Electronic Supplementary Material (ESI) for Analyst.

Harnessing Long-lived Visible Phosphorescence to Eliminate Background Interference from Fingermark Images

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Supporting Information

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S1. General methods and synthesis of doped 4-**tpt** fingerprint powder

General methods

All chemicals used in this study were obtained from Sigma-Aldrich as analytical grade or better and used without further purification. Green Fluro-Magnetic Print Powder (Sirche Greencharge Powder) was sourced from Optimum Technology, Australia. Photoluminescent measurements were recorded at room temperature using a Cary Eclipse Fluorescence Spectrophotometer by Agilent Technologies using the solid sample holder accessory. Spectral data were interpreted using the Cary Eclipse software. ^{1}H-NMR spectra were recorded at 298 K on a Jeol ECS-400 spectrometers with the chemical shifts (δ) reported in parts per million (ppm) and referenced to deuterated chloroform ($CDCl_3$). The spectral data were analysed using either the software MestReNova (version 12), or TopSpin 4.0.8. Scaning Electron Microscopy images were recorded using a Hitachi S3400-N SEM. The system was equipped with Oxford Instruments EDX systems, running INCA software (version 7). Powder X-ray diffraction patterns were collected using the Rigaku Miniflex 600 (Cu Kα, λ = 1.5406 Å) over a 2θ range from 5 - 40 or 5 - 70 degrees with a step size of 0.02 degrees and a count time of 1 second/step. Software CrystalDiffract (version 6) was used to interpret the diffraction patterns. Forensic documentation of fingermark evidence was conducted in a dark room using either the Superlite M05 or S04 light sources, and a Sony α7 digital camera. The camera ISO setting was 160000 combined with a shutter speed of 1/10 s. Latent fingerprints were processed either by careful dusting the prints with a soft brush (squirrel hair) or by applying the powders directly to the fingermark and blowing away excess powder with pressurised airflow.

Synthesis of doped 4-tpt

The metastable form of 2,4,6-tris(4-pyridyl)-1,3,5-triazine was synthesised according to a modified literature procedure.[1] To a nitrogen-charged round bottomed flask were added 4-cyanopyridine (5.00 g, 48 mmol), 18-crown-6 (500 mg, 1.89 mmol), potassium hydroxide (125 mg, 2.23 mmol), mesitylene (2.25 mL) and pyridine (0.225 mL). Once the mixture was combined, it was heated at 250 °C for 4 hours with stirring. After this time, the mixture was slowly cooled to room temperature. The beige precipitate was isolated by filtration, washed twice with fresh pyridine and dried under vacuum. The washed and dry material appeared as a cream-coloured fine powder (Yield: 3.0 g; 60%). The inclusion of pyridine in the synthesis in this ratio to mesitylene yielded a product doped with 7.3% pyridinium salt. Omitting the pyridine as a solvent yielded undoped 4-tpt as confirmed by ^{1}H-NMR spectroscopy (ESI, S2).

Modifying the adhesion properties of the doped 4-**tpt** was achieved by dissolving 366 mg of rosin (*i.e.* (2R,3S,4S,5R,6R)-2-(hydroxymethyl)-6-[(E)-3-phenylprop-2-enoxy]oxane-3,4,5-triol) in neat isopropanol (20 mL). Doped 4-**tpt** (1.442 g) was then suspended in this rosin solution. The solvent was then removed from the mixture using a rotary evaporator, and the resultant solid was transferred to a drying dish and left to completely air dry over 48 hours. The off-white powder was then transferred to an agate mortar and pestle and ground for 1-2 minutes to homogenise any large clumps of powder. The resultant powder had an off-white appearance and a free-flowing consistency.

S2. Selected ^{1}H-NMR spectra for the 4-**tpt** powders.

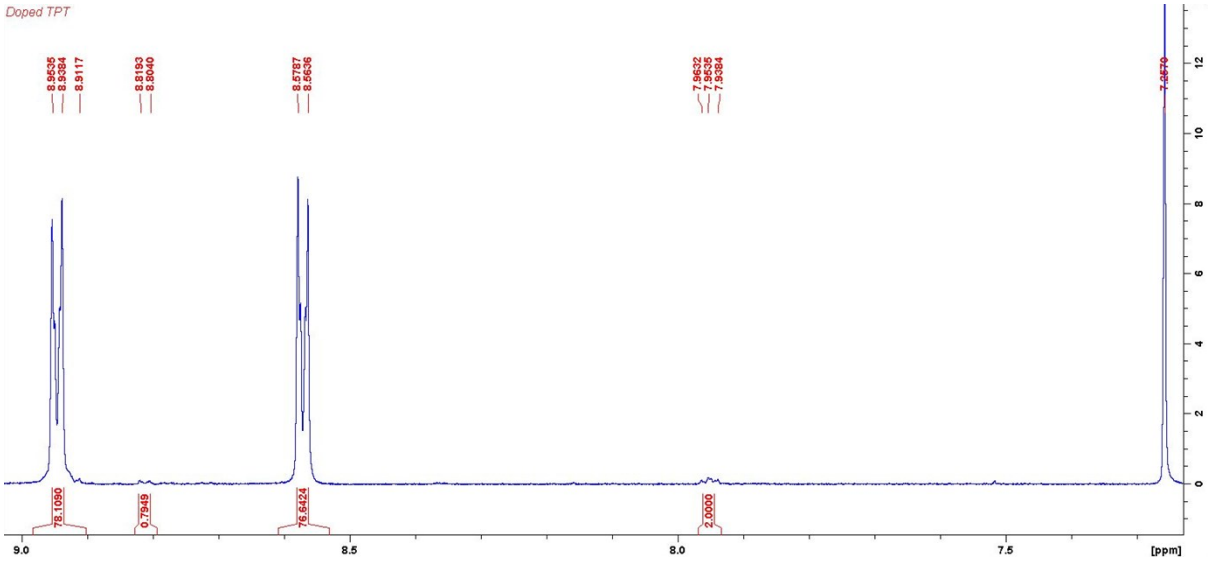

Fig. S1: ^{1}H-NMR expansion of the doped 4-**tpt** powder. The doublet of doublets at 8.57 and 8.94 ppm correspond to the 4-**tpt** resonances. The small triplet at 7.95 ppm, multiplet at 8.81 ppm and overlapped multiplet at ca. 8.91 ppm correspond to the PyH dopant (see Fig. S2 for enlargement). The ratio of dopant to tpt present in the as-synthesised was calculated to at (1 : 12.77) based on the resonances at 7.95 and 8.57 ppm respectively. This gave the reported dopant ratio of 7.3%.

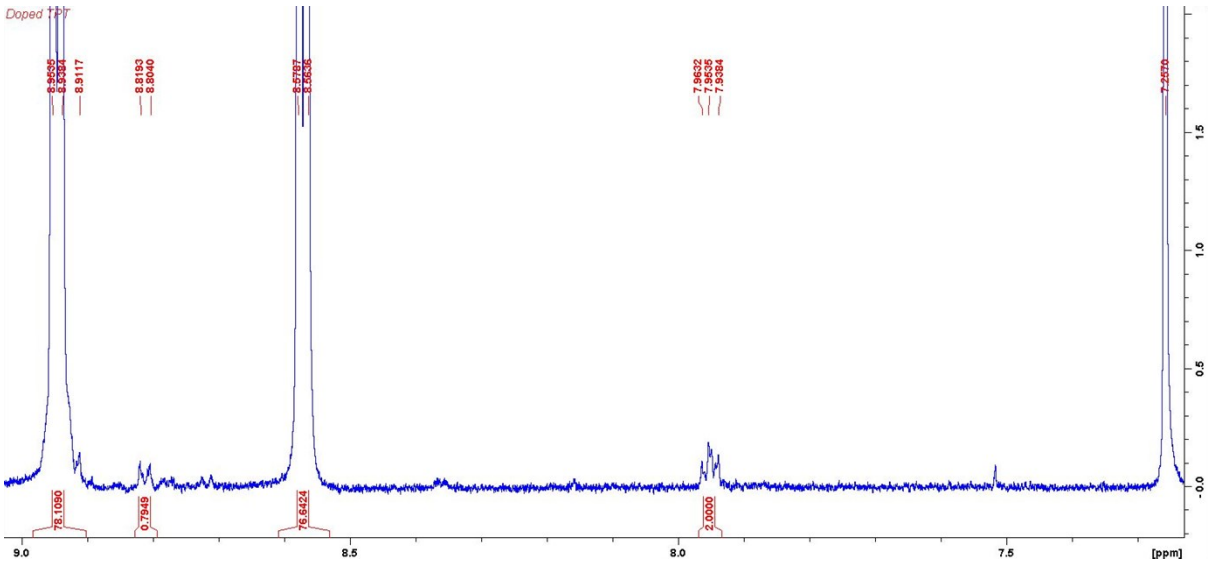

Fig. S2: A zoomed in version of Fig. S1 showing the PyH resonances in greater detail.

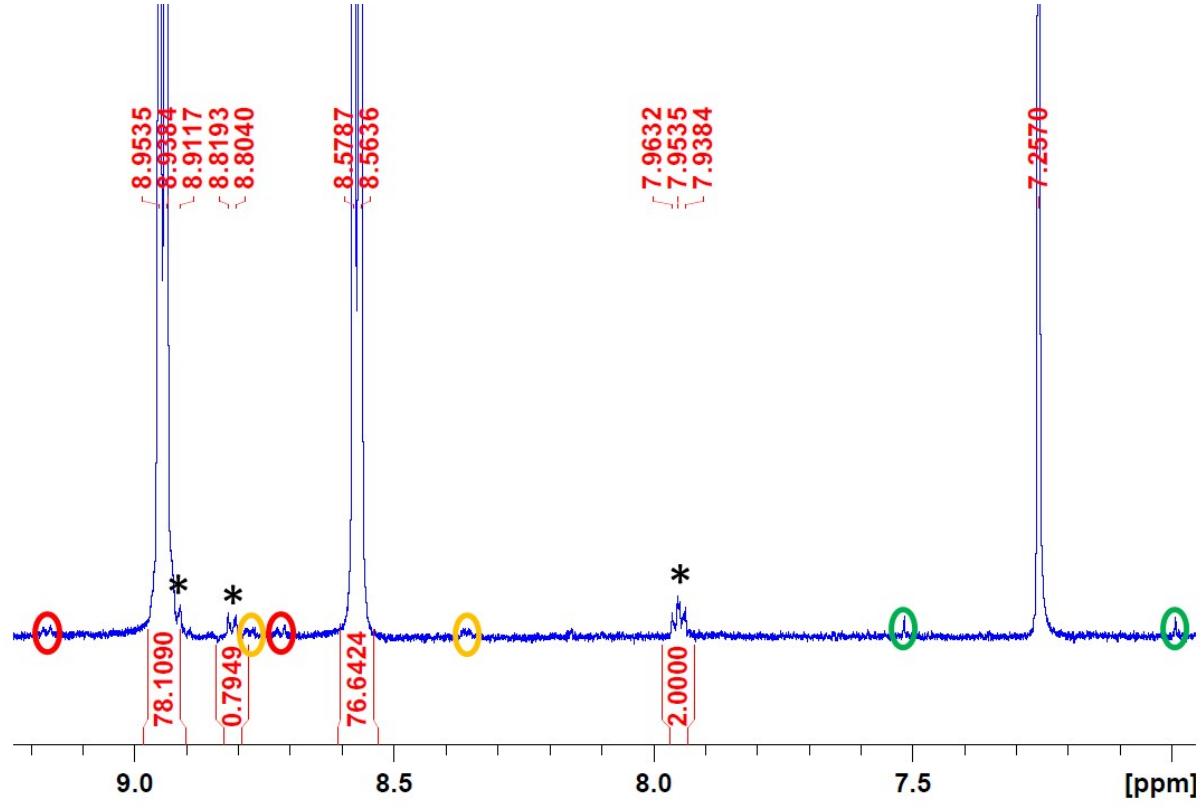

Fig. S3: An enlargement of Fig. S1 highlighting the location of satellites derived from both 4-**tpt** resonances and the CDCl3 peak highlighting the unique locations of the PyH resonances (shown asterisked).

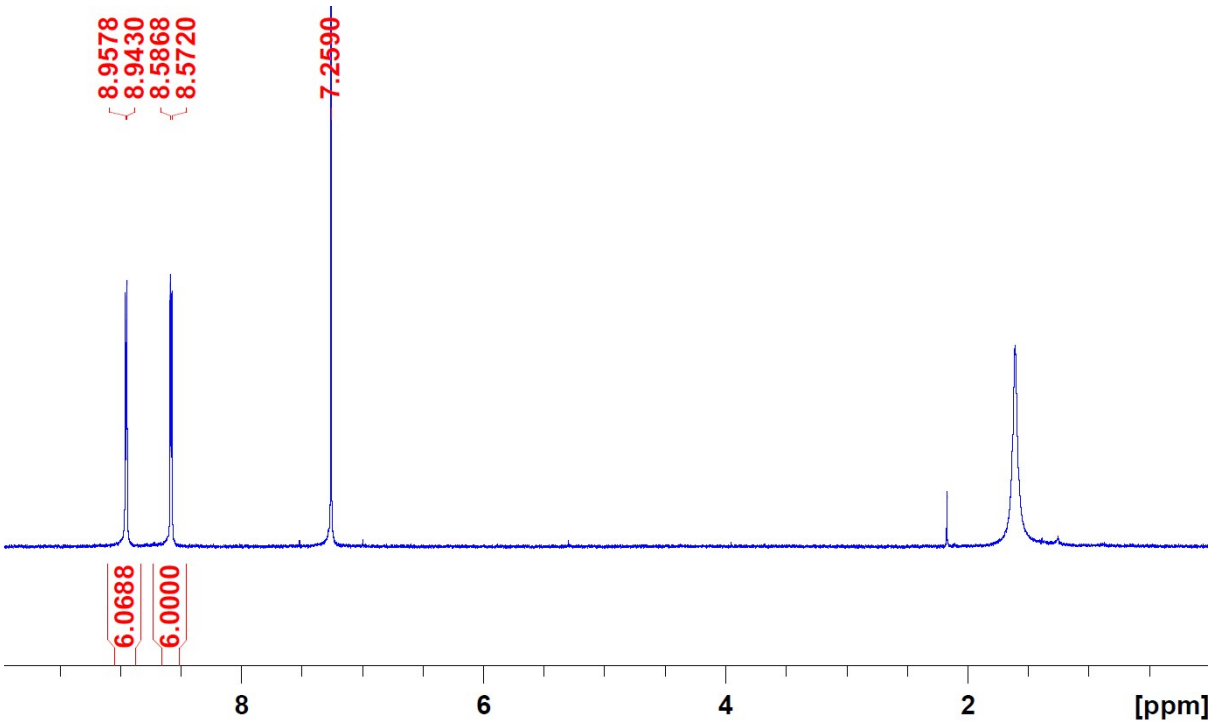

Fig. S4: ^{1}H-NMR spectrum of undoped 4-**tpt** made by omitting pyridine from the synthesis.

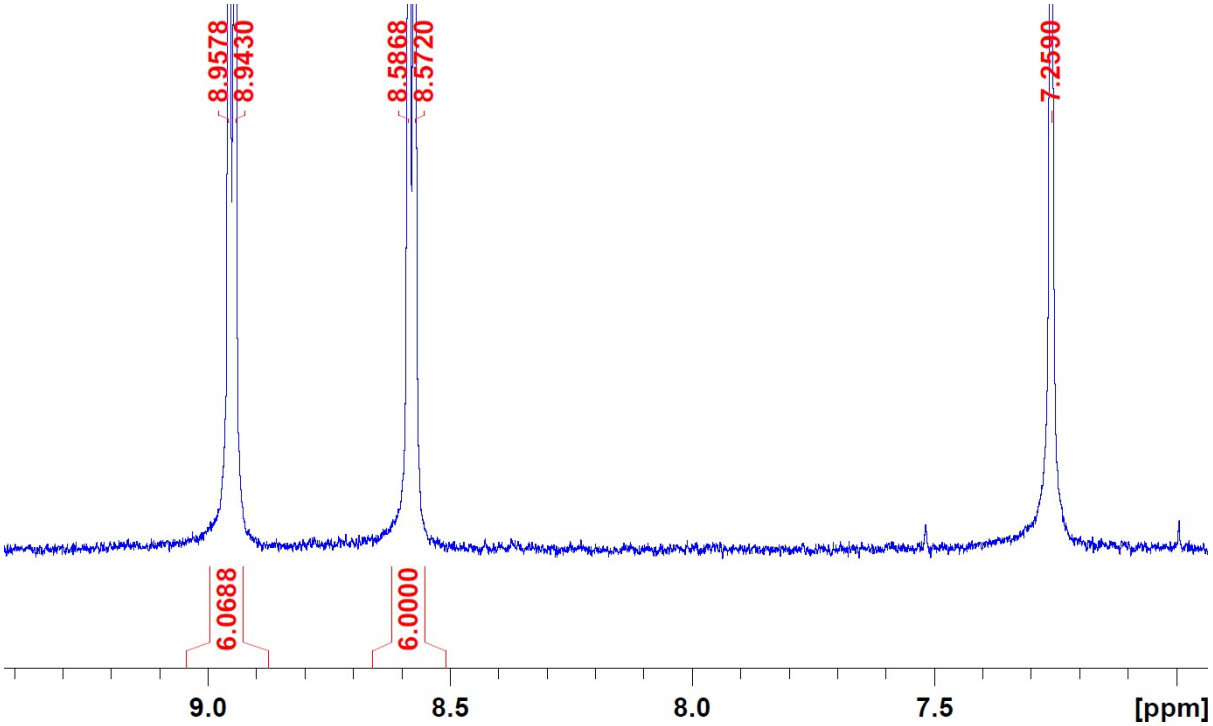

Fig. S5: A zoomed in version of the ^{1}H-NMR spectrum shown in Fig. S4 of undoped 4-**tpt**.

S3. Powder X-ray diffraction (PXRD) patterns of the metastable 4-**tpt** polymorph.

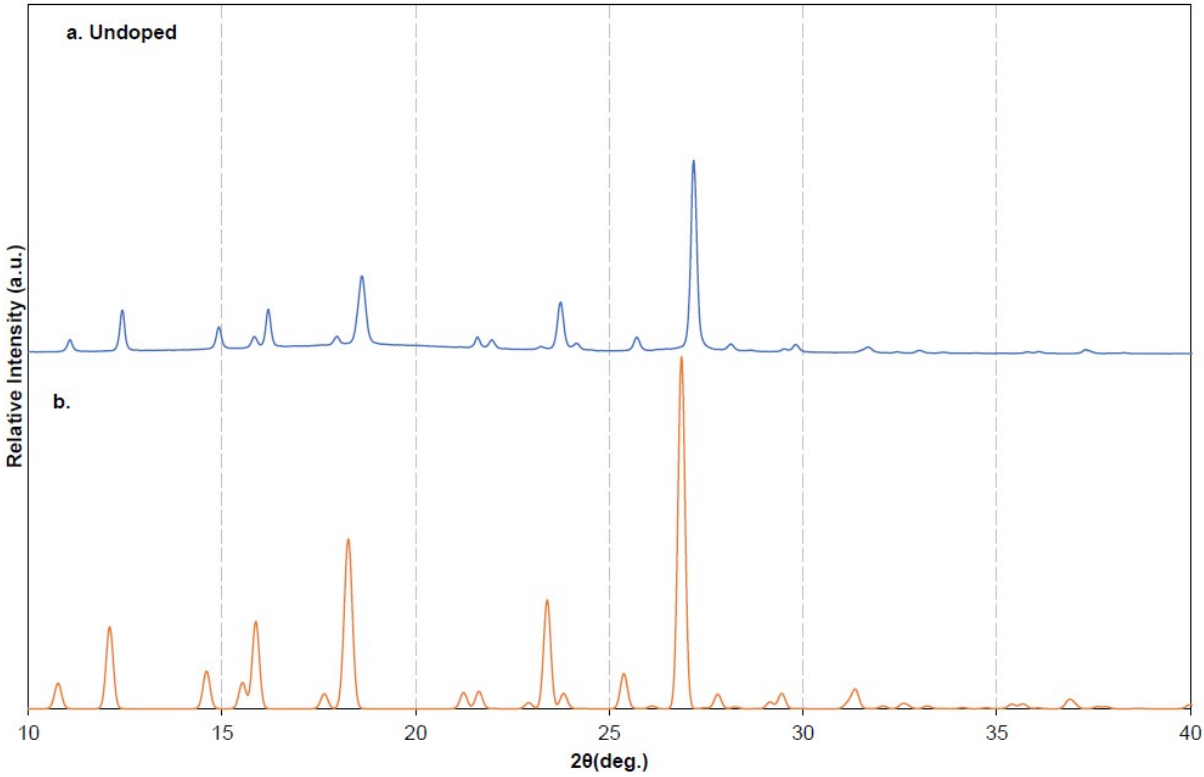

Fig. S6: Top (blue trace): undoped 4-**tpt** as-synthesised. Bottom (orange trace): the predicted PXRD pattern for the metastable form of **tpt** as reported in the literature.[2]

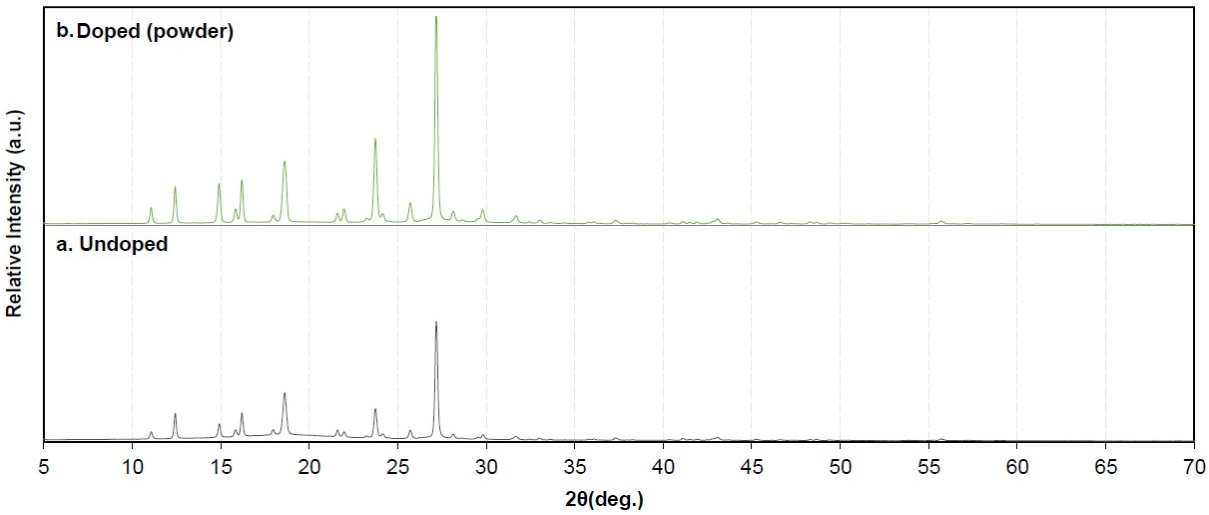

Fig. S7: Bottom (black trace): undoped 4-**tpt** as-synthesised. Top (green trace): doped 4-**tpt** as synthesised. It can be seen that the metastable form is retained upon doping.

S4. Influence of pyridine doping on fluorescent intensity.

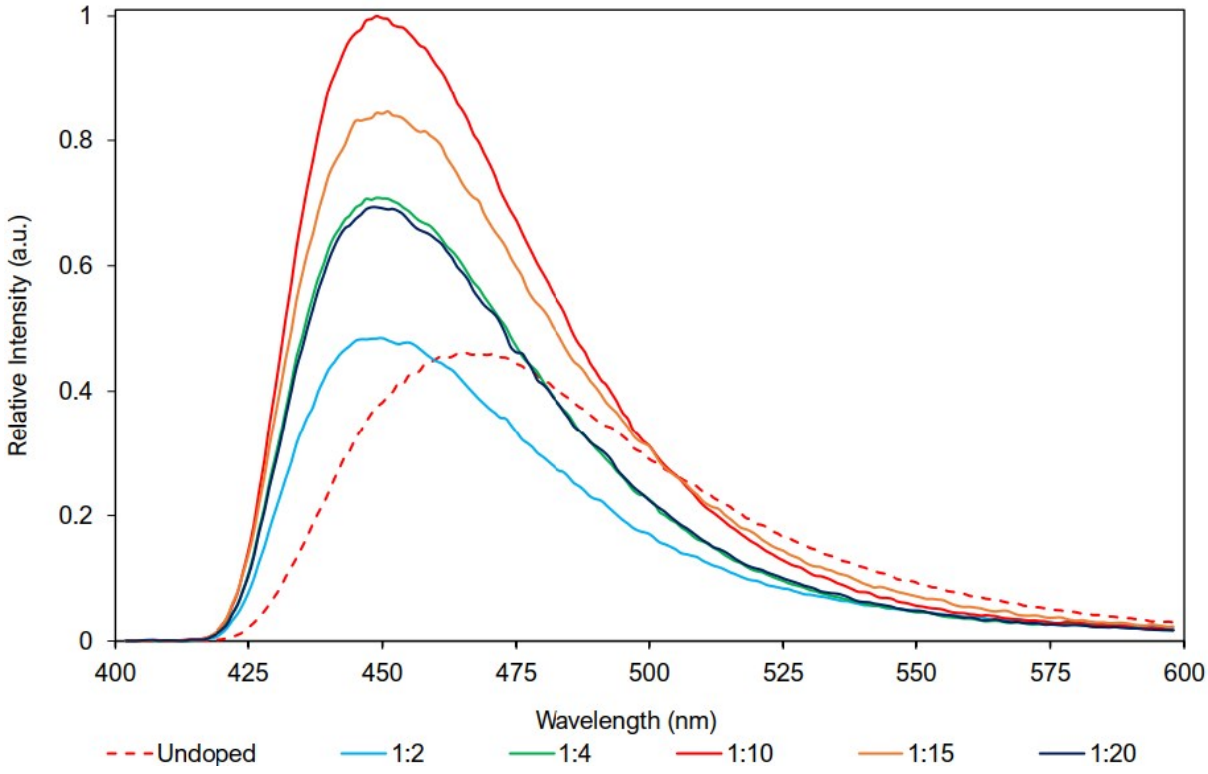

Fig. S8: The effect of altering the ratio of pyridine to mesitylene when synthesising the 4-**tpt** powder. The ratios above correspond to Pyridine:Mesitylene ratios used in the reaction solvent. Adding no pyridine gave the 'undoped' dashed red trace. The as-synthesised doped material had a ratio of pyridine (0.225 mL) to mesitylene (2.25 mL) corresponds to the 1:10 trace. The quantities of reagents used was kept constant with that reported in section S1, and the total volume of solvent mixture used was kept to ~2.5 mL.

S5. Scanning electron microscopy images of as-synthesised doped 4-**tpt**.

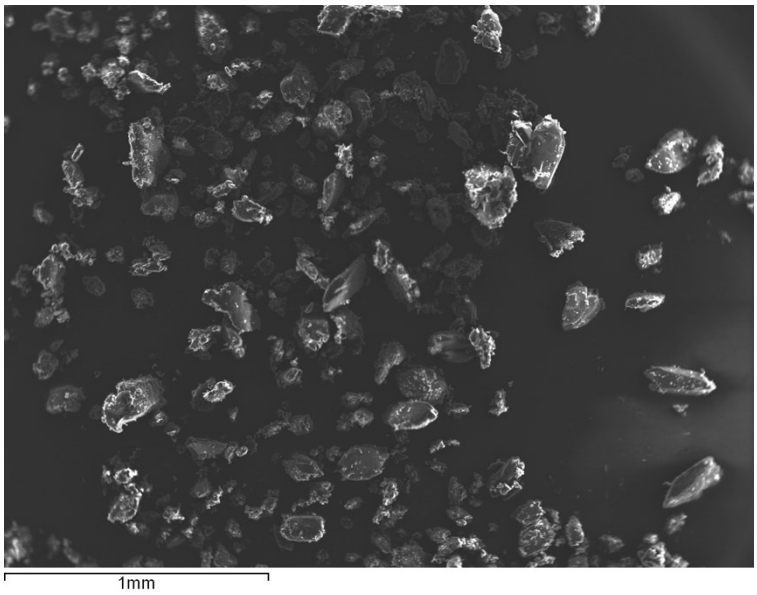

Fig. S9: A general cross-section of sizes for the as-synthesised doped 4-**tpt**. While a range of sizes are evident, an average particle diameter of 145 μm can be inferred (see Fig. S10 for a representative enlargement).

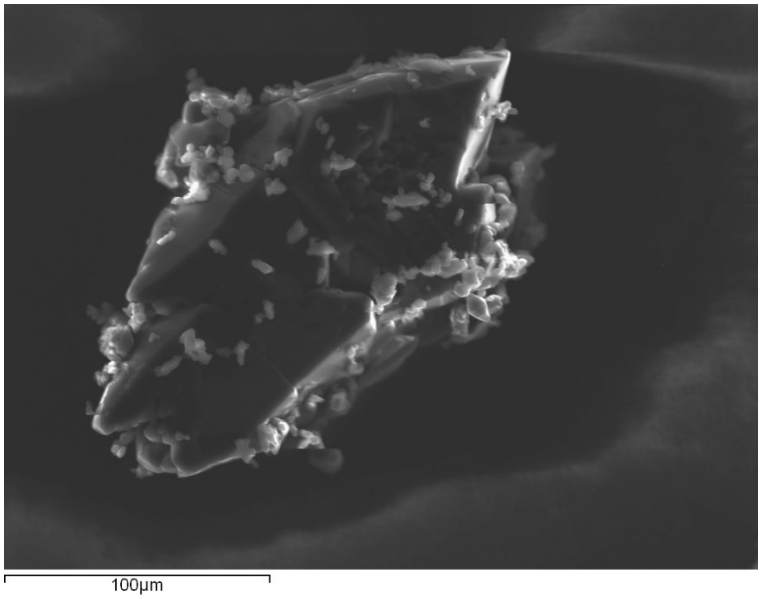

Fig. S10: A magnified image of a representative particle drawn from the same sample shown in Fig. S9.

S6. Fingermarks on additional surfaces treated with 4-**tpt** fingerprint powder.

White tile:

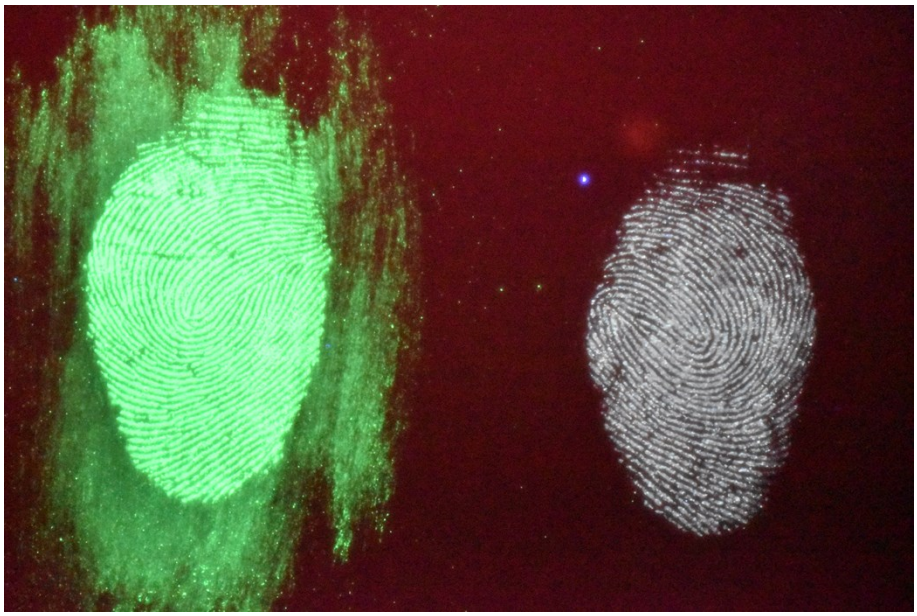

Fig. S11: Both commercial Fluro-Magnetic Print Powder (left) and doped 4-**tpt** powder (right) under UV Irradiation (λ = 365 nm). Surface is white tile.

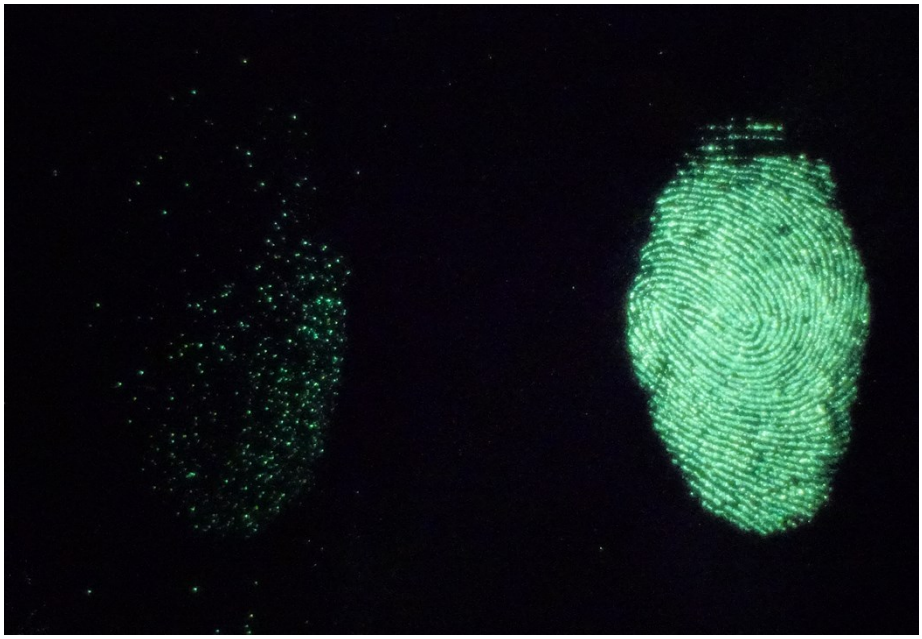

Fig. S12: Phosphorescent afterglow imaging.

Glossy barcode:

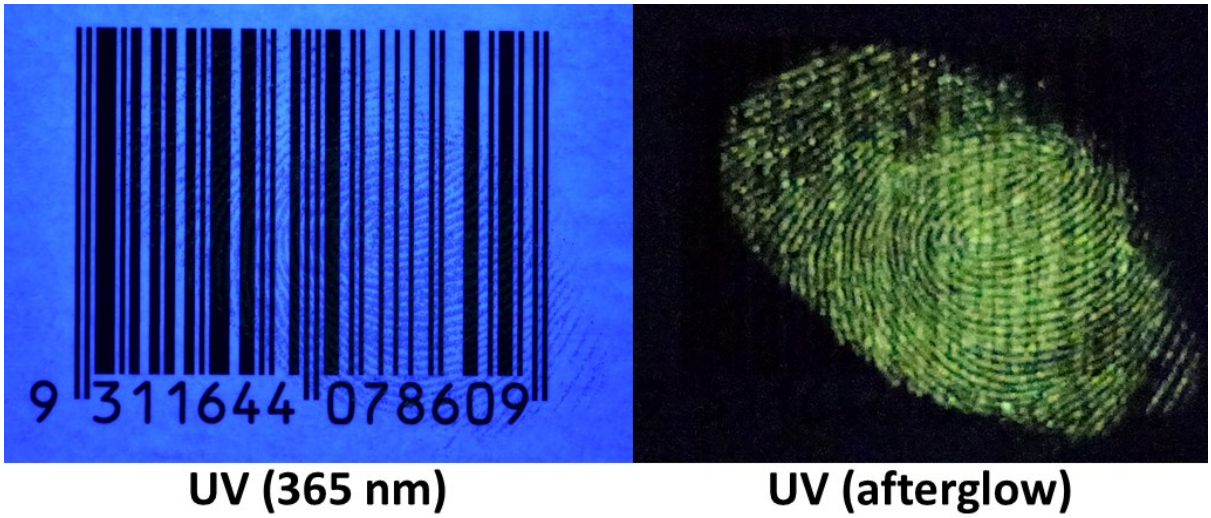

Fig. S13: Constant UV (left) and phosphorescent afterglow imaging (right). Note: only 4-**tpt** powder shown.

Glossy map:

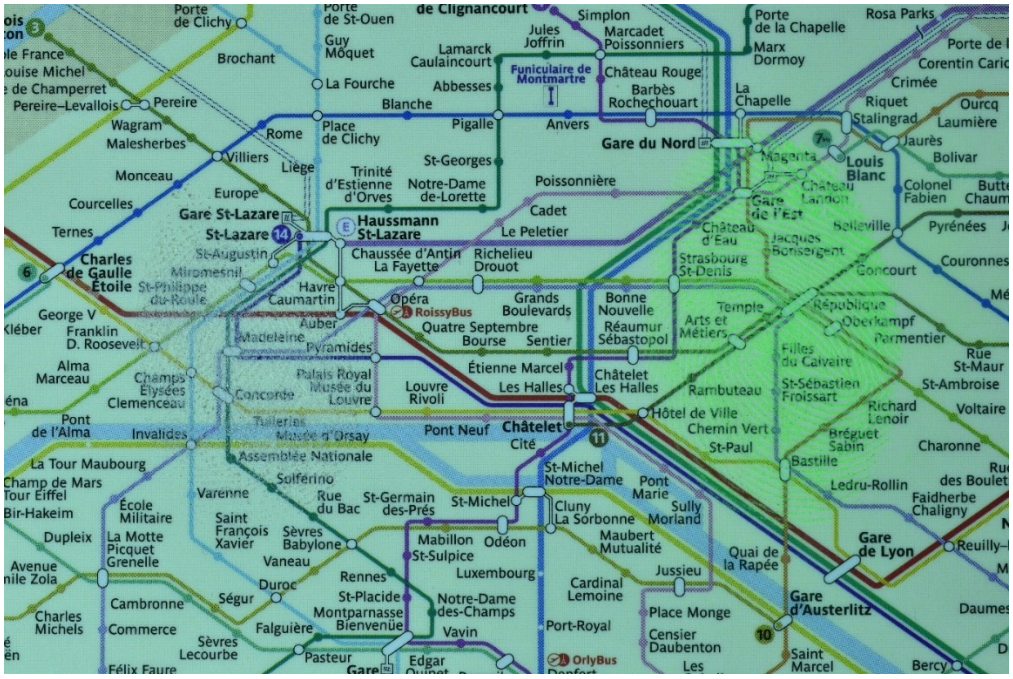

Fig. S14: Both commercial Fluro-Magnetic Print Powder (right) and doped 4-**tpt** powder (left) under white light.

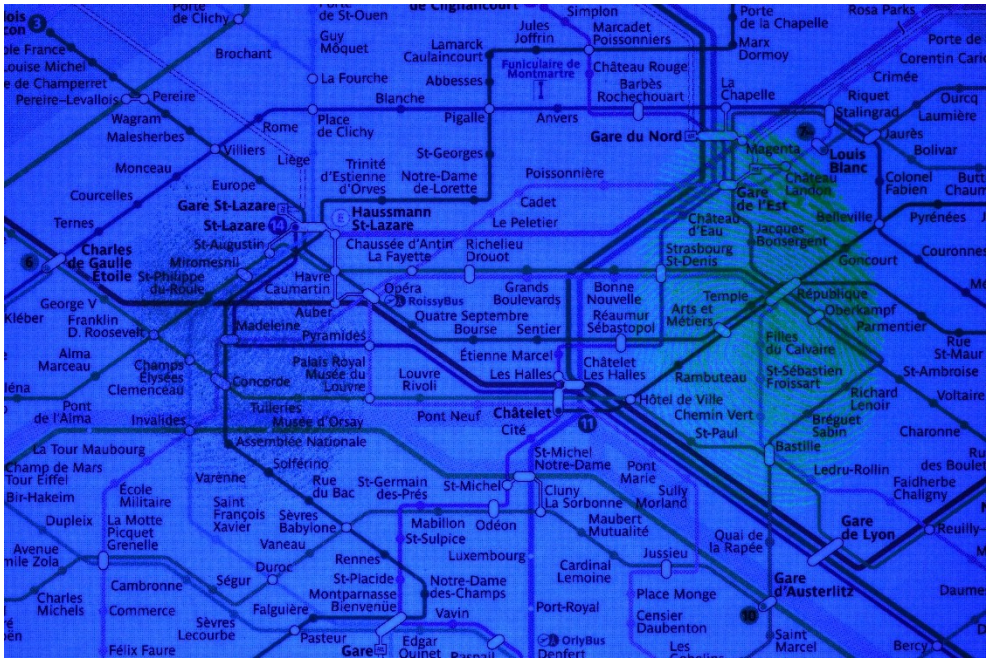

Fig. S15: Both commercial Fluro-Magnetic Print Powder (right) and doped 4-**tpt** powder (left) under UV Irradiation (λ = 365 nm).

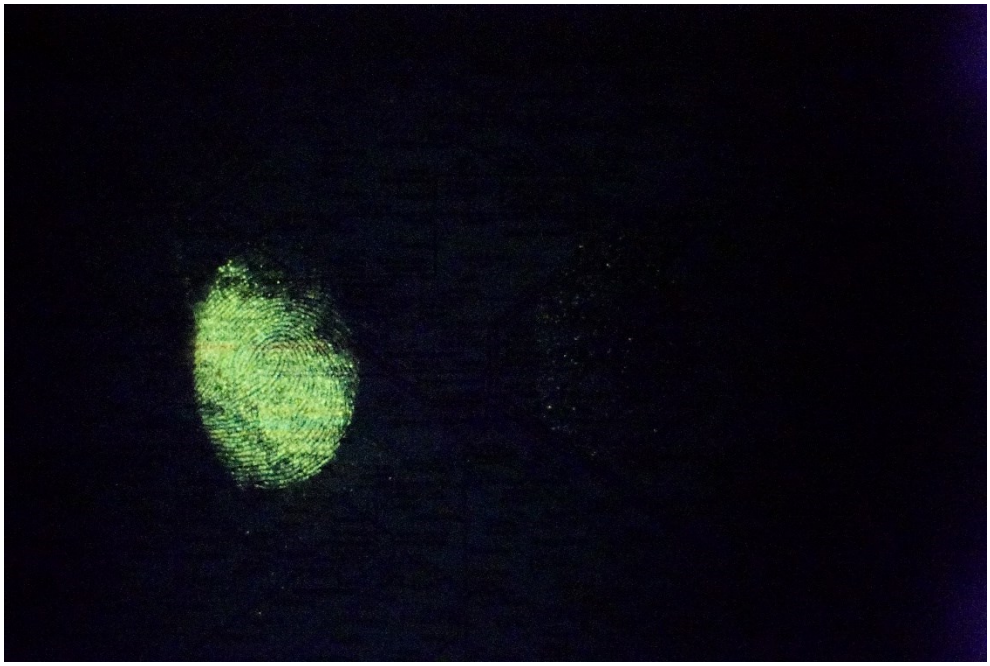

Fig. S16: Phosphorescent afterglow imaging showing only the 4-**tpt** powder.

S7. References

[1] Barrios, L. A.; Ribas, J.; Aromi, G.; Ribas-Arino, J.; Gamez, P.; Roubeau, O.; Teat, S. J. *Inorganic Chemistry*, **2007**, *46*, 7154–7162.

[2] Yuan, L.; Xing, M.; Pan. F. *Acta Cryst.* **2019**, *B75*, 987–993.