odén, S.; von Hofsten, B. *Nature* **1954**, 173, 449-450.
- a) Friedman, M.; Williams, L. D. *Bioorg. Chem.* **1974**, 3, 267-280. b) Grigg, R.; Malone, J. F.; Mongkolasavaratana, T.; Thianpatanagul, S. *J. Chem. Soc., Chem. Commun.* **1986**, 421-422.
- Grigg, R.; Mongkolasavaratana, T.; Pounds, C. A.; Sivagnanam, S. *Tetrahedron Lett.* **1990**, 31, 7215-7218.
- a) Hauze, D. B.; Petrovskaja, O.; Taylor, B.; Joullié, M. M.; Ramotowski, R.; Cantu, A. A. *J. Forensic Sci.* **1998**, 43, 744-747. b) Ramotowski, R.; Cantu, A. A.; Joullié, M. M.; Petrovskaja, O. *Fingerprint Whorld* **1997**, 23, 131-140.
- Almog, J.; Glasner, H. *J. Forensic Sci.* **2010**, 55, 215-220.
- Selected recent examples: a) Fritz, P.; van Bronswijk, W.; Lewis, S. W. *Anal. Methods* **2013**, 5, 3207-3215. b) Frick, A. A.; Busetti, F.; Cross, A.; Lewis, S. W. *Chem. Commun.* **2014**, 50, 3341-3343. c) Bentolila, A.; Totre, J.; Zozulila, I.; Levin-Elad, M.; Domb, A. J. *Macromolecules* **2013**, 46, 4822-4828.
- a) Cantu, A. A. *Forensic Sci. Rev.* **2001**, 13, 29-64. b) Burow, D.; Seifert, D.; Cantu, A. A. *J. Forensic Sci.* **2003**, 48, 1094-1101. c) Cantu, A. A.; Johnson, J. L. In *Advances in Fingerprint Technology Second Edition*; Lee, H. C., Gaensslen, R. E. Eds.; CRC Press: Boca Raton, 2001; pp 242-247.
- Schnetz, B.; Margot, P. *Forensic Sci. Int.* **2001**, 118, 21-28.
- Selected references: a) Stauffer, E.; Becue, A.; Singh, K. V.; Thampi, K. R.; Champod, C.; Margot, P. *Forensic Sci. Int.* **2007**, 168, e5-e9. b) Hazarika, P.; Russell, D. A. *Angew. Chem. Int. Ed.*

- 2012**, *51*, 3524-3531. c) Becue, A.; Scoundrianos, A.; Champod, C.; Margot, P. *Forensic Sci. Int.* **2008**, *179*, 39-43.
13. a) Taylor, B. M.; Joullié, M. M. *Tetrahedron* **1998**, *54*, 15121-15126. b) Petrovskaia, O.; Taylor, B. M.; Hauze, D. B.; Carroll, P. J.; Joullié, M. M. *J. Org. Chem.* **2001**, *66*, 7666-7675.
14. a) Sametband, M.; Shweky, I.; Banin, U.; Mandler, D.; Almog, J. *Chem. Commun.* **2007**, 1141-1144. b) Jaber, N.; Lesniewski, A.; Gabizon, H.; Shenawi, S.; Mandler, D.; Almog, J. *Angew. Chem. Int. Ed.* **2012**, *51*, 12224-12227. c) Shenawi, S.; Jaber, N.; Almog, J.; Mandler, D. *Chem. Commun.* **2013**, *49*, 3688-3690.
15. Dreher, S. D.; Lim, S. -E.; Sandrock, D. L.; Molander, G. A. *J. Org. Chem.* **2009**, *74*, 3626-3631.
16. Kotiaho, A.; Lahtinen, R.; Efimov, A.; Lehtivuori, H.; Tkachenko, N. V.; Kanerva, T.; Lemmetyinen, H. *J. Photochem. Photobiol. A—Chemistry* **2010**, *212*, 129-134.
17. Prasad, B. L. V.; Stoeva, S. I.; Sorensen, C. M.; Klabunde, K. J. *Langmuir* **2002**, *18*, 7515-7520.
18. According to guidelines published by the International Fingerprint Research Group (IFRG), the obtained latent fingerprint images are of Phase 1 (pilot studies). International Fingerprint Research Group *J. Forensic Ident.* **2014**, *64*, 174-200.