Near Infrared Laser Dyes for the Detection of Latent Fingermarks

by

Scott Chadwick

A thesis submitted for the

Degree of Doctor of Philosophy (Science)

University of Technology, Sydney

Certificate of authorship and originality

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of the requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all the information sources and literature used are indicated in the thesis.

NAME

DATE

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Abbreviations

¹³C NMR Carbon 13 spectroscopy

¹H NMR Hydrogen-1 (proton) nuclear magnetic resonance spectroscopy

AA Acetic acid

Ala Alanine

ATR-FTIR Attenuated Total Reflectance Fourier Transform Infrared

CB Cyanobloom

CCD Charged-coupled device

CdCl₃ Deuterated chloroform

CdS Cadmium sulfide

CdTe Cadmium telluride

CdTe-MMT Cadmium telluride montmorillonite

CTAB Cetyl trimethylammonium bromide

 Δ^9 -THC Δ^9 -Tetrahydrocannabinol

DESI-MS Desorption electrospray ionisation-mass spectrometry

DEUS Digital enclosed ultra-violet imaging system

DFO 1,8-Diazafluoren-9-one

DMAB p-Dimethylaminodbenzaldehyde

DMF Dimethyl formamide

DMSO Dimethyl sulfoxide

DMSO-d₆ Deuterated dimethylsulfoxide

DNA Deoxyribonucleic acid

Em Emission

ESA Europium-doped strontium aluminate

Ex Excitation

FRET Forster resonance energy transfer

FTIR Fourier transform infrared spectroscopy

GD Good development

Gly Glycine

His Histidine

IND 1,2-Indanedione

IND-Zn 1,2-Indanedione zinc

Leu Leucine

LED Light emitting diode

λmax Wavelength of maximum absorbance or luminescence

LOD Limit of detection

Lys Lysine

Matrix-assisted laser desorption ionization mass spectroscopy

MALDI-MSI in

imaging

MeOH Methanol

MAO Monoamine oxidase

MHz Megahertz

MMD Multi metal deposition

mp Melting point

ND No development

NIN Ninhydrin

NIR Near-infrared

NMR Nuclear magnetic resonance spectroscopy

OPSC Optically pumped semi-conductor

Orn Ornithine

PC UV PolyCyano UV

PD Physical developer

PD Poor development

Phe Phenylalanine

QD Quantum dots

R6G Rhodamine 6G

RAY Rhodamine 6G, Ardrox™ and basic yellow 40 dye mixture

RH Relative humidity

RP Ruhemann's purple

RUVIS Reflected ultra-violet imaging system

SDS Sodium dodecyl sulfate

Ser Serine

SMD Single metal deposition

SPR Small particle reagent

SPR UV Small particle reagent ultra-violet

SSP Sticky side powder

STaR 11 Styryl 11 and rhodamine 6G mixture

Scientific working group on friction ridge analysis, study and

SWGFAST technology

SWGIT Scientific working group on imaging technology

TEC Thenoyl europium chelate

TECTOPO Thenoyl europium trioctylphosphine oxide

Thr Threonine

THF Tetrahydrofuran

TIFF Tagged image file format

Tyr Tyrosine

UTS University of Technology Sydney

UV Ultra violet

Val Valine

VMD Vacuum metal deposition

VSC Video spectral comparator

Zn-RP Zinc Ruhemann's purple complex

Abstract

The near infrared region (700 nm – 2000 nm) of the electromagnetic spectrum provides significant potential for fingermark detection. Many ubiquitous commercial surfaces give luminescent interferences that can present a challenge for latent fingermark enhancement. Background interference from these types of surfaces can be reduced when viewed in the near infrared region. The development of near infrared luminescent techniques for latent fingermarks would improve the possibility of imaging an exploitable fingermark. This research aimed to develop methods for near infrared detection of latent fingermarks across a number of different surface types and assess the effectiveness of the developed techniques by comparing them to conventional detection methods.

A mixture of two dyes, styryl 11 and rhodamine 6G (STaR 11), was coated onto a range of metal oxide powders to produce a luminescent fingerprint powder. This was applied as a dry powder for fingermarks on non-porous surfaces as well as a suspension for developing fingermarks on adhesive and wetted surfaces. The dry powder was successful in developing fingermarks and gave comparable results to a commercially available luminescent fingermark powder. The suspension for adhesive surfaces was able to develop fingermarks however when compared to the commercial method, the developed fingermarks were of significantly poor quality. The suspension for wetted surfaces, when used in conjunction with the EcoSpray® device (a pressurised sprayer which delivers the suspension in a fine mist to prevent fingermark damage), had shown significant promise when compared to conventional luminescent SPR. Ultimately, however, the suspension was unable to develop natural fingermarks, which affected its potential for routine use.

Styrylisatin was trialled as a potential near infrared luminescent amino acid sensitive reagent for the detection of latent fingermarks on porous surfaces. Styrylisatin was successfully synthesised, however there were several issues that made it unsuitable for use as a fingermark detection technique. Despite attempts to optimise the formulation, the sensitivity of styrylisatin to amino acids was not improved, thus it was not pursued any further.

The use of one-step luminescent cyanoacrylate (PolyCyano UV®) was also explored in this research and compared to conventional cyanoacrylate development subsequently stained with rhodamine 6G and STaR 11. PolyCyano UV® developed fingermarks were assessed for

development and visualisation under UV illumination as well as how they performed in a sequence. PolyCyano UV® developed fingermarks were applied successfully in sequence with rhodamine 6G and STaR 11. Sequencing allowed the developed marks to be visualised in the luminescence mode for two different visible wavelength regions as well as in the near infrared region, which was found to improve the possibility of imaging an exploitable fingermark.

A range of imaging systems are available to forensic laboratories, however, the suitability of these systems for near infrared imaging has not been explored in any published study. Four imaging systems (Condor, Fuji IS Pro, Poliview IV and VSC 6000) were compared based on their ability to image fingermarks developed with STaR 11 magnetic powder and cyanoacrylate developed fingermarks stained with STaR 11. Overall, the Poliview IV and VSC 6000 were found to give the best imaging capabilities of all the systems tested. Generally the VSC 6000 was better suited for well-developed fingermarks; however the Poliview IV produced better quality images for poorly developed fingermarks. The Fuji IS Pro was suitable as a lab based near infrared camera; however when used for field purposes it displayed a significant decrease in effectiveness.

The research has successfully developed a range of fingermark detection techniques that are luminescent in the near infrared region. These techniques can be used in conjunction with conventional techniques to improve and possibly increase the number of exploitable fingermarks.