



A new methodology for the visualization of latent fingermarks on the sticky side of adhesive tapes using novel fluorescent dyes



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ABSTRACT

Three novel fluorescent dyes were evaluated for the detection of latent fingermarks on different types and colors of adhesive tapes. Compared with the conventional reagents used to reveal latent fingermarks on these surfaces, these new fluorescent dyes have many advantages. They are highly selective to fingermarks, require only a simple procedure, do not need pre- or post-treatment, have high thermal and photochemical stability, are low in cost and use only water as a solvent. In addition, the emitted fluorescence creates a sharp contrast with the fingermark surface, meaning the fingermarks can be clearly visualized and photographed when excited with longwave ultraviolet light (365 nm).

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1. Introduction

Fluorescence imaging has become an extremely important tool in forensic science as a method for the detection of latent evidences [1]. At a crime scene, sometimes the marks are not visible, such as in the case of fingermarks, thus the development of new methodologies that allow this mark to become visible is very important.

Adhesive surfaces, such as the adhesive side of tapes, have relevant features for the detection of latent fingermarks. For example, the receptive nature of adhesive tape allows fingermark residues to be retained when these surfaces are touched by papillary ridges. Furthermore, the difficulty in handling tapes when wearing gloves means that the handling (e.g. in crimes) is generally carried out with bare hands, which means there could be a latent fingermark anywhere on the tape surface. The high uses of adhesive tape for immobilize victims (e.g., rape, robbery and kidnapping) or building an explosive device make it an important physical evidence for identifying criminals.

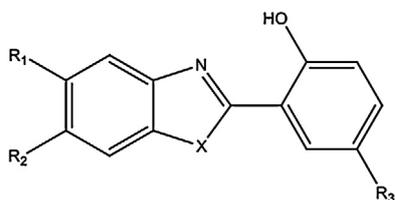
For the non-adhesive side of the tapes, it can be relatively easy to detect and visualize the fingermarks. Black, metallic, fluorescent or colored powders and cyanoacrylate fuming usually produce good results [2–5]. However, for the adhesive side, many problems

arise due to the difficult nature of the surface. The application of dyes, e.g., Crystal Violet (or Gentian Violet) dissolved in water (in some cases with the addition of phenol), is one of the most used procedure for this purpose [6]. Crystal Violet reacts with the fatty acids and lipids in sweat and produces a purple color [7]. This technique often requires additional procedures, such as dye sublimation to another surface to visualize the revealed fingermark, especially for dark adhesive tapes [6,8–10]. Crystal Violet has other limitations, such as low selectivity for fingermarks, which often leads to the entire staining of the tape's surface. The intense purple color of the dye also makes it difficult or impossible to photograph fingermarks on dark adhesive tapes (e.g. black electrical tape).

Other methodologies for adhesive tapes include alternate black powder, ash gray powder, Liqui-Drox, sticky-side powder, ray dye and phase transfer catalyst-based formulation [2,3,5,8,9,11–13]. However, all these methodologies have important limitations, like low selectivity for fingermarks, again, often leading to the entire staining of the tape's surface.

The novel fluorescent dyes reported in this article [14,15] can overcome the limitations inherent to Crystal Violet and other commercial dyes, and they show high efficiency in the detection of latent fingermarks in a short time. They detected only fingermarks, do not stain the surface of all the tested tapes and have high efficiency in staining the fingermarks, even when used in very dilute solutions. Only water is required to prepare the dye. No pre- or post-treatment of the surface (except to rinse the adhesive tape

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HB-7, X=S, R₁=H, R₂=H, R₃=SO₃H
HB-9, X=O, R₁=H, R₂=CH₃, R₃=SO₃H
HB-11, X=O, R₁=SO₃H, R₂=H, R₃=NH₂

Scheme 1. Structures of the novel fluorescent dyes.

with water) is required to show great fingerprint sharpness. In addition, the dyes have high thermal and photochemical stability as well as being low in cost.

2. Materials and methods

All reagents and solvents used in the synthesis and purification of the compounds were purchased from Sigma–Aldrich, Acros or Merck and were used without further purification. Spectroscopic solvents (Merck) were used to prepare samples for spectroscopic characterization. All dyes were characterized by infrared (IR) spectroscopy, ¹H- and ¹³C-NMR spectroscopy, ultraviolet–visible (UV–vis) spectroscopy, fluorescence spectroscopy and mass spectrometry. ¹H- and ¹³C-NMR spectra were obtained with a Varian INOVA-300 and Bruker Avance - 400. Infrared (IR) spectra were obtained using a Mattson Galaxy Series 3000 FT-IR in KBr and the mass spectra in a Shimadzu GCMS - QP20105 with quadrupole analyzer. The absorption spectra were obtained using a Varian Cary-50 spectrometer. The fluorescence spectra were obtained with a Hitachi spectrometer, model F-4500. An ultraviolet light source with a 365 nm wavelength (black light lamp: 46 W, 50/60 Hz- Golden®) was used for visualising and photograph developed fingerprints. Sometimes, a photographic orange barrier filter was used to eliminate the background fluorescence. The fingerprint samples were treated with different fluorescent dyes and photographed using a digital camera (NIKON D600, macro mode, 60 mm f/3.2D) or (Canon EOS 1100D, macro mod96e, 55 mm f/3.5–5.6D) under white light or ultraviolet light of 365 nm, with no camera filters.

2.1. Synthesis of the HB-7, HB-9 and HB-11 fluorescent dyes

The fluorescent dyes named HB-7, HB-9 and HB-11, used in this study (Scheme 1), were previously synthesized, purified and characterized in our laboratory by the present authors [14] and they are patent pending in the National Institute of Intellectual Property (Brazilian Patent Agency - BR 10 2014 0309420) [15]. All dyes are water-soluble and fluorescent in the blue–green region when exposed to longwave UV light. Fig. 1 shows the normalized

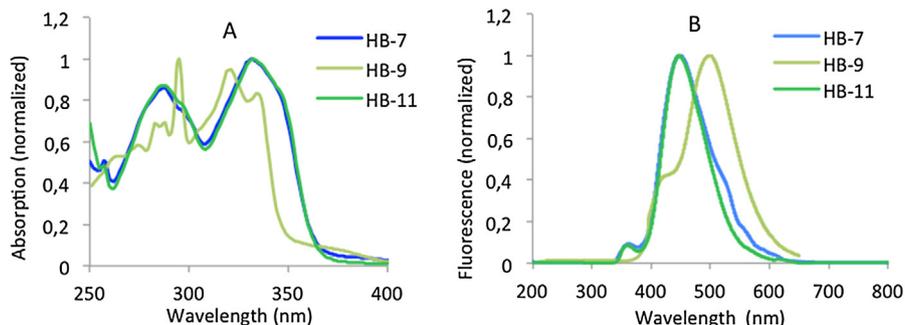


Fig. 1. (A) Normalized absorption and (B) fluorescence emission spectra of HB-7, HB-9 and HB-11 in water (excitation wavelength of 324 nm).

Table 1

Absorption and fluorescence emission data for HB-7, HB-9 and HB-11.

Dyes	λ_{max} absorption (nm)	λ_{max} emission (nm)	Stokes shift	ϵ_{max} ($\times 10^6 \text{ L mol}^{-1} \text{ cm}^{-1}$)
HB-7	331	449	118	0.42
HB-9	320	499	179	0.35
HB-11	329	447	118	0.38

absorption and fluorescence spectra of HB-7, HB-9 and HB-11 in water, obtained using excitation wavelength of 324 nm. The Stokes shift values were 118, 179 and 118 nm for HB-7, HB-9 and HB-11, respectively. These values are summarized in Table 1 and they are consistent with compounds which undergo excited-state intramolecular proton transfer (ESIPT).

Fig. 2 shows the novel fluorescent dyes in the solid state under white light (A), ultraviolet light of 365 nm (B) and in aqueous solution under ultraviolet light of 365 nm (C), where we can see an intense fluorescence emission.

2.2. Latent fingerprint samples

Fingermarks samples were impressed on four different types and colors of adhesive tapes (listed in Section 2.3) by three individuals (two males and one female) of unknown donor capabilities. The fingerprints were deposited after rubbing the donor's finger onto an oily part of the face (charged fingerprints), and then five fresh successive depositions of the same finger were made on brown tape to obtain a depletion series of fingerprints, each time presenting subsequently fewer quantities of deposited material (a sequential study). Other fingerprint samples were taken from donors without replenishment (natural fingerprints). This served to produce fingerprints with varying amounts of residues. A time study involving detecting of previously deposited latent fingerprints on different tape surfaces was conducted. Fingerprints were deposited on black (electrical tape) and brown tape substrates and were developed 0 (fresh fingerprint), 2, 8, and 15 days later. The substrates were stored under ambient conditions. The environment was hot, dry, and dusty. The temperature varied from 24 to 32 °C. All experiments were performed in triplicate.

2.3. Performance on different types of adhesive tapes

Different types of adhesive tapes common to forensic cases were used to study the potential of the novel dyes in revealing the latent fingerprints. Other adhesive tapes such as plaster tapes, surgical tapes and tapes of different colors and brands were also tested. Although they produced good results, they are not presented in this work. The four types of adhesive tapes discussed in this work are shown in Table 2.

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