

# Fluorescent TiO<sub>2</sub> powders prepared using a new perylene diimide dye: Applications in latent fingerprint detection

## ABSTRACT

A new, highly fluorescent dye was synthesised using oleylamine combined with a perylene dianhydride compound. The new dye was characterised by <sup>1</sup>H NMR, UV-visible spectroscopy and fluorescence spectroscopy as well as quantum yield. The dye was adsorbed onto titanium dioxide nanostructured particles for use as a fingerprint detection powder. The new fluorescent powder was applied to latent fingerprints deposited onto different non-porous surfaces and compared with commercial fluorescent powders.

The powder exhibits strong fluorescence at 650-700 nm under excitation at 505 nm. On glass surfaces, the new powder gave images showing tertiary-level detail of the fingerprint ridges with almost no background development. Compared with current magnetic fluorescent powders, the new powder was slightly weaker in fluorescence intensity but produced significantly less background development, resulting in a better contrast between the fingerprint and the substrate.

## 1. Introduction

One of the most common types of physical evidence found at crime scenes is fingerprint evidence. Fingermarks at a scene or on items submitted to the laboratory may be visible or they may be latent; latent marks require enhancement for them to be adequately exploited [1]. This work focuses on latent fingermarks on typical non-porous surfaces such as glass, plastic, metal, and gloss-painted surfaces. Fingerprint residues left on non-porous surfaces are not absorbed therefore their original form is often maintained. For fixed surfaces at a crime scene, powdering remains the primary fingerprint detection method [2]. This physical method of enhancement relies on the mechanical adherence of powders to the moisture and/or oily components of the skin ridge deposits [3].

Nanocrystalline titanium dioxide ( $\text{TiO}_2$ ) has been investigated extensively due to its interesting optical, electrical, and photocatalytic properties. It is commonly used as a functional material, adsorbent, cosmetic, catalyst, and gas sensor [4-6]. There are several reports describing the use of  $\text{TiO}_2$  particles in latent fingerprint development. Saunders used a  $\text{TiO}_2$  particle suspension to visualize fingermarks on porous and non-porous surfaces in 1996 [7]. It was proposed that there is no advantage in using nanoparticulate  $\text{TiO}_2$  although limited characterization data about the particles used was presented. Wade [8] found that micron-sized titanium dioxide particles gave good results developing latent fingermarks on dark non-porous surfaces where it could be used as a white fingerprint powder or a white small particle reagent. Bergeron showed that  $\text{TiO}_2$  particles in methanol could enhance the visualisation of blood prints on non-porous and semi-porous surfaces [9]. Polimeni et al. [10] and Cucè et al. [11] reported that suspended  $\text{TiO}_2$  particles developed latent fingermarks on wet surfaces. Williams [12] showed that  $\text{TiO}_2$  could be applied in a paste form with a brush, sprayed on as a solution, or evidence could be submerged in the reagent itself to develop prints on both sides of dark coloured electrical tapes and duct tapes.

Perylene and perylene diimide compounds are widely utilized synthetic dyes. They were applied initially as vat dyes and pigments due to their chemical inertness as well as their broad

range of colours, red to violet and even black [13]. More recently they have been investigated as n-type semiconductors [13,14], in electrophotography [15] and photovoltaics [16]. Of interest to the current work is their high fluorescence quantum yield and photostability [13-16].

In a previous article [17], we reported the use of oleylamine-stabilised gold and silver nanoparticles for visualizing latent fingerprints. These particles developed latent fingerprints on non-porous surfaces with minimal background staining. We attributed their preferential binding to the fingerprint ridges, which contain oily components, to the lipophilic nature of the long alkyl chain substituents. Titanium dioxide on its own may not show good contrast on some surfaces as it is plain white, however it does deposit on fingerprint ridges as mentioned above. We anticipated that combining TiO<sub>2</sub> particles with a robust fluorescent dye bearing lipophilic substituents may increase the utility of TiO<sub>2</sub> in latent fingerprint detection.

In this work, we report the synthesis and characterization of a new perylene diimide derivative, the preparation of TiO<sub>2</sub> particles coated with the new dye, and their use as fluorescent powders for the detection of latent fingerprints.

## **2. Experimental**

### *2.1. General*

Oleylamine, imidazole, and 3,4,9,10-perylenetetracarboxylic dianhydride were purchased from Aldrich and used as received. Degussa P25 titanium dioxide was purchased from Degussa. Titanium dioxide (<5 micron particle size) was purchased from Aldrich.

A BVT 3000 Bruker Spectrospin was used as to record <sup>1</sup>H NMR spectra. Spectra were referenced internally to residual protic solvent (CHCl<sub>3</sub>, δ 7.26). UV-visible spectra were recorded on a Varian Cary 3E UV-Visible Spectrometer. Fluorescence spectra of the dye in solution and of the dye absorbed onto titanium dioxide particles were recorded on a Varian Cary Fluorescence Spectrometer. Fingermarks were imaged on a Rofin Poliview, with illumination by a Rofin Polilight PL10.

## 2.2. Synthesis and Characterisation of the *N,N'*-Dioleoyl-3,4,9,10-perylenedicarboximide dye, **1** (see Scheme 1)

3,4,9,10-Perylenetetracarboxylic dianhydride (1.0 g, 2.54 mmol) and imidazole (12 g) were heated with stirring in a round bottom flask at 160 °C. After all of the imidazole had melted, the perylenetetracarboxylic dianhydride formed a suspension. Oleylamine (1.8 ml, 5.4 mmol) was then added to the mixture. The resultant mixture was stirred for 4 hours at 160°C and then, before it completed cooling; ethanol (20 mL) was added to dissolve the remaining imidazole. Aqueous HCl (30 mL, 2 M) was added and the mixture was allowed to stand for approximately 1 hour. The dark brown precipitate was collected by vacuum filtration and washed with distilled water. The product was purified by column chromatography on silica gel (dichloromethane/acetone 20:1). Yield was 0.49 g (21%) of a deep red waxy material. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 25°C): δ = 0.87 (broad t, 6H, CH<sub>2</sub>CH<sub>3</sub>), 1.25 – 2.01 (m, 56H, CH<sub>2</sub>), 4.19 (t, J = 15 Hz, 4H, CH<sub>2</sub>N), 5.34 (m, 4H, CH=CH), 8.50 – 8.63 ppm (m, J = 13 Hz, 8H, arom. CH): UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> = 457 (17480), 488 (47300), 524 (74640). Fluorescence (CH<sub>2</sub>Cl<sub>2</sub>, λ<sub>ex</sub> 488 nm): λ<sub>max</sub> = 535, 574, 618. Fluorescence Quantum Yield (CH<sub>2</sub>Cl<sub>2</sub>, λ<sub>ex</sub> 525 nm) 0.4.

## 2.3. Preparation of dye-coated TiO<sub>2</sub> particles

To prepare TiO<sub>2</sub> coated with **1**, 10 mL of a 10 mM solution of the fluorescent dye in dichloromethane was added to 0.3 g of TiO<sub>2</sub> particles. Immediately the TiO<sub>2</sub> particles turned pink. The mixture was allowed to settle and the solution decanted off and the remaining powder was rinsed six times with 10 mL of dichloromethane and the particles were allowed to dry in air.

## 2.4. Application to Fingerprint Detection

Fingermarks were deposited after wiping fingers over the forehead in succession and then recharged with sebum from the forehead. All fingerprint marks were from the one donor who gave

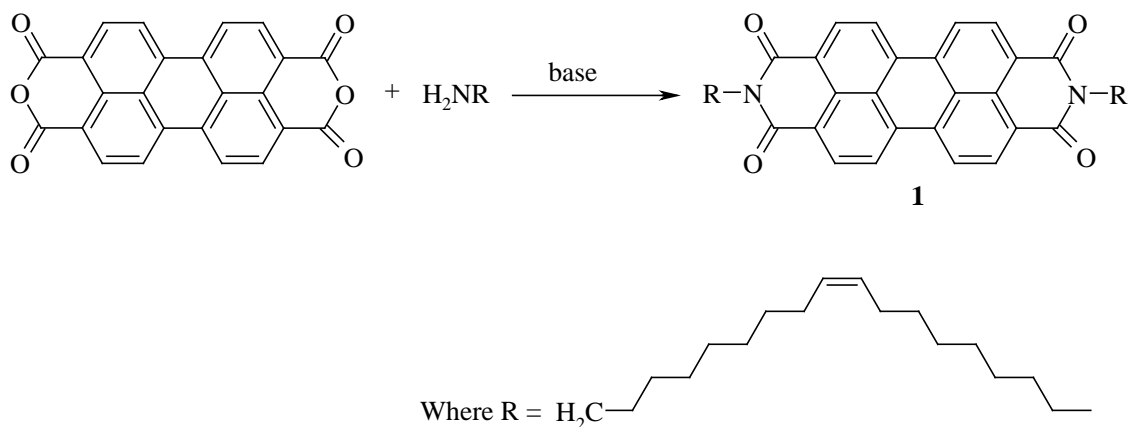
good quality prints. The middle print deposited in each set was bisected for comparison between the perylene dye/titanium dioxide particles and other fingerprint powders. The left hand side of deposited prints was powdered with fluorescent dye/TiO<sub>2</sub> particles. The right hand side of the surface was developed with either Blitz Green or Black Emerald fluorescent magnetic powders. Each pair was examined and images were taken with a Poliview image capture system (Rofin Australia) using 505 nm illumination and a 575 nm long-pass barrier filter. A microscope image in transmission mode was acquired on a Leica DMLM microscope.

Glass (microscope slides), plastic (polyethylene bags) and painted wood (from dismantled furniture) were used for comparison experiments as non-porous substrates. 6-Optitech brushes, Blitz Green and Black Emerald fluorescent magnetic powders were purchased from Lightning Powder, USA.

We anticipated that particles coated with long chain alkyl groups, providing a lipophilic surface, would be attached to the lipid components of the fingerprint. To investigate this further, an oil mark experiment was conducted. Mineral oil was diluted with volatile solvents and a circular pipette tip was used as a stamp to deposit a ring on glass. The sample was allowed to evaporate at room temperature and then brushed with the fluorescent TiO<sub>2</sub> powder in the same fashion as described above for fingerprints.

### 3. Results and Discussion

#### 3.1. Dye synthesis and characterisation

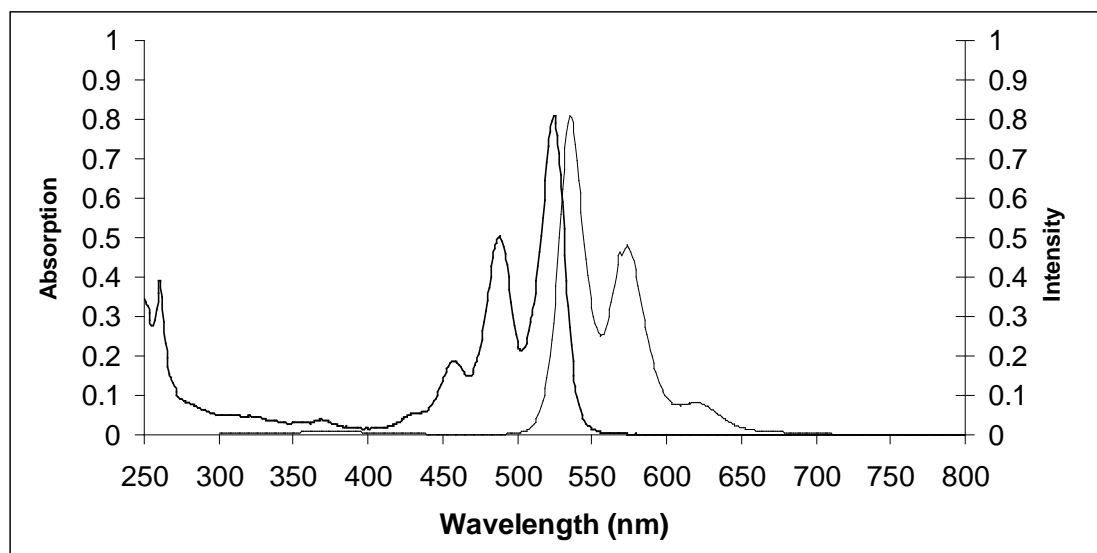


**Scheme 1.** Synthesis of new perylene diimide compound **1**.

The synthesis of the new dye, **1**, was achieved by modification of a literature procedure [18]. The reaction of oleylamine with 3,4,9,10-perylenetetracarboxylic dianhydride in imidazole at 160 °C, followed by purification by silica column chromatography gave **1** in 21% yield (Scheme 1).

The  $^1\text{H}$  NMR spectrum contains signals assigned to the perylene protons at  $\delta$  8.50 – 8.63, in agreement with chemical shifts reported for similar compounds [18, 19]. A signal at  $\delta$  5.34 is assigned to the protons associated with the carbon-carbon double bonds located in the C18 chains. This chemical shift is virtually unchanged compared to that of free oleylamine. A signal at  $\delta$  4.19 is assigned to the protons directly adjacent to the N atoms. This resonance is significantly shifted compared to that of the free amine, which is observed at  $\delta$  2.68, and is consistent with the expected shielding due to the close proximity to the planar aromatic core. The remainder of the signals assigned to the alkyl chain are seen in the region  $\delta$  0.87 – 2.01.

The UV-visible spectrum of **1** is typical of perylene diimide compounds [20] with strong absorption bands at 457, 488 and 524 nm, as shown in Figure 1, assigned to  $\pi$ - $\pi^*$  transitions [21].

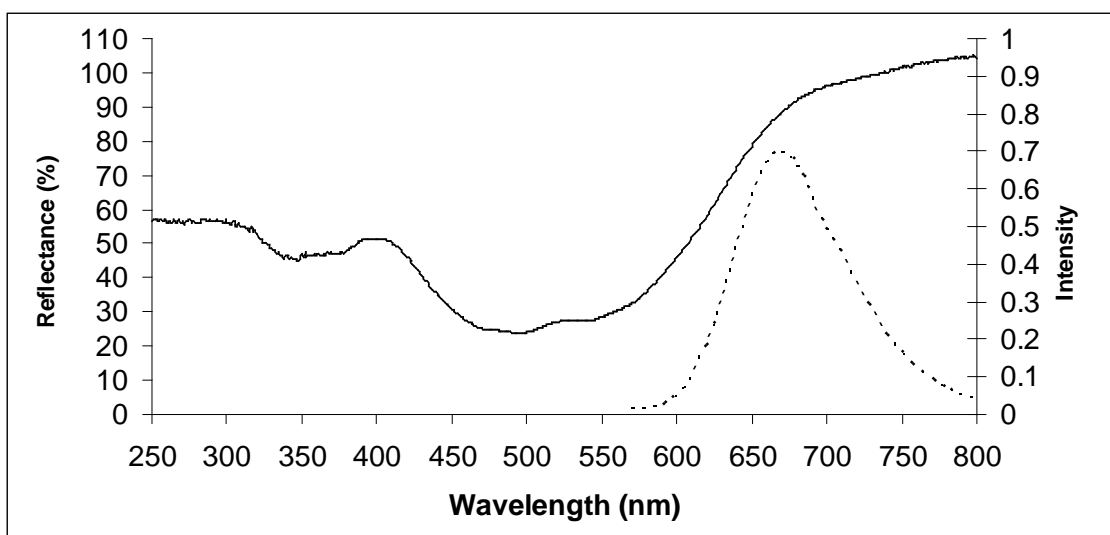


**Figure 1.** UV-visible absorbance (solid line) and emission (dashed line, excitation at 488nm) spectra of **1** in dichloromethane.

Fluorescence maxima are observed at 535, 574 and 618 nm in dichloromethane solutions of **1** (Figure 1, dashed line) and are also typical for this class of compound [22]. A fluorescence quantum yield of 0.4 (in dichloromethane solution) was measured using Rhodamine 6G as reference. The quantum yield of **1** is moderate in comparison with some other modified perylene dyes [20, 23-25].

### 3.2. Dye-coated $\text{TiO}_2$ particles

The new perylene dye readily adsorbs onto  $\text{TiO}_2$  particles. A 10 mmol solution of **1** in dichloromethane added to  $\text{TiO}_2$  particles followed by rinsing six times with dichloromethane gave a pink coloured powder.

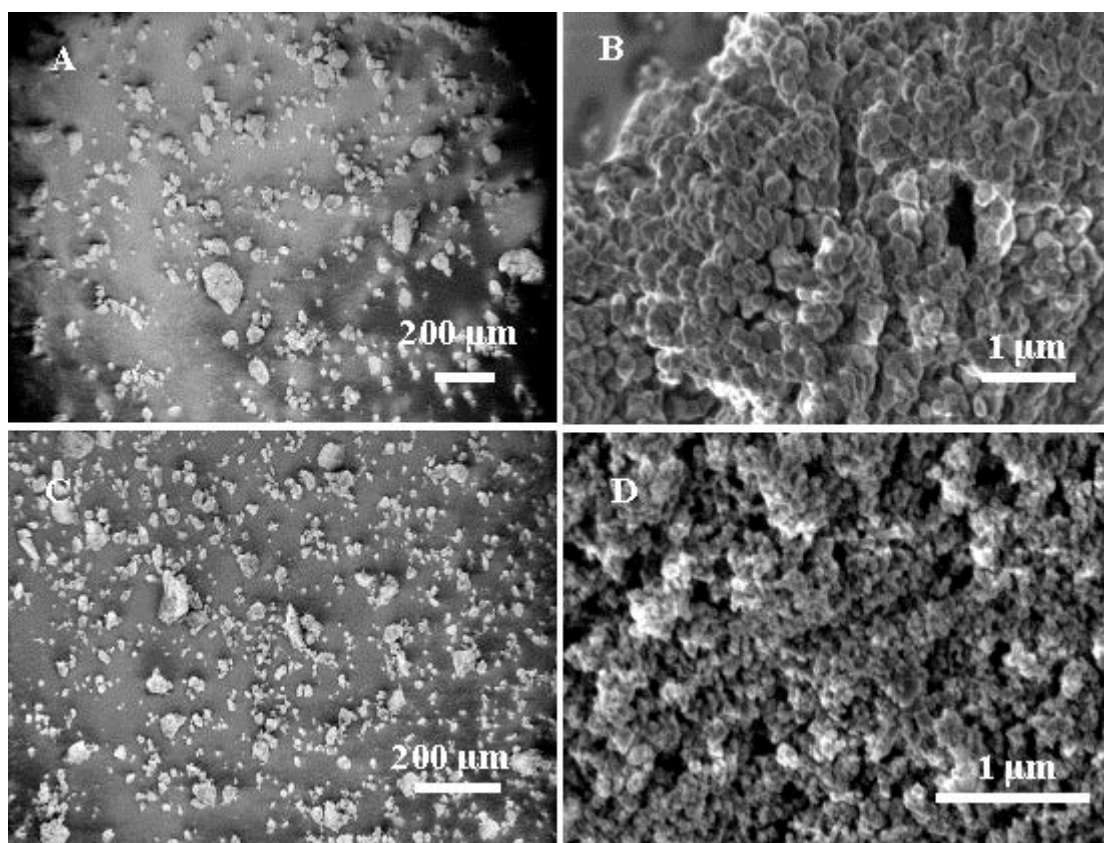


**Figure 2.** Reflectance (solid line) and emission (dashed line, excitation at 524 nm) spectra of  $\text{TiO}_2$  particles coated with **1**.

Figure 2 shows the reflectance spectrum of dye-coated  $\text{TiO}_2$  particles. Instead of the three absorption bands observed in solution, a broad band with a minimum reflectance at 495 nm is observed, similar to other perylene diimide dyes [22, 26].

The emission spectrum of  $\text{TiO}_2$  particles coated with **1** exhibits a broad fluorescence band with a peak at 670 nm (Figure 2). The emission peaks observed at 535 and 574 nm in solution are absent in the surface-adsorbed sample. The band observed at 670 nm may be assigned to an excited-state dimer (excimer) emission resulting from a high surface concentration of the dye [27, 28].





**Figure 3.** SEM images of TiO<sub>2</sub> powders after coating with **1**. A: Aldrich TiO<sub>2</sub> particles . B: Magnified Aldrich TiO<sub>2</sub> particles revealing nanostructure. C: Degussa P25 TiO<sub>2</sub> particles. D: Magnified Degussa P25 TiO<sub>2</sub> particles revealing nanostructure.

The microstructure of two different commercial TiO<sub>2</sub> powders was investigated using a scanning electron microscope (SEM). SEM images of the powders recorded before and after adsorption of **1** showed that applying the dye had no significant effect on aggregation, so only images of the dye-coated particles are presented here for discussion. Figure 3 shows that Aldrich (< 5 μm) particles (Figure 3A) and Degussa P25 TiO<sub>2</sub> particles (Figure 3C) exist predominately as aggregates of smaller particles with many larger than 10 μm. It is apparent from Figure 3B and 3D that the TiO<sub>2</sub> aggregates consist of quite different sized primary particles. In Figure 3B, the primary particle size varies from ~100 to 500 nm in diameter (Aldrich product), while in Figure 3D (Degussa P25) the primary particle size is close to 20 nm (as specified by the manufacturer at [www.degussa.com](http://www.degussa.com)). Thus the surface area and roughness of the Degussa particles may be expected to be much higher than that of the Aldrich particles. This may have some influence on the number of dye molecules that can

bind to each particle, even though the overall particle sizes are comparable. This also highlights the importance of distinguishing between genuine nanoparticles, which are distinct, non-aggregated particles with nanometer-size diameters, and nanostructured particles, which may be up to microns in diameter.

### *3.3. Application to fingerprints*

The new fluorescent powders were applied to fingerprints on several different surfaces and compared with other commercial fluorescent powders. The common surfaces such as glass, polyethylene bags and painted wood were all examined in the same manner. The fluorescent dye itself was not suitable for powdering because of its waxy texture, possibly due to liquid crystalline properties [29].



**Figure 4.** Fresh fingerprints on glass developed with; (left) perylene dye/TiO<sub>2</sub> particles, and (right) untreated TiO<sub>2</sub> particles, under 505 nm illumination and viewed using a 575 nm long pass filter.

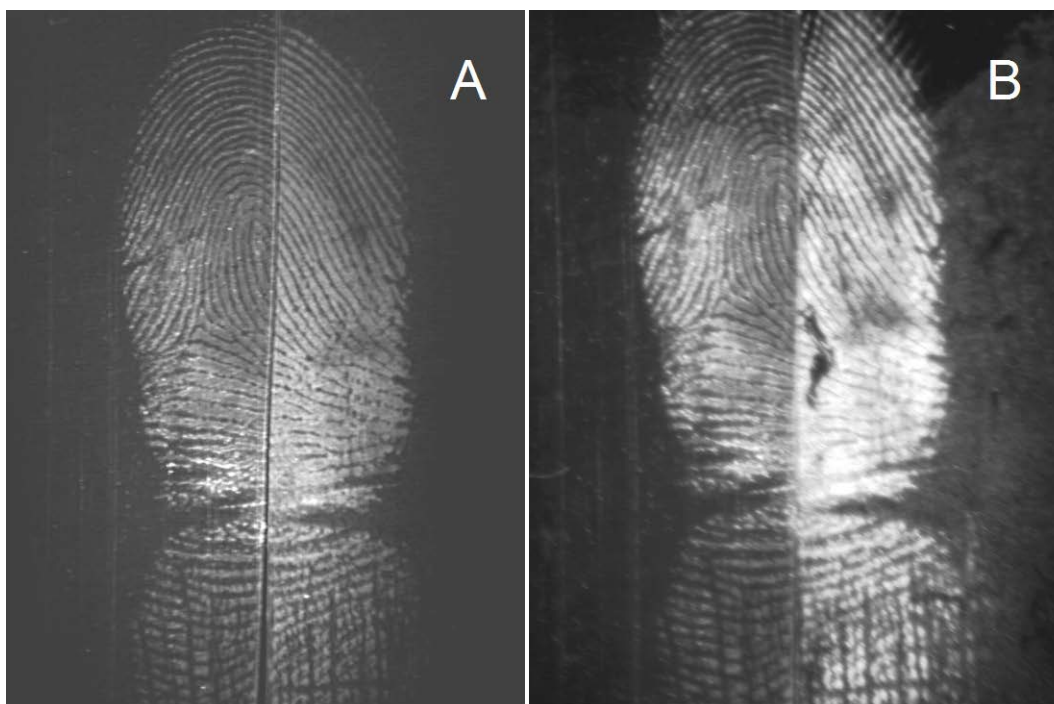
Untreated  $\text{TiO}_2$  powder deposited on latent fingermarks is limited in potential due to its white colour, which gives poor contrast on common non-porous surfaces such as glass and plastic. Using illumination at 505 nm,  $\text{TiO}_2$  particles coated with **1** revealed detailed fluorescent fingermarks on glass and polyethylene (as expected from the fluorescence spectroscopy experiments) without significant background development. Figure 4 shows a comparison of fingermarks developed with dye-coated  $\text{TiO}_2$  particles (left) and uncoated particles (right) on glass. Fingermarks were very poorly developed on painted wood surfaces.



**Figure 5.** Fresh fingermarks on glass developed with; (left) perylene dye/ $\text{TiO}_2$  particles (Degussa brand), and (right) perylene dye/  $\text{TiO}_2$  particles (Aldrich brand) in reflection mode under white light illumination.

The effectiveness with which powder adheres to fingerprint ridges may depend on the size and shape of the particles; small, fine particles generally adhere more easily than large, coarse ones [3]. Thus, particle differences may affect the quality of fingermarks developed with powders. In comparisons of the two types of commercial  $\text{TiO}_2$  particles coated with **1**, similar performance was observed although in some cases the Degussa P25 powder produced clearer

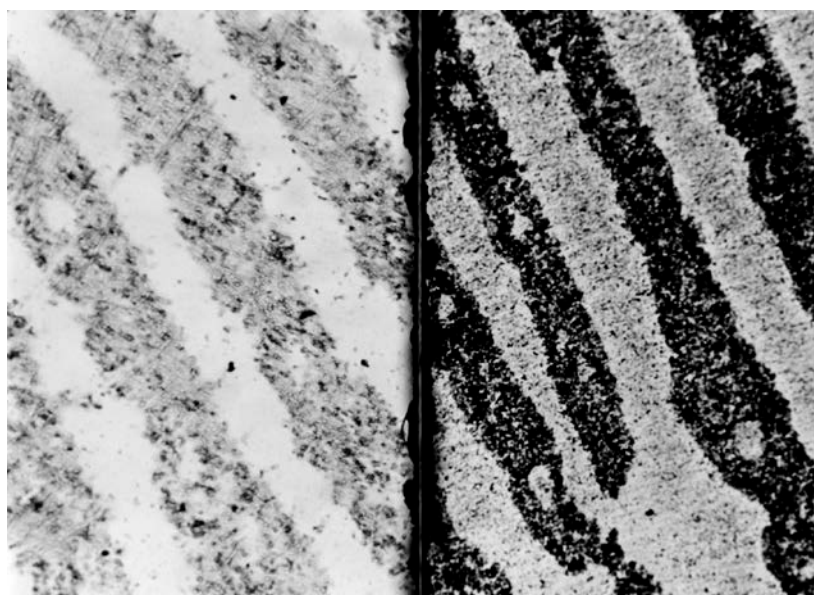
fine-level development of fingerprints. Figure 5 shows an example of this. Note that tertiary level detail is clearly visible.



**Figure 6.** Comparison of perylene dye on  $\text{TiO}_2$  and commercial fluorescent powders, viewed using a 575 nm longpass filter and 505 nm illumination. **A:** (left) perylene dye/ $\text{TiO}_2$  particles (Degussa), and (right) Black Emerald fluorescent magnetic powder powder on polyethylene. **B:** (left) fluorescent dye/ $\text{TiO}_2$  particles (Degussa), and (right) Blitz Green fluorescent magnetic powder on polyethylene.

Comparison experiments with some commercial fluorescent powders were performed. Black Emerald and Blitz Green fluorescent magnetic powders were used for this comparison (Figure 6). On glass and polyethylene, the new powder worked well but neither the commercial powders nor the new powder were successful on painted wood. Under 505 nm illumination, the new  $\text{TiO}_2$  powder exhibited weaker fluorescence than the commercially available powders. Despite the strong fluorescence exhibited by the commercial powders, heavy background development can reduce the contrast between ridge detail and the

background. The new dye absorbed onto nano-structured TiO<sub>2</sub> particles showed minimal background development under all conditions.

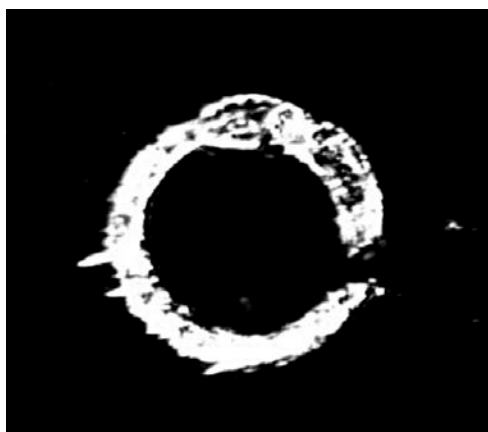


**Figure 7.** Fresh fingermarks on glass developed with; (left) perylene dye/TiO<sub>2</sub> particles (Degussa brand), and (right) Black Emerald fluorescent magnetic powder. This image was taken in transmission mode with white light illumination. Fingermark ridges are shown as the darker features. Note that the right-hand side image shows considerably more powder was deposited in the fingermark valley regions compared to the image on the left.

It may be argued that the minimal background development observed in the fluorescence images of the new powder may be due to the lower luminescence of the powder, and thus was simply less visible in the background. To investigate this, developed fingermarks on glass were imaged in transmission mode with white light. Figure 7 shows a comparison of fingermarks developed using the new powder with those developed using a commercial powder, Black Emerald. In these images, the ridges appear as dark features. It is apparent that the new powder adheres to the fingermark ridges and shows little affinity for the glass surface. The Black Emerald powder also adheres to the ridges but significantly more powder is observed in the valley regions compared to the new powder. These findings demonstrate a

significant advantage of the new formulation with respect to minimal background interference. However, because the use of the new fluorescent powder results in less intense ridges when compared to commercial powders, the overall advantage of the new powder may be less obvious in some situations. The final choice of the examiner should be assessed on a case-by-case basis.

The fluorescent dye/TiO<sub>2</sub> powder also gave satisfactory results when applied to fingerprints that had been kept in storage for 1 month. The detail enhancement was slightly less than with fresh prints, but the powder still revealed clear images.



**Figure 8.** A ring-shaped mineral oil mark developed using perylene dye on TiO<sub>2</sub> particles (Degussa) with 505 nm illumination and viewed using a 575 nm longpass filter.

An experiment with mineral oil demonstrated that the new powder is attracted to oily residues. Figure 8 shows a ring-shaped oil mark clearly developed using the new powder. Development of oil marks on glass using the commercial powders described above gave similar results to those using fingerprints; the powders adhered to the oily deposit together with some background staining. Although this does not prove that the new powder exclusively targets the oily components of fingerprints, the difference in surface properties between the new powder and existing powders may account for the lack of background development using with the new powder.

#### **4. Conclusion**

A new fluorescent dye was synthesised through the reaction of oleylamine and 3,4,9,10-perylenetetracarboxylic dianhydride and adsorbed onto titanium dioxide particles to yield a fluorescent powder. Analysis of the new powders using SEM showed that the two commercial powders have different nanostructures but similar overall particle sizes. The fluorescent dye/TiO<sub>2</sub> powder exhibited strong fluorescence under 505 nm excitation and developed fingermarks on glass and polyethylene with minimal background staining. A comparison between the new fluorescent powder and two commercial fluorescent powders showed that, although the commercial powders had greater fluorescence intensity, they also demonstrated greater background development in comparison to the new dye/TiO<sub>2</sub> powder. None of the powders worked well to develop fingermarks on a painted wood surface. We are currently expanding our research in this area to investigate the use of non-aggregated, dispersed titanium dioxide nanoparticles as fingerprint powders as well as the application of other metal oxide particles.

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