Title:

"Use of quantum dots in aqueous solution to detect blood fingermarks on non-porous surfaces"

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Abstract

A new and original reagent based on the use of highly fluorescent cadmium telluride (CdTe) quantum dots (QDs) in aqueous solution is proposed to detect weak fingermarks in blood on non-porous surfaces. To assess the efficiency of this approach, comparisons were performed with one of the most efficient blood reagents on non-porous surfaces, Acid Yellow 7 (AY7). To this end, four non-porous surfaces were studied, i.e. glass, transparent polypropylene, black polyethylene, and aluminium foil. To evaluate the sensitivity of both reagents, sets of depleted fingermarks were prepared, using the same finger, initially soaked with blood, which was then successively applied on the same surface without recharging it with blood or latent secretions. The successive marks were then cut in halves and the halves treated separately with each reagent. The results showed that QDs were equally efficient to AY7 on glass, polyethylene and polypropylene surfaces, and were superior to AY7 on aluminium. The use of QDs in new, sensitive and highly efficient latent and blood mark detection techniques appears highly promising. Health and safety issues related to the use of cadmium are also discussed. It is suggested that applying QDs in aqueous solution (and not as a dry dusting powder) considerably lowers the toxicity risks.

Keywords:

Detection; latent fingermarks; blood; nanoparticles; quantum dots; luminescence; Acid Yellow 7

Introduction

In the frame of an investigation on crime scene or related evidence, one of the major goals for investigators is the detection of fingermarks that were left on objects or surfaces by individuals. Most of the time, these marks are not visible since they are composed of a small amount of sweat or other secretions, invisible to the naked eye. They are said to be "latent" and require the application of physical, chemical or physico-chemical processes to permit their visualization. Numerous techniques are currently dedicated to this purpose [1] among which it is possible to distinguish those based on chemical detection (e.g. ninhydrin) because they imply the reaction between a reagent and secretion components (e.g. proteins, amino acids), those based on physico-chemical processes (physical developer, multi- or single-metal deposition,…) whose efficiency will be influenced by chemical parameters (pH, surfactant, …), and finally, the techniques based on physical processes (e.g. powdering) which are characterised by a low sensitivity since they only adhere to secretions through physical interactions, without a specific affinity for them. All the existing techniques are, however, more or less limited in their application or efficiency. For example, the nature of the surface (porous, non-porous), whether the surface has been wet or not, the composition of the secretions (sebaceous, eccrine, blood-contaminated), or the age of the fingermarks are such parameters that cannot be controlled by investigators but will play a major role in the capability of a technique to be able to highlight the existing latent fingermarks. There is a continuing quest for developing new efficient techniques (or improving existing ones) with an enhanced sensitivity towards secretions, a range of compatibility as wide as possible with various surfaces, and a detection mode allowing the observation of marks on dark or patterned surfaces. This last point is one of the reasons why the use of luminescence to detect fingermarks is preferred compared to the colorimetric techniques that only stain the marks. Additionally, aqueous formulations are generally preferred for their lower toxicity and ease of

application (on crime scene surfaces, for example) compared to toxic or highly flammable organic solvents that require work to be conducted under safe laboratory conditions.

During the last decade, several studies have focused on the development of new detection methods based on the use of nanoparticles (NPs) to detect fingermarks, and more particularly functionalized NPs [2]. One possibility consists of designing new powders, to be used as dusting agents, with enhanced capabilities compared to classical ones: Choi et al. [3] proposed gold NPs on which aliphatic chains were grafted to increase the powder affinity for sebaceous secretions. The same strategy has been applied with functionalized titanium dioxide NPs, on which a fluorescent dye and aliphatic chains were grafted. They were used as a powder on fingermarks through application with a brush [4]. In the same context, aluminium oxide NPs have been coated with two types of molecules, *i.e.* Eosin Y (a fluorescent dye) and a hydrophobic chain [5], and, finally, silica NPs were combined with fluorescent dyes to permit the detection of latent fingermarks on various surfaces [6]. Another research strategy consists of trying to enhance existing physico-chemical techniques based on NPs: some authors have demonstrated that it is possible to use functionalized gold NPs to enhance the deposition of silver in the physical developer process [7]; others have modified the classical multimetal deposition technique by depositing zinc oxide on gold, instead of silver, to obtain luminescent fingermarks [8]. Introducing luminescence in an existing technique that is otherwise limited to light coloured or transparent surfaces increases its application field to black or patterned surfaces, which constitutes an important improvement. Finally, new original techniques taking advantage of the properties of NPs were proposed: Leggett et al. [9] showed that binding an antibody to gold NPs allows the detection of specific drug metabolites in a fingermark. Other works focused on the use of quantum dots (QDs) to detect fingermarks: in 2000, researchers tried to use cadmium sulphide nanocrystals to stain cyanoacrylate by combining them with

dendrimers [10]. However, the immersion times were too long (24h), the working solution was unstable, and it did not constitute an alternative to existing cyanoacrylate stains. More recently, researchers stabilized QDs in petroleum ether by grafting aliphatic chains on their surface and tried to detect sebaceous fingermarks on silicon wafers and paper substrates [7]. The results were encouraging for the silicon substrate, but not for paper due to high background luminescence.

We propose in this paper a method based on the use of highly luminescent QDs in aqueous solution to detect blood fingermarks on non-porous surfaces. Contrary to previous forensic research involving QDs, a water-based formulation is proposed here. In this approach, we take advantage of the strong affinity of QDs for haemoglobin [11] to apply them as blood fingermark sensors, without the need for a surfactant or any organic solvent.

The choice of QDs arose from the fact that this class of nanoparticles has very promising attributes for forensic applications: they are spherical semiconductor nanocrystals with a diameter of a few nanometers (1-10 nm). They can be soluble in water or in organic solvents, depending on their external surface coating. Moreover, their outer surface can easily be functionalized with chemical groups to offer new functionalities, such as molecular targeting. For all these reasons, they are widely used in cellular biology to dye different components of the cells or tissues [12], which can be observed simultaneously under a single excitation source, or used in the conception of electronic components such as lasers and diodes [13]. For this study, QDs were synthesized in water for the following reasons: first, water is a user-friendly solvent compared to most organic solvents; second, synthesizing QDs in organic solvents requires using organometallic species at high temperature (~300°C), contrary to the synthesis in water, performed at 100°C (boiling point of water). One of the most interesting

properties of QDs is that they are highly luminescent in solution due to their nano-structure and composition. Moreover, their emission spectrum is quite narrow, with an emission wavelength directly proportional to their size (Figure 1).

Material and Methods

All chemicals were purchased from Sigma-Aldrich and were of high purity grade. No further purification was required before use.

Synthesis of the quantum dots

Cadmium telluride (CdTe) quantum dots (QDs) were synthesized in water by combining two protocols found in the literature [14, 15]. First, tellurium powder (31.9 mg; 0.25 mmol) was mixed with sodium borohydride (30 mg; 0.793 mmol) in an appropriate flask filled with an inert atmosphere (nitrogen). Two millilitres of bidistilled water were then injected using a syringe and the reaction was performed until all the tellurium powder was dissolved (~2 hours). Second, in another flask, cadmium chloride (92 mg; 0.502 mmol) was dissolved in 100 mL bidistilled water. Thioglycolic acid (TGA; 45 μL; 0.651 mmol) was then added to the mixture and the pH of the solution was adjusted to a value of 11.6 by adding sodium hydroxide (1M). Nitrogen was allowed to bubble through the solution for 30 minutes. Finally, 2 mL of the sodium hydrogen telluride (NaHTe) solution, prepared in the first step, were quickly injected to the flask using a syringe, under strong stirring. The solution was then left under reflux at 100°C. One of the great advantages of this synthesis is the ability to choose the diameter of the QDs of interest by stopping the reaction when the desired size is obtained. This can easily be done by observing the colour of the solution in the flask and removing the heat source at the appropriate time, since the colour of the QDs is directly linked to their size.

The reaction time varies from 10 minutes (small particles, light orange solution, green luminescence) to several hours (large particles, dark red solution, red luminescence).

QDs staining solution

The QDs staining solution has to be prepared just before use. The working solution was prepared by diluting the concentrated QDs solution 10 times (1 volume of QDs in 9 volumes of deionized water) and by lowering the pH to a value of 3.5, using concentrated TGA (liquid).

Fingermark deposition

In this study, blood fingermarks were deposited on four different substrates: glass, transparent polypropylene, black polyethylene bags and aluminium foil. To be able to assess the sensitivity of the QDs to detect faint blood marks, the donor finger was first pricked using a blood lancet to allow the covering of the fingertip with blood. The first apposition was done on a sheet of paper to decrease the quantity of blood on the skin. After that, 12 successive appositions of the same finger were made on one of the substrates, without pricking again, to obtain a depletive series of fingermarks presenting less and less blood. The same procedure was followed for each substrate to be tested. After only a few successive depositions, the blood fingermarks were no longer visible to the naked eye. The fingermarks were stored in the dark for 3 weeks before being immersed in staining solutions. It should be noted that only one donor was used in this study. Indeed, contrary to the detection of latent fingermarks, for which the composition of the secretions is strongly influenced by the donor (and thus the efficiency of the detection techniques), we assumed here that only haemoglobin was to be targeted. When referring to published haemoglobin levels in blood samples, we found that the normal ranges for adult males and females are 13.5-18 g/mL and 12-16 g/mL, respectively

[16]. Consequently, the sex or the number of donors was expected to have little (if any) affect on the efficiency of the method.

Fingermark detection protocol

The detection of the latent fingermarks by QDs was performed as follows (Figure 2): (1) the samples were immersed in a solution of 5-sulfosalicylic acid in water (2.3%, w/v) for 10 minutes; (2) they were then briefly rinsed with water and (3) immersed in the QD staining solution for 20 minutes under light stirring using a rotating platform/shaker; (4) the samples were finally rinsed with water and observed in the luminescence mode using a Mini-Crimescope® 400 set at a UV excitation wavelength of 300-400 nm.

Efficiency of the method

To be able to judge the actual efficiency and sensitivity of this method, we visually compared the results obtained using the QD-based formulation with those obtained using an existing efficient blood reagent, in this case Acid Yellow 7 (AY7). AY7 generates luminescent fingermarks and has been identified as being the most effective reagent to detect blood fingermarks on non-porous surfaces [17], especially when small quantities of blood are present. The comparison between the two methods was performed by cutting the series of fingermarks in halves before dipping them in their respective staining solutions (QDs for the left halves and AY7 for the right halves). By doing this, we can achieve an objective comparison in terms of ridge quality, luminescence and sensitivity. The AY7 was applied according to the procedure recommended by the product supplier (http://www.bvda.com/EN/prdctinf/en_acid_yellow_7.html).

Results

The synthesis as described resulted in quantum dots (QDs) presenting a strong luminescence in water. The QDs are stabilized in solution by the thioglycolic acid (TGA) absorbed on their surface. By stopping the reaction after 60 minutes, we obtained an aqueous solution of QDs presenting a strong and narrow luminescence emission peak centred in the green region (540 nm) – See Figure 3. This nanoparticle size was chosen as the one giving the most intense emission.

Additionally, it was observed that if the freshly-synthesized QD solutions were stored in transparent glass bottles and left in sunlight (close to a window) for several days or weeks, their luminescence capabilities considerably increased, even quadrupled after 13 days under such conditions. This point will be discussed further.

The four substrates, on which the sets of depletion blood marks were deposited and aged for 3 weeks, were cut in half and treated according to the described procedures. The results are summarized in Table 1, which gives an indication of the performance of both methods towards the depleted marks. The results were further analyzed according to two parameters:

- the quality of the detected fingermarks; and
- the sensitivity of the methods.

Both methods detected fingermarks on the four substrates that were tested. The ridges were clearly defined in terms of detail, with observable 3rd level characteristics (pores and ridge contours). Both methods showed very good affinity and selectivity for the blood contaminated ridges, since the substrate backgrounds remained unstained. When comparing both halves of the fingermarks for the first five depletions, the quality of development was almost equal

between the two methods, with performance unable to be differentiated in term of quality (Figure 4).

While techniques behaved equally well for the first depletions, differences in terms of sensitivity began after the sixth deposition and was closely related to the nature of the surface. No major difference appears between QD and AY7 for glass, transparent polypropylene and black polyethylene surfaces. As can be seen in Table 1, both techniques permitted detection of fingermarks up to the depletions #10, 7, and 8, respectively, with a difference of one depletion in favour of one or the other. This difference is not significant. However, for aluminium, AY7 stopped detecting the latent blood fingermarks after depletion #9, whereas QDs continued to give good results in terms of ridge pattern and minutiae detail (Figure 5A) even up to the last depletion (#12). A second depletion series made on aluminium foil, and composed of 17 successive fingermarks, showed positive results for QDs up to the 17^{th} fingermarks (Figure 5B). The results were faint but, after image enhancement, ridges could be clearly seen and minutiae identified. This point will be discussed hereafter.

Discussion

Synthesis of quantum dots (QDs)

The synthesis of the QDs as described in this paper was relatively easy to perform and did not require high temperatures, such as may be the case with syntheses in organic solvents. The production of green luminescent particles required a reflux time (at 100° C) of one hour. The solutions were stable over time and were strongly luminescent. Moreover, 100 mL of concentrated QD solutions were obtained and were used to prepare 1 L of working solution after dilution by a factor 10. For all these reasons, we propose that such a protocol is further investigated for applications in this field.

Role played by the thioglycolic acid (TGA)

TGA plays several roles in the production of QDs in aqueous solution. First, it participates in the early stages of the synthesis, when the particles are forming [18]. Then, it is assumed that the particles in solution are covered by a TGA shell, preventing them from coalescing and facilitating their dissolution in water, similar to the role played by citrate ions towards silver and gold nanoparticles [19, 20]. Finally, it seems to be also involved in the increase of luminescence of the solution when exposed to sunlight. Indeed, according to Bao et al. [21], the photodegradation of TGA molecules, induced by sunlight, leads to the formation of a cadmium sulphide (CdS) shell around the cadmium telluride (CdTe) quantum dots. This is called a "core/shell" structure. The two main advantages of "core/shell" QDs are both increased stability and more intense luminescence, compared to the corresponding "core" QDs. It should be noted that their ability to develop fingermarks is not influenced by this phenomenon as we were able to obtain results using a working solution prepared by using a concentrated solution of CdTe exposed to sunlight for 30 days. Consequently, we recommend leaving the solution to "age" close to a window for several days prior to use.

Ability to detect blood fingermarks / comparison with Acid Yellow 7 (AY7)

In agreement with the literature [11], we observed that quantum dots possess an affinity for blood, because of the presence of haemoglobin. When immersing non-porous surfaces bearing weak fingermarks in blood in the QD solution, clear and well-defined ridges were observed without background staining. This resulted in very good contrast, particularly on the black polyethylene surface. When comparing the results with those achieved using AY7, QDs were equally efficient on three of the four substrates. Both techniques were able to detect depletive series of fingermarks up to the 7^{th} to 10^{th} deposition, depending on the surface. It has to be

noted that, at this level, the bloody fingermarks were essentially "latent" since they were not visible to the naked eye before any chemical treatment. QDs showed excellent behaviour and outperformed AY7 on aluminium, since it was possible to detect fingermarks up to the 17th deposition whereas AY7 stopped detecting ridges after the 9th. At this stage of depletion, one could wonder if there was still blood present on the marks (since the 17 depositions were performed continuously without stopping or loading with blood). We were not able to clarify this point as it can be assumed that the very small amount of secretion that was left in the range of the 15th or 17th deposition may be composed of only sweat secreted by the fingertip pores, even during the deposition process. This would mean that no more blood was present and it would explain why AY7 was not capable of detecting such traces. It would also mean that QDs are able to detect classical latent fingermarks on non-porous surfaces. Preliminary tests performed on fresh sebaceous marks (which were loaded with secretions by rubbing the fingers on the forehead) deposited on aluminium showed a positive result (Figure 6). However, the immersion time was longer, around 30 minutes. Contrary to AY7, the QD-based detection method presented here is thus not limited to blood fingermarks. After optimization, it may consequently constitute a new versatile technique allowing the detection of bloody or classical "latent" fingermarks on non-porous surfaces.

Application protocol

The times required to prepare and apply both solutions were mainly driven by the immersion times in the working solution, which amount to 20 minutes for QDs and 10 minutes for AY7. Such time values are similar to those required by other commonly used blood detection techniques (Acid Violet 17, Amido Black or 3,3'-Diaminobenzidine). At this point, we can say that processing times are similar, even if we are currently trying to lower the time required when using QDs.

Costs related to the use of nanoparticles instead of regular reagents

The QD formulation and application protocol presented in this article is a relatively inexpensive alternative compared to existing techniques since one litre of working solution (obtained by diluting 100 mL of the concentrated solution with water) costs less than US$1 (US$0.25 at 2009 prices). By comparison, one litre of working solution for Acid Yellow 7 costs almost US$5. The costs are largely due to the use of organic solvents in the Acid Yellow 7 formulation (ethanol, acetic acid), whereas the QD technique only uses water. It should also be noted that choosing to synthesize the QDs yourself considerably lowers the costs compared to the purchase of QDs through chemical resellers. For example, 50 mg of CdTe QDs (540 ± 5 nm emission maximum) that could be solubilized in water cost almost US$400 at 2009 prices if purchased by PlasmaChem GmbH – Germany (http://www.plasmachem.com). This quantity permits the preparation of almost 1 L of working solution similar to the one used in this study. Such costs would certainly decrease if the use of nanoparticles for forensic applications became widespread.

Health and Safety issues

One disadvantage of the method presented in this paper is the toxicity of cadmium. The risks related to the use of cadmium-based NPs were greatly lowered by the fact that they were synthesized and applied in aqueous solution (without drying them or using them as dusting powders). However, we strongly recommend use under safe laboratory conditions (e.g. fume cupboards). Moreover, we are planning to synthesize alternative QD species that do not contain cadmium. Another solution is to synthesize core/shell QDs, with a zinc sulphide or zinc telluride shell surrounding the CdTe core. The surrounding shell is highly stable and

greatly diminishes the toxicity of the resulting QD. This point will be of prime interest in the future use of QDs in the detection of fingermarks.

Conclusions

The results obtained for the detection of blood fingermarks on non-porous surfaces using highly luminescent quantum dots (QDs) in aqueous solution are promising. We have demonstrated that the detection was successful when immersing the samples in an acidic solution (pH 3.5) of CdTe (/CdS) QDs in water, for 20 minutes. To be able to assess the actual efficiency of this new method, depletive series of blood fingermarks were prepared on the following four non-porous surfaces: glass, transparent polypropylene, black polyethylene, and aluminium. The results were comparable to those obtained with the classical and very efficient blood reagent Acid Yellow 7 (AY7) in most instances. On the other hand, AY7 was outclassed when detecting very weak bloodmarks on aluminium foil, both in terms of selectivity and sensitivity. However, this may have been due to the fact that the QD solution was detecting true "latent" impressions (i.e. total absence of blood).

In contrast to other scientific studies performed on the subject of functionalized nanoparticles, we chose to target the detection of fingermarks by nanoparticles in (aqueous) solution. This is a major aim of our research strategy, since immersion in a solution allows for greatly enhanced sensitivity of the method. Indeed, contrary to a physical interaction (such as when dusting with a powder), the use of immersion baths requires a chemical or physico-chemical affinity between the reagent in solution and some components of the secretions. We chose to promote the use of aqueous solutions in order to allow their application on crime scene surfaces, which would constitute an added advantage over other techniques and this goal is within reach. This approach avoids the use of toxic or highly flammable organic solvents.

Functionalized nanoparticles, and more particularly quantum dots, show great promise as new efficient, sensitive and selective fingermark detection agents as demonstrated in this paper. We took advantage of the affinity of the QD for haemoglobin and are now concentrating our efforts at developing more efficient functionalized nanoparticles capable of specifically targeting latent fingermarks on various surfaces. Suitable molecular targets present among the various components of natural secretions are currently being studied. Such targets must be present in most latent fingermarks and in sufficient quantities to permit adequate development. Luminescent nanoparticles will have to be tuned, in terms of synthesis and functionalization, so that they develop luminescence at different wavelengths and specifically target those molecules. Finally, this research has focused on the detection of marks on non-porous surfaces, but we have indications that such approaches could be directed towards marks on porous supports. Finally, a great deal of attention is dedicated to finding reactants with the lowest documented toxicity so that the techniques may be transferred to non laboratory environments such as at the crime scene itself.

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Figure captions

Figure 1

(a) Evolution of the luminescence emission for cadmium telluride quantum dots of increasing size (from left to right), illuminated under UV light (300-400 nm) using a Mini-Crimescope® 400. (b) Emission spectra obtained for the illustrated samples using a Perkin Elmer LS-50B luminescence spectrophotometer. The spectra were normalized to 1.0 to illustrate the progression of the maxima of intensity to higher wavelengths as the quantum dots are growing in size. The samples were obtained by removing a small amount (2.5 mL) of concentrated quantum dots from the reaction mixture at different reaction time.

Figure 2

Schematic representation of the experimental procedure used for fingermark detection in this study.

Figure 3

Excitation (dotted line) and emission (continuous line) spectra of the solution, containing cadmium telluride quantum dots, that was used in this study to detect fingermarks. The nanoparticles were obtained by stopping the reaction after 60 min (synthetic protocol as described in the Material and Methods section), so that their maximum emission was centred in the green range of the visible spectrum. Spectra were obtained using a Hitachi F-2500 spectrophotometer.

Figure 4

Examples of results that were obtained for the first depletions of traces using cadmium telluride quantum dots (left halves) and Acid Yellow 7 (right halves). Supports and illustrated

depletion #: (A) glass – #4, (B) transparent polypropylene - #4, (C) black polyethylene - #3, (D) aluminium - #5. The samples were excited in the UV range (300-400 nm) using a Mini-Crimescope 400.

Figure 5

(a) Illustration of the result obtained for the 10^{th} depletion mark on aluminium foil, detected using quantum dots (left half) and Acid Yellow 7 (right half). This depletion illustrates the transition that has been observed in term of sensitivity between the two techniques. It can be seen that, at this point, Acid Yellow 7 no longer permitted the visualization of complete fingermark ridges (only isolated dots can be seen along the ridges), whereas this was still the case with the quantum dots. (b) Illustration of the 17^{th} successive fingermark deposited on aluminium foil still showing ridges in green luminescence for quantum dots (left half), whereas Acid Yellow 7 (right half) did not give any result. The luminescent halo near the edge of the aluminium foil (for the quantum dots) was due to an inadequate rinsing time, leaving quantum dots in the extremity of the sample when drying it. Each mark is presented in colour and in greyscale after digital enhancement (contrast adjustment).

Figure 6

Illustration of a non-bloody latent fingermark deposited on aluminium foil and immersed for 30 minutes in a working solution of quantum dots. It should be emphasized that the mark was very fresh (< 1 day) and charged with natural secretions by rubbing the finger on the forehead before deposition.

Table caption

Table 1

Summary of the results obtained when treating the depletion series (up to 12 successive fingermark depositions) of blood fingermarks on the four substrates, using quantum dots (QDs) and Acid Yellow 7 (AY7). (+) stands for clearly visible ridges with sufficient quality to see minutiae, (±) stands for ridges that are slightly visible but not sufficient to perform an analysis in terms of minutiae positioning, (-) stands for no visible reaction between the reagent and the ridges.

Figure 1
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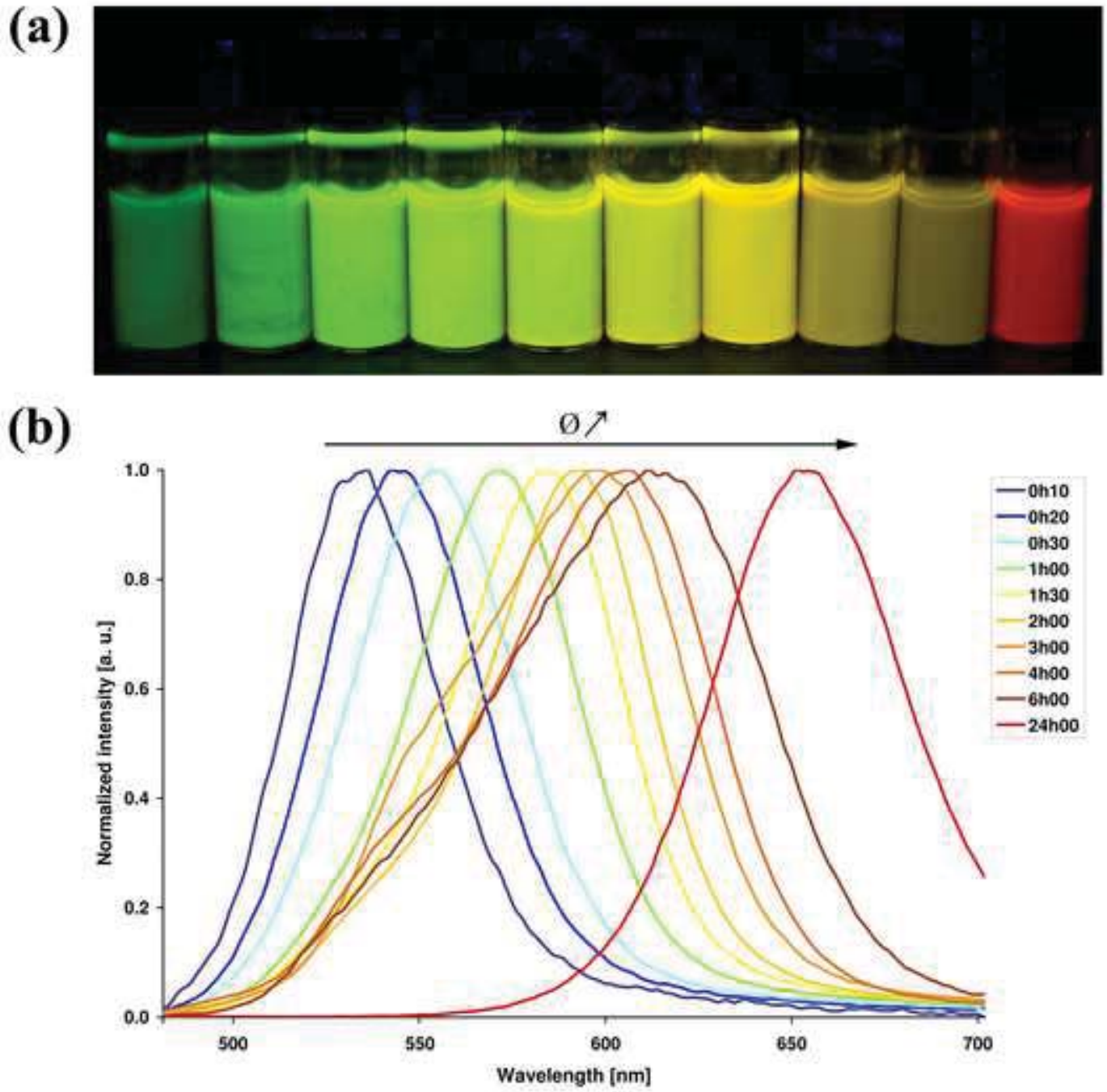

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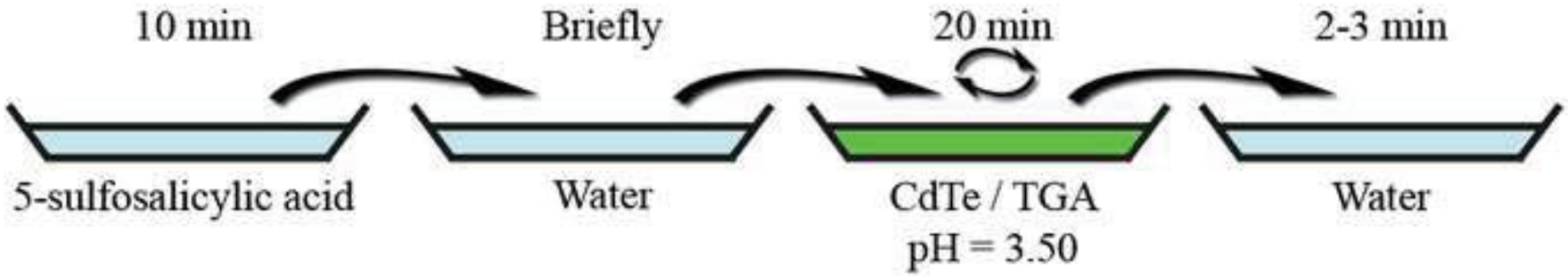

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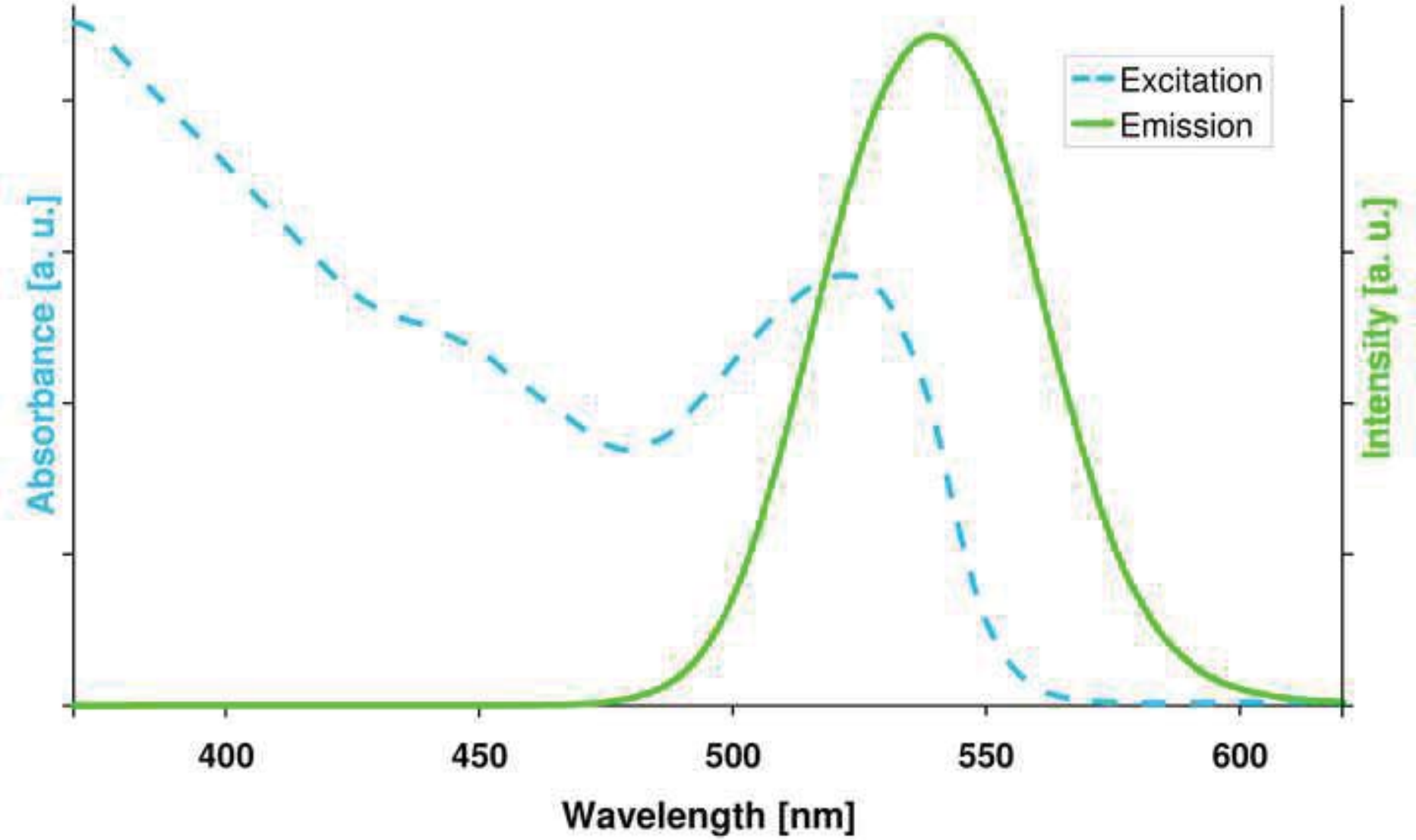

Figure 4

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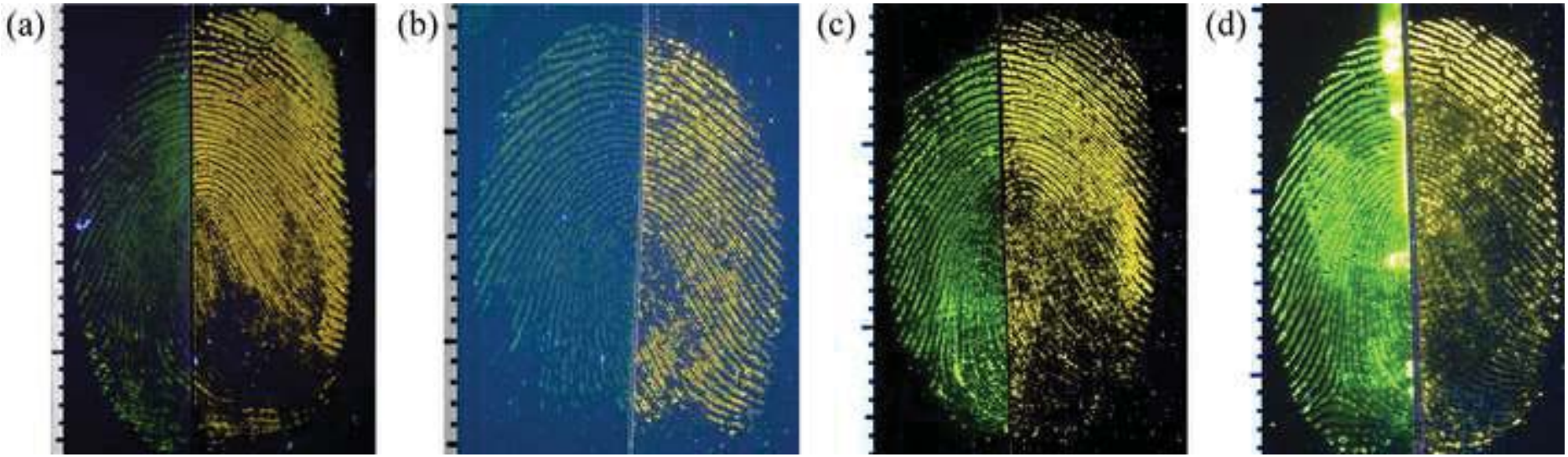

Figure 5
Click here to download high resolution image

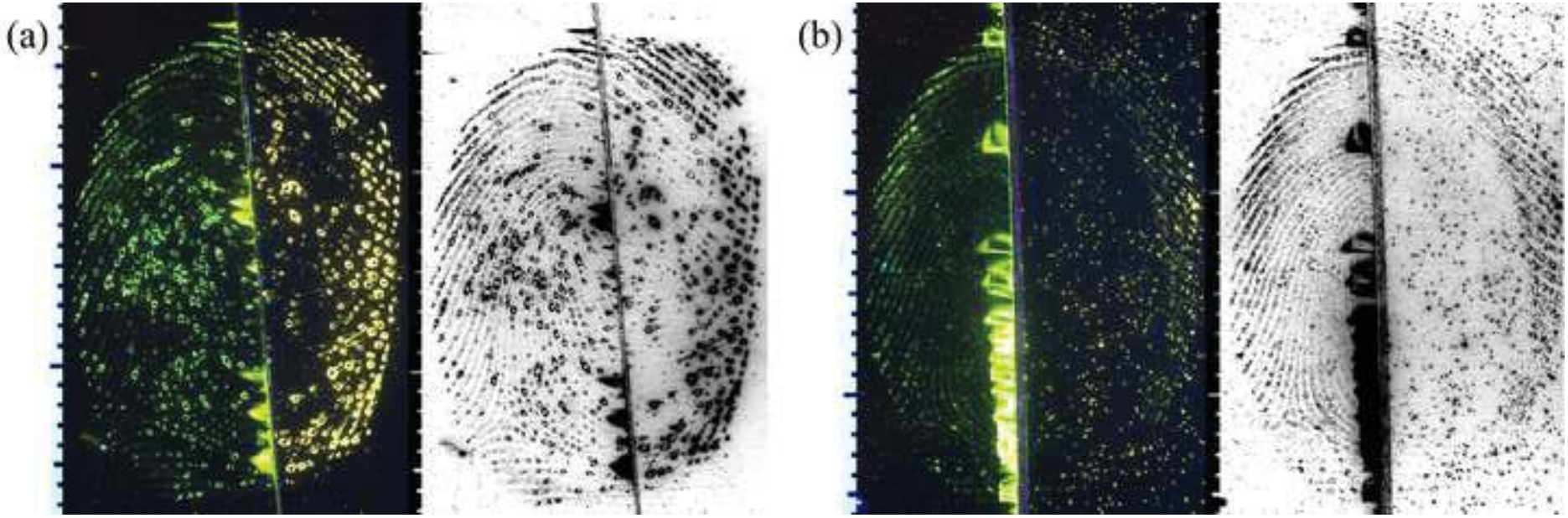

Figure 6
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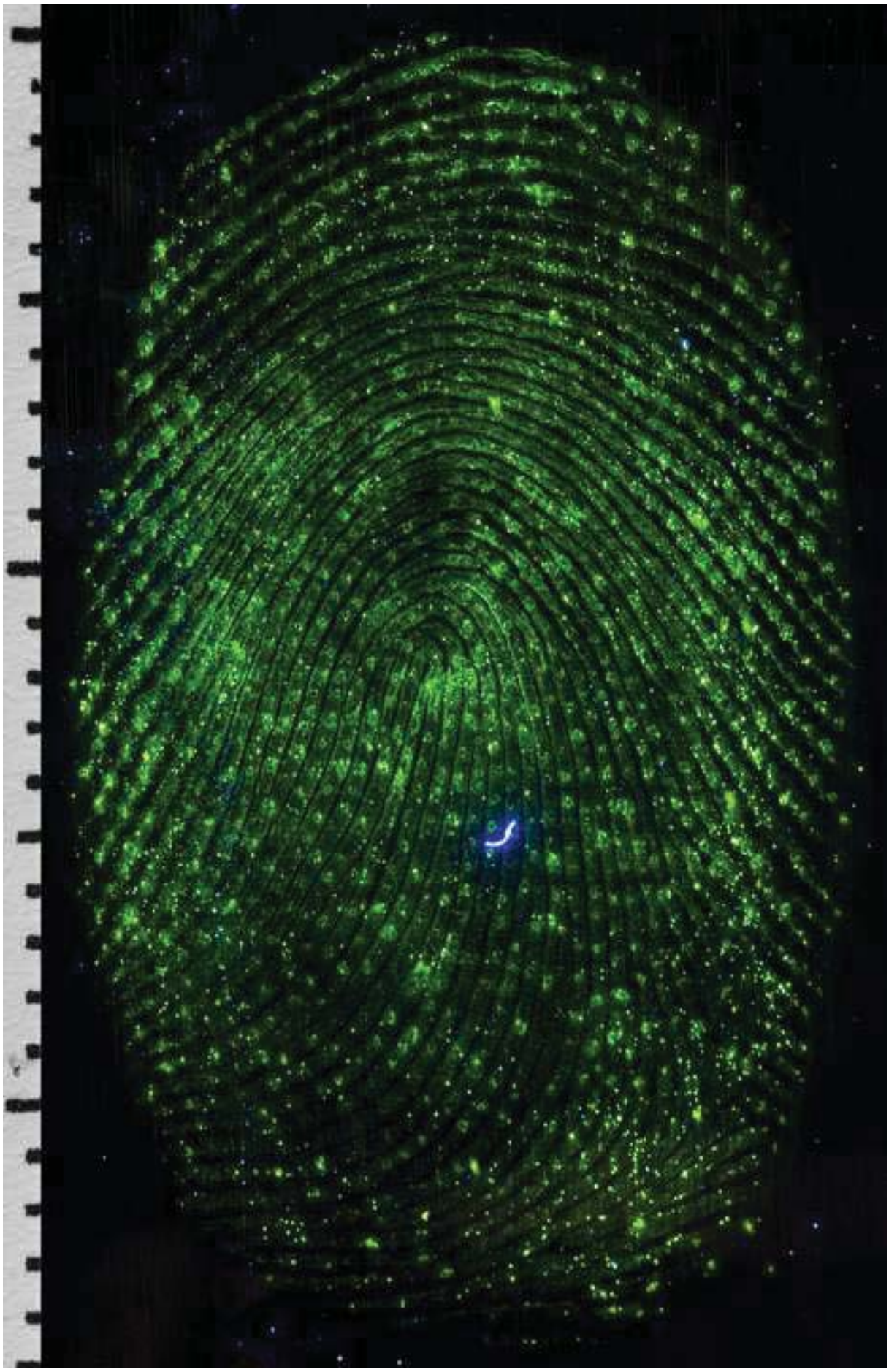

Table 1

Table 1

	Glass		Transparent polypropylene		Black polyethylene		Aluminium	
Depletion n°	**QDs**	**AY7**	**QDs**	**AY7**	**QDs**	**AY7**	**QDs**	**AY7**
1	+	+	+	+	+	+	+	+
2	+	+	+	+	+	+	+	+
3	+	+	+	+	+	+	+	+
4	+	+	+	+	+	+	+	+
5	+	+	+	+	+	+	+	+
6	+	+	+	+	+	±	+	+
7	+	+	±	±	±	-	+	+
8	±	+	-	-	±	±	+	+
9	±	±	-	-	-	-	+	+
10	±	±	-	-	-	-	+	-
11	-	-	-	-	-	-	+	-
12	-	-	-	-	-	-	+	-