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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<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>$^{13}$C NMR</td>
<td>Carbon 13 spectroscopy</td>
</tr>
<tr>
<td>$^1$H NMR</td>
<td>Hydrogen-1 (proton) nuclear magnetic resonance spectroscopy</td>
</tr>
<tr>
<td>AA</td>
<td>Acetic acid</td>
</tr>
<tr>
<td>Ala</td>
<td>Alanine</td>
</tr>
<tr>
<td>ATR-FTIR</td>
<td>Attenuated Total Reflectance Fourier Transform Infrared</td>
</tr>
<tr>
<td>CB</td>
<td>Cyanobloom</td>
</tr>
<tr>
<td>CCD</td>
<td>Charged-coupled device</td>
</tr>
<tr>
<td>CdCl$_3$</td>
<td>Deuterated chloroform</td>
</tr>
<tr>
<td>CdS</td>
<td>Cadmium sulfide</td>
</tr>
<tr>
<td>CdTe</td>
<td>Cadmium telluride</td>
</tr>
<tr>
<td>CdTe-MMT</td>
<td>Cadmium telluride montmorillonite</td>
</tr>
<tr>
<td>CTAB</td>
<td>Cetyl trimethylammonium bromide</td>
</tr>
<tr>
<td>$\Delta^9$-THC</td>
<td>$\Delta^9$-Tetrahydrocannabinol</td>
</tr>
<tr>
<td>DESI-MS</td>
<td>Desorption electrospray ionisation-mass spectrometry</td>
</tr>
<tr>
<td>DEUS</td>
<td>Digital enclosed ultra-violet imaging system</td>
</tr>
<tr>
<td>DFO</td>
<td>1,8-Diazafluoren-9-one</td>
</tr>
<tr>
<td>DMAB</td>
<td>p-Dimethylaminobenzaldehyde</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethyl formamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl sulfoxide</td>
</tr>
<tr>
<td>DMSO-d$_6$</td>
<td>Deuterated dimethylsulfoxide</td>
</tr>
<tr>
<td>DNA</td>
<td>Deoxyribonucleic acid</td>
</tr>
<tr>
<td>Em</td>
<td>Emission</td>
</tr>
<tr>
<td>ESA</td>
<td>Europium-doped strontium aluminate</td>
</tr>
<tr>
<td>Ex</td>
<td>Excitation</td>
</tr>
<tr>
<td>FRET</td>
<td>Forster resonance energy transfer</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>GD</td>
<td>Good development</td>
</tr>
<tr>
<td>Gly</td>
<td>Glycine</td>
</tr>
<tr>
<td>His</td>
<td>Histidine</td>
</tr>
<tr>
<td>IND</td>
<td>1,2-Indanedione</td>
</tr>
<tr>
<td>IND-Zn</td>
<td>1,2-Indanedione zinc</td>
</tr>
<tr>
<td>Leu</td>
<td>Leucine</td>
</tr>
<tr>
<td>LED</td>
<td>Light emitting diode</td>
</tr>
<tr>
<td>$\lambda_{\text{max}}$</td>
<td>Wavelength of maximum absorbance or luminescence</td>
</tr>
<tr>
<td>LOD</td>
<td>Limit of detection</td>
</tr>
<tr>
<td>Lys</td>
<td>Lysine</td>
</tr>
<tr>
<td>MALDI-MSI</td>
<td>Matrix-assisted laser desorption ionization mass spectroscopy imaging</td>
</tr>
<tr>
<td>MeOH</td>
<td>Methanol</td>
</tr>
<tr>
<td>MAO</td>
<td>Monoamine oxidase</td>
</tr>
<tr>
<td>MHz</td>
<td>Megahertz</td>
</tr>
<tr>
<td>MMD</td>
<td>Multi metal deposition</td>
</tr>
<tr>
<td>mp</td>
<td>Melting point</td>
</tr>
<tr>
<td>ND</td>
<td>No development</td>
</tr>
<tr>
<td>NIN</td>
<td>Ninhydrin</td>
</tr>
<tr>
<td>NIR</td>
<td>Near-infrared</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance spectroscopy</td>
</tr>
<tr>
<td>OPSC</td>
<td>Optically pumped semi-conductor</td>
</tr>
<tr>
<td>Orn</td>
<td>Ornithine</td>
</tr>
<tr>
<td>PC UV</td>
<td>Polycyano UV</td>
</tr>
<tr>
<td>PD</td>
<td>Physical developer</td>
</tr>
<tr>
<td>PD</td>
<td>Poor development</td>
</tr>
<tr>
<td>Phe</td>
<td>Phenylalanine</td>
</tr>
<tr>
<td>QD</td>
<td>Quantum dots</td>
</tr>
<tr>
<td>QD</td>
<td>Quantum dots</td>
</tr>
<tr>
<td>R6G</td>
<td>Rhodamine 6G</td>
</tr>
</tbody>
</table>
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
SWGFAST  |  Scientific working group on friction ridge analysis, study and 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
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 fingerprint 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.