

Real-Time Visualization of Latent Fingermarks with Level 3 details based on Solid State Emissive Organic Fluorophore Using Powder Dusting Method

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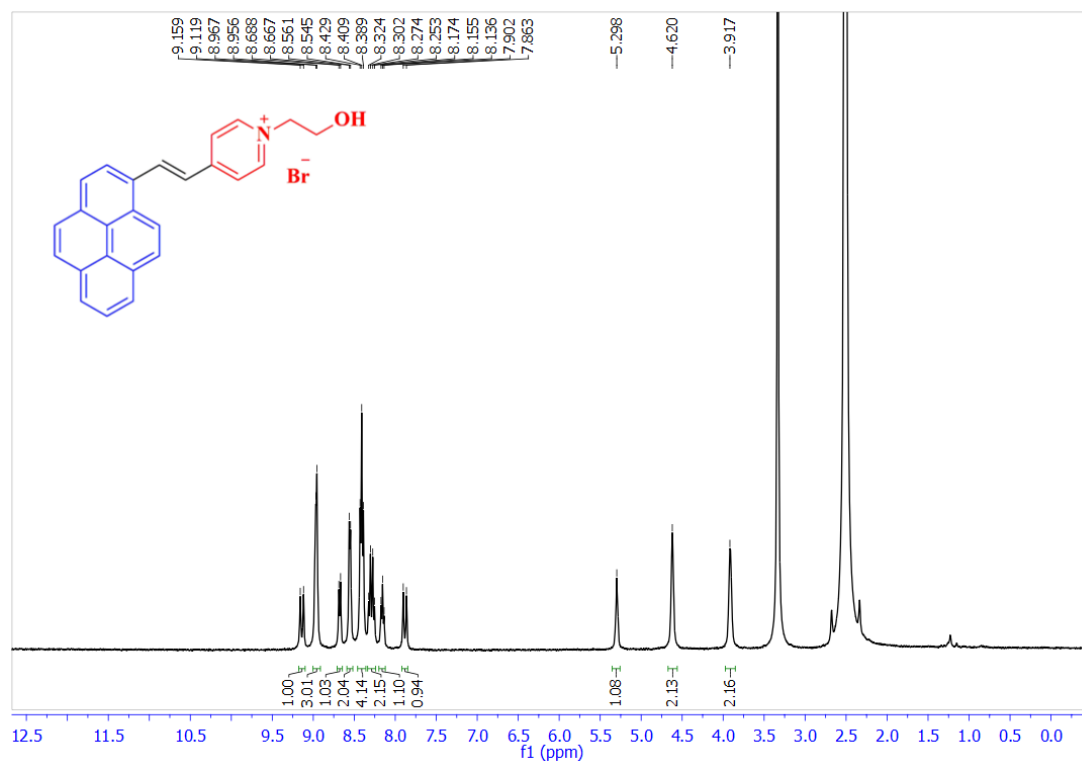


Figure S1. ¹H NMR spectrum of probe Py-Pr-OH in DMSO-*d*₆.

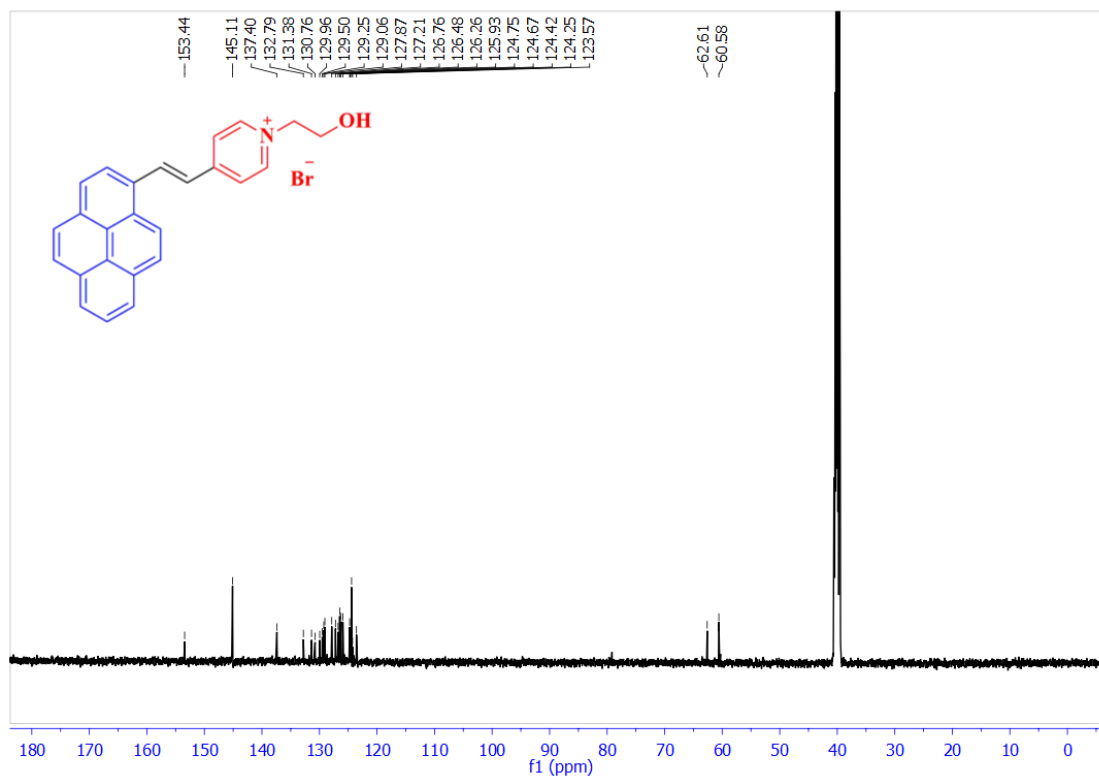


Figure S2. ¹³C NMR spectrum of probe Py-Pr-OH in DMSO-*d*₆.

Single Crystal X-Ray Diffraction:

The single crystal X-ray diffraction data of the **Py-Pr-OH** crystals were collected on a Microfocus D8 venture Bruker APEX 3 diffractometer equipped with a CCD area detector and having MoK α radiation ($\lambda = 0.71069\text{\AA}$). SAINT program (v. 8.38A) was used for data reduction, which were analyzed for agreement using XPREP. All these software were included in the APEX 3 software suite (v 2017.3-0).^{S1} Absorption correction was carried out with the SADABS program.^{S2} The crystal structure were solved using SHELXT (version 2018/2)^{S3} program and refined by refined using SHELXL-2014.^{S4-S6}. The positions of H-atoms were calculated and refined isotopically. Crystallographic data of **Py-Pr-OH** have been deposited with the Cambridge Crystallographic Data Centre (CCDC) under deposition no 2249837 and the crystallographic parameters are given in Table S1, supporting information.

Table S1. Single crystal X-ray parameters of **Py-Pr-OH** at 298 K

Compound	Py-Pr-OH
CCDC deposit No.	2249837
Chemical formula	C ₂₅ H ₂₀ Br N O
M_r	430.33
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
$a / \text{\AA}$	7.9403(5)
$b / \text{\AA}$	9.8325(6)
$c / \text{\AA}$	25.0359(16)
$a / ^\circ$	90
$b / ^\circ$	90
$g / ^\circ$	90
$V / \text{\AA}^3$	1954.6(2)
Z_s	4
$\rho_{\text{calc}} / (\text{g cm}^{-3})$	1.462
μ / mm^{-1}	2.118
F_{000}	880
$\theta_{\text{min}} / ^\circ$	2.22
$\theta_{\text{max}} / ^\circ$	21.30
Reflections collected	4375
Independent reflections	2934
GoF	1.115
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0445$ $wR_2 = 0.949$
R indices (all data)	$R_2 = 0.0952,$ $wR_2 = 0.1207$

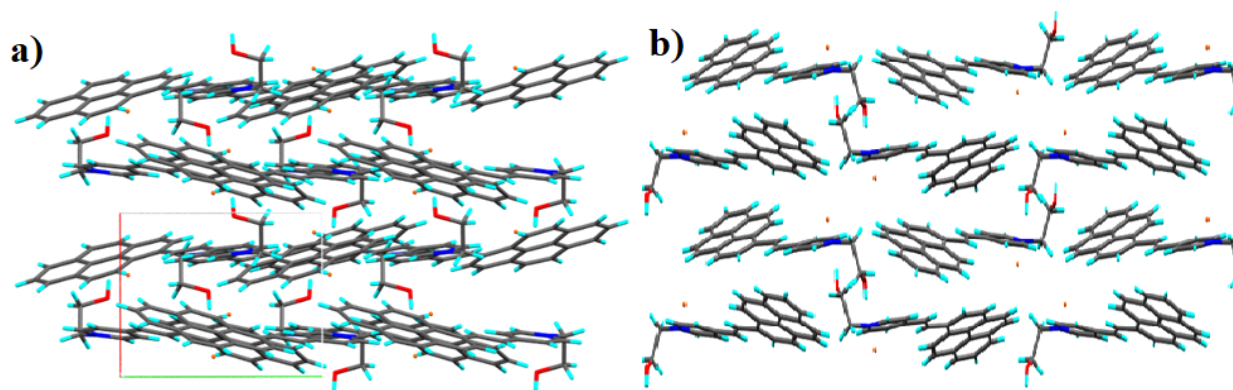


Figure S3. a) Packing of the molecules when viewed along c -axis. b) Packing of the molecules when viewed along b -axis.

Table S2. Solvent dependent properties of Py-Pr-OH in different solvents

Solvent	Py-Pr-OH λ_{ex} (nm)	Py-Pr-OH λ_{ex} (nm)	Py-Pr-OH ϵ M ⁻¹ cm ⁻¹
MeOH	450	569	51,000@450 nm
EtOH	456	567	48,000@456 nm
2-Pr-OH	454	567	44,000@454 nm
THF	446	566	20,000@446 nm
ACN	444	569	42,000@444nm
DMF	445	567	40,000@445nm
DMSO	446	568	40,000@446 nm
H ₂ O	438	571	38,000@438 nm

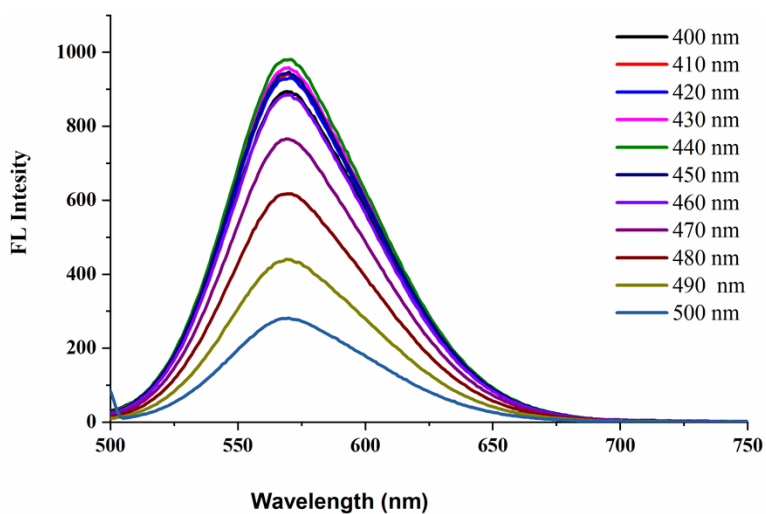


Figure S4. Fluorescence spectra of Py-Pr-OH (10 μ M) with different excitation wavelengths at room temperature in methanol.

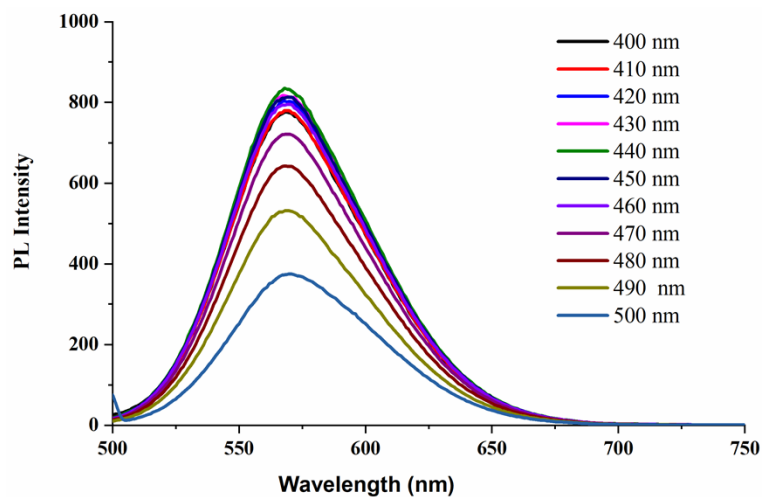


Figure S5. Fluorescence spectra of Py-Pr-OH (10 μM) with different excitation wavelengths at room temperature in ethanol.

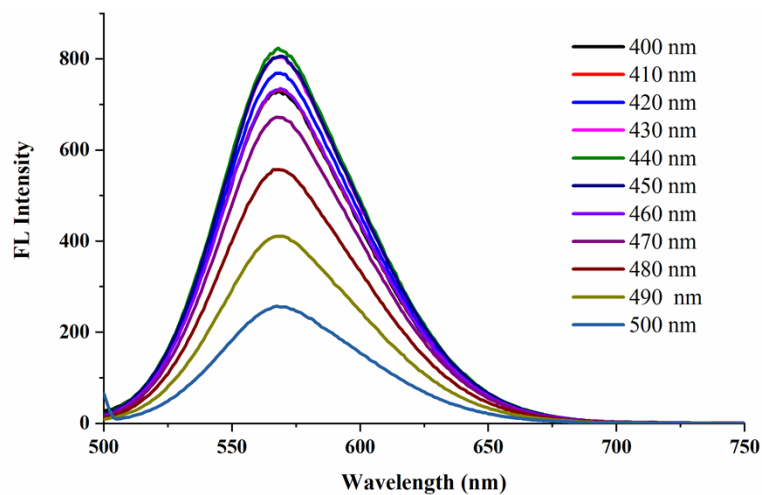


Figure S6. Fluorescence spectra of Py-Pr-OH (10 μM) with different excitation wavelengths at room temperature in 2-Propanol.

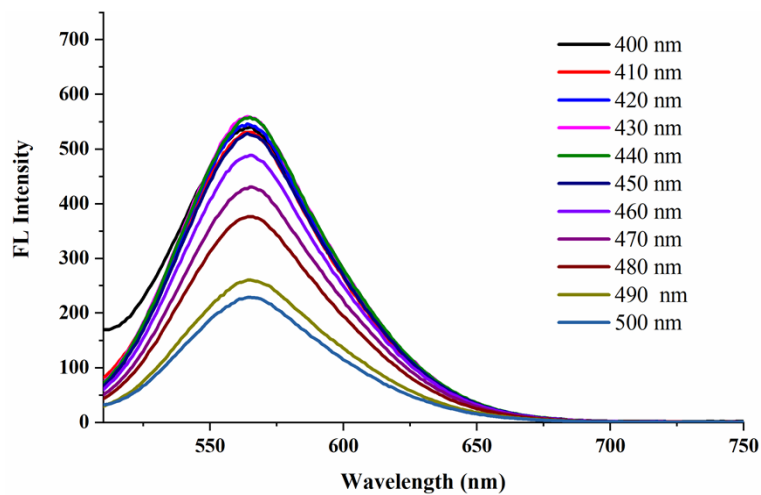


Figure S7. Fluorescence spectra of **Py-Pr-OH** (10 μ M) with different excitation wavelengths at room temperature in THF.

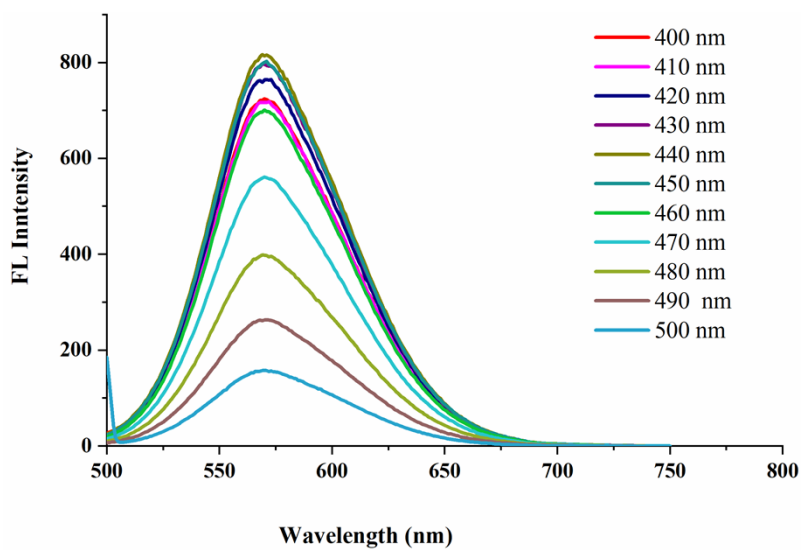


Figure S8. Fluorescence spectra of **Py-Pr-OH** (10 μ M) with different excitation wavelengths at room temperature in acetonitrile.

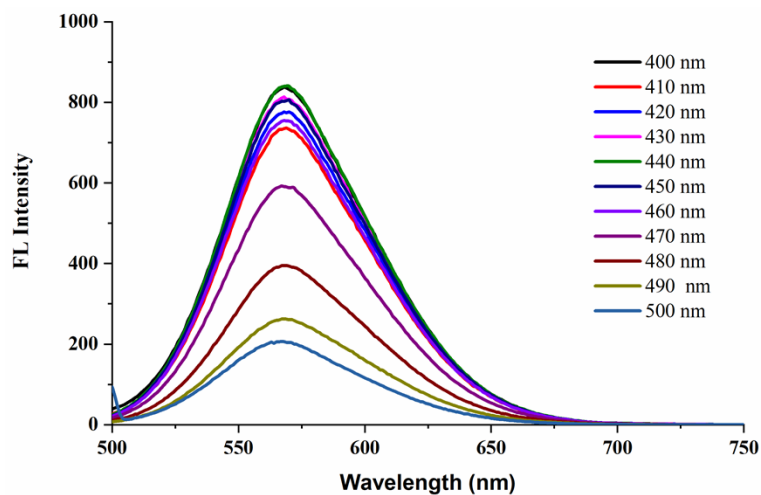


Figure S9. Fluorescence spectra of Py-Pr-OH (10 μM) with different excitation wavelengths at room temperature in DMF.

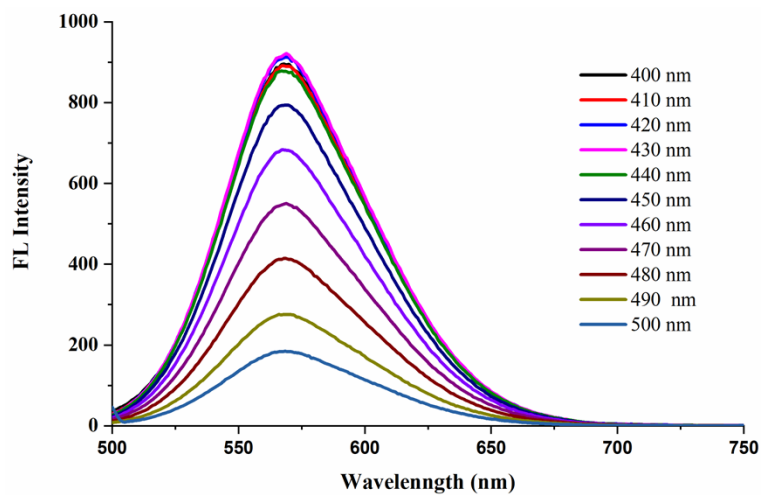


Figure S10. Fluorescence spectra of Py-Pr-OH (10 μM) with different excitation wavelengths at room temperature in DMSO.

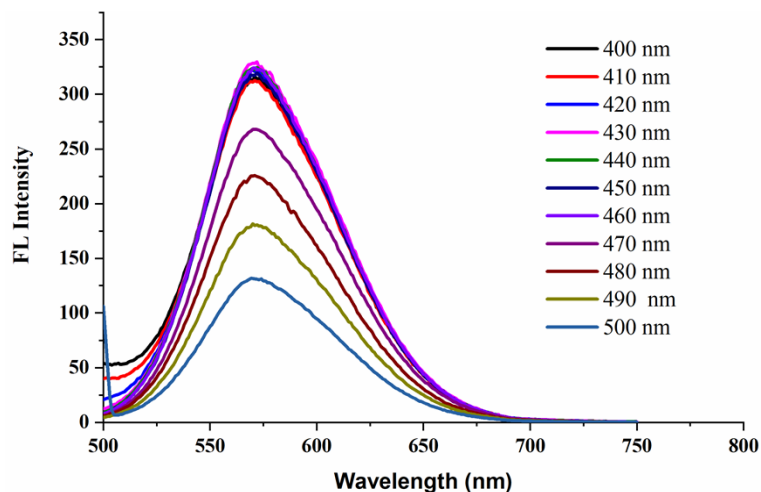


Figure S11. Fluorescence spectra of **Py-Pr-OH** (10 μ M) with different excitation wavelengths at room temperature in water.

Quantum yield calculation

$$\Phi_S = \Phi_R I_S/I_R * A_R/A_S$$

Φ_S – Quantum yield of sample; Φ_R – Quantum yield of reference (Fluorescein = 0.79)

I_S – Integrated fluorescent area of sample; I_R – Integrated fluorescent area of sample.

A_R – Absorbance of reference; A_S – Absorbance of sample

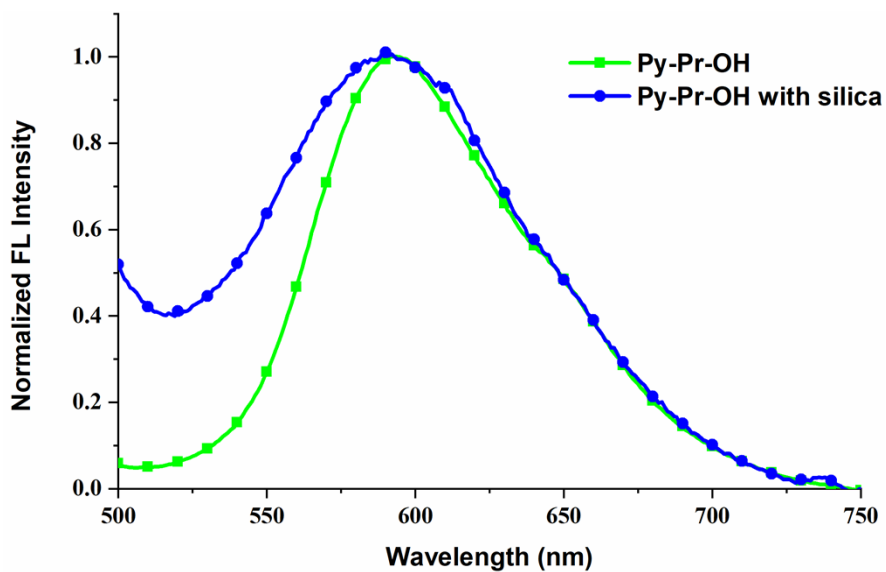


Figure S12. Normalized solid state emission spectra of **Py-Pr-OH** and **Py-Pyr-OH** with silica.

LFM development Powder preparation procedure

To the suspension of **Py-Pr-OH** in DCM, silica gel (230-400 mesh) was added. The solvent was evaporated in rotary evaporator. The silica adsorbed material was further grinded to make it free flow, and was further used for LFMs development procedure.

LFM development procedure by powder dusting method

FMs were collected from volunteers, asked to touch their fingers lightly on the chosen substrate surfaces such as tinfoil, paper currency, ceramic tile, plastic, plywood, CD, coin etc.). The LFM developing fluorescent smoothly brushed on their surfaces the images were captured using mobile phone camera.

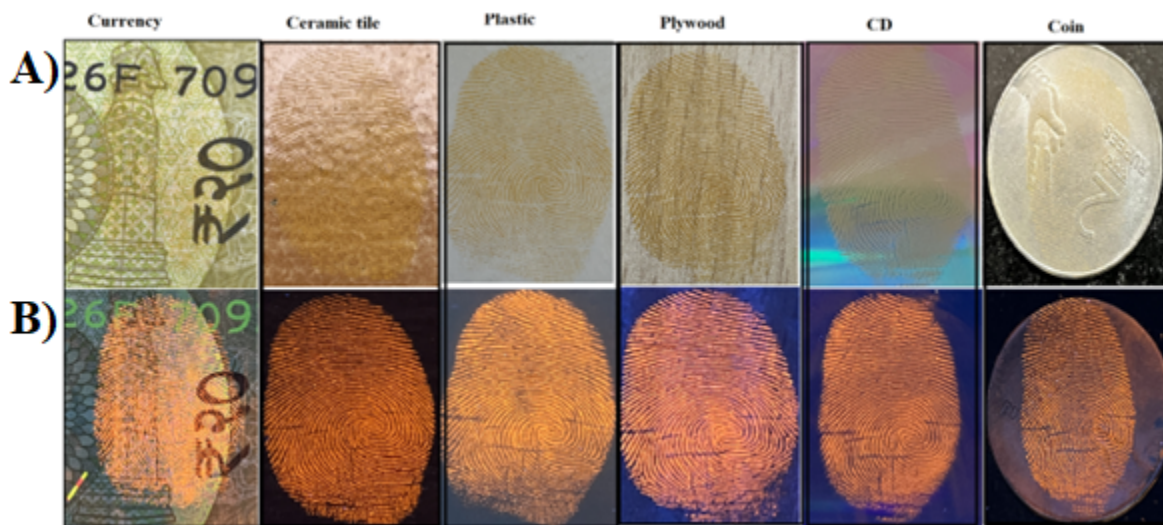


Figure S13. LFM developed on various non-porous substrates such as currency, ceramic tile, plastic, plywood, CD, coin A) under daylight, B) under UV light.

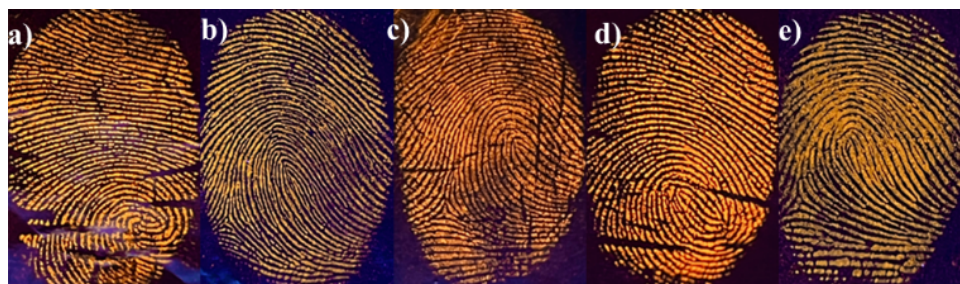


Figure S14. LFM developed on aluminium foil of different volunteers a) volunteer 1; b) volunteer 2; c) volunteer 3; d) volunteer 4; e) volunteer 5.

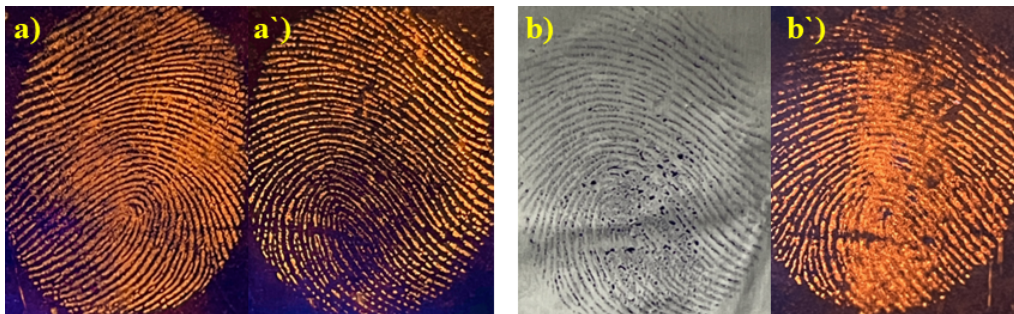


Figure S15. LFM developed on aluminium foil for aged sample a) after 7 days a') after 15 days in ambient atmosphere and Stained sample b) before treatment; b') After treatment with **Py-Pr-OH**.

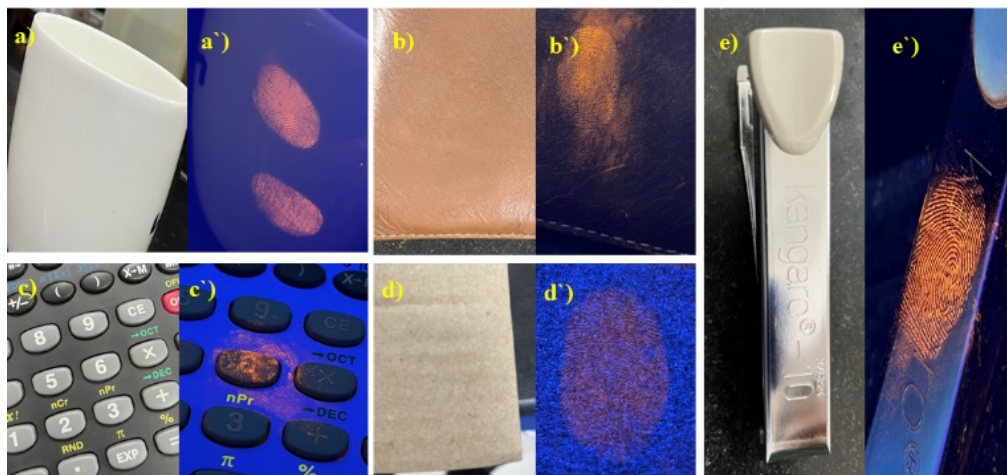


Figure S16. LFM developed on surfaces of common objects like a) coffee mug b) leather wallet c) calculator d) cardboard e) stapler under under day light a') coffee mug b') leather wallet c') calculator d') cardboard e') stapler under 365 nm UV light.

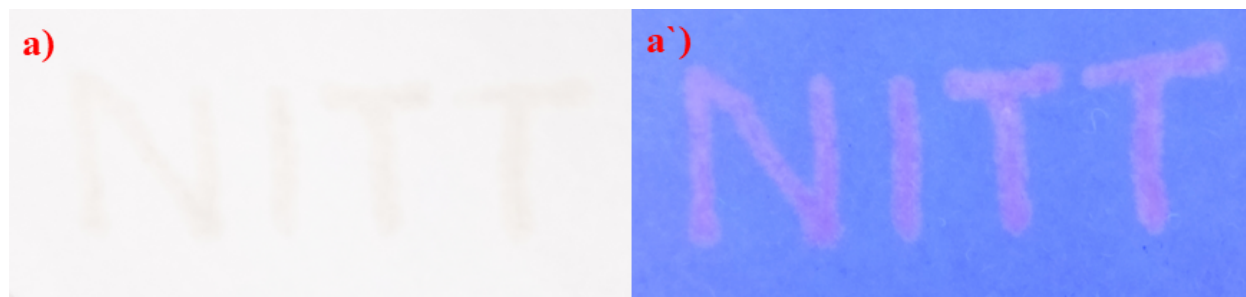


Figure S17. Anticounterfeiting labeling using **Py-Pr-OH** a) under natural light a') UV light (365nm)

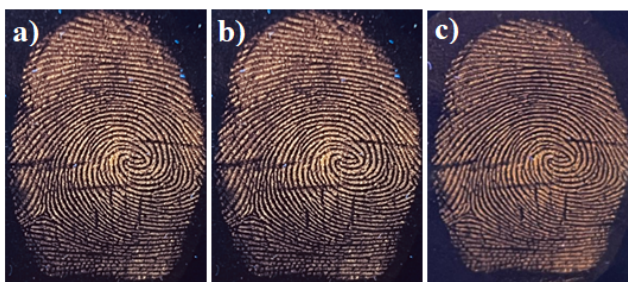


Figure S18. Fluorescence image of LFP developed using **Py-OH** after a) 7 days; b) 14 days; c) 30 days of ageing.

References:

- S1. APEX3, version 2017.3-0, and SAINT, version 8.38A, Bruker AXS Inc., Madison, WI, 2012, URL: <https://www.bruker.com>
- S2. Sheldrick, G. M. SADABS, University of Göttingen, Göttingen, Germany, 1996 (part of Bruker APEX3 software package (version 2017.3-0): Bruker AXS, 2017).
- S3. Sheldrick, G. M. SHELXTL XT – Crystal Structure Solution, version 2014/4, Bruker AXS, 2010–2014.
- S4. Sheldrick, G. M. SHELXL2014. University of Göttingen, Germany, 2014.
- S5. Sheldrick, G. M. *Acta Crystallogr. A* **2015**, *71*, 3–8.
- S6. Sheldrick, G. M. *Acta Crystallogr. A* **2008**, *64*, 112–122.