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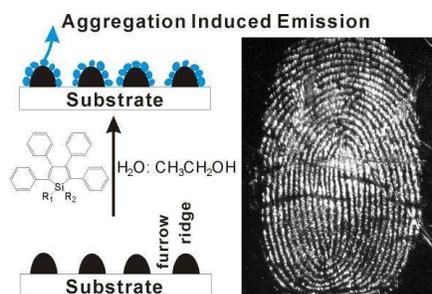
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## Enhancing the visualization of latent fingerprints by aggregation induced emission of siloles

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## Enhancing the visualization of latent fingerprints by aggregation induced emission of siloles

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The aggregation-induced emission of two silole compounds was explored for enhancing the visualization of latent fingerprints on wet non-porous surfaces. This effect was proved to stem from the hydrophobic interaction between the silole aggregates and the fingerprint residues.

Fingerprints are the impressions left by the raised portion of the friction skin that is featured with a series of lines corresponding to ridges and grooves. It is the pattern of these ridges and grooves that renders each fingerprint unique. Since the late 19<sup>th</sup> century, fingerprints have been used in forensic investigations to establish the identity of an individual, and continue to be an important tool in our daily life for many other purposes, such as access control, safety inspection, and individual credentials.<sup>1-2</sup> The most common form of fingerprint evidence is latent fingerprints (LFPs), which are present but invisible to naked eyes and require some means of “development” to enhance the visual contrast between the prints and their backgrounds.<sup>3</sup>

The past two decades have witnessed great innovation of instrumental and synthetic techniques employed successfully for fingerprint detection. For example, chemical imaging techniques utilizing Raman,<sup>4-5</sup> FTIR,<sup>6-8</sup> and mass spectrometry,<sup>9-11</sup> have significantly improved the study of fingerprint composition because of their ability to identify and map the compounds present in fingerprint residues. Additionally, the application of nanoparticles (NPs), including gold NPs,<sup>11-15</sup> TiO<sub>2</sub> particles,<sup>16</sup> nano-structured ZnO,<sup>17</sup> and quantum dots,<sup>18-19</sup> for fingerprint detection has also attracted considerable interest.<sup>3</sup>

LFPs also can be detected by fluorescence approaches which exhibit a much higher sensitivity than those based on color formation.<sup>20</sup> Almog et al. have reported that fluorescent CdSe/ZnS NPs stabilized by octadecaneamine can develop LFPs deposited on silicon wafers under UV illumination.<sup>19</sup> A highly fluorescent conjugated polymer film has been used for nondestructive fingerprint detection, on the basis of swelling-induced emission due to the permeation of oily components in LFPs into the film.<sup>21</sup> Russell et al. have presented the combination of immunomagnetic beads with fluorescence imaging to detect drugs and drug metabolites within LFPs and simultaneously provide fluorescence images of the print to enable individual identification.<sup>22-25</sup>

Despite numerous analytical processes that have already been proposed for fingerprint detection, the most widely used method at a scene of a crime is still powder dusting.<sup>26</sup> Apparently,

brushing magnetic and/or luminescent powders on LFPs has some drawbacks, e.g., inevitable destruction of the fingerprint details and health hazard to the examiners. In a preliminary work, we reported an alternative fluorescence approach to enhance the visualization of LFPs on the basis of the aggregation induced emission (AIE) of the tetraphenylethene (TPE, its structure is shown in Fig. 1a).<sup>27</sup> Since the overall process is performed in solutions and does not involve powder treatment, it is more user-friendly and faster. AIE is a newly developed phenomenon observed with some silole and TPE luminogens, which are practically non-luminescent in the solution state but become strongly emissive when forming aggregates.<sup>28-33</sup> This phenomenon is exactly opposite to the aggregation-caused quenching (ACQ) effect, in which the emission of organic fluorophores is attenuated when their concentrations are increased or when they are aggregated in the solid state.

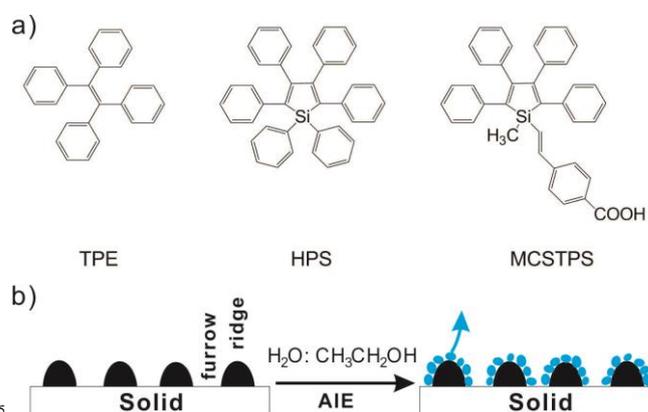
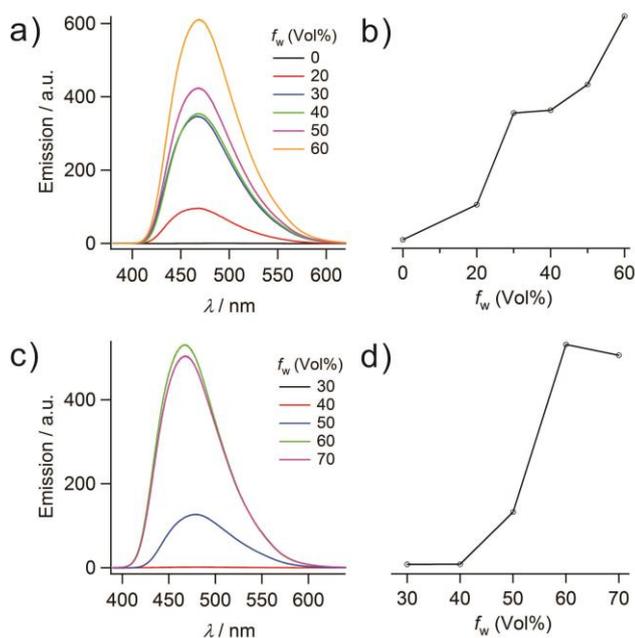


Fig. 1 (a) Molecular structures of TPE, HPS and MCSTPS. (b) Schematic illustration of the fingerprint enhancement by AIE.

In this work, we further explored the AIE strategy, using two 2,3,4,5-tetraphenylsiloles (as shown in Fig. 1a) with different 1,1-substituents on the ring silicon atoms, i.e., 1,1,2,3,4,5-hexaphenylsilole (HPS) and 1-methyl-1-(4-carboxystyrene)-2,3,4,5-tetraphenylsilole (MCSTPS), for the enhancement of the LFPs on various surfaces. As we shall show, both HPS and MCSTPS aggregates formed in the ethanol-water mixture can absorb preferentially onto the ridges of sebum-rich fingerprints, thus generate emission under UV illumination and enhance sufficiently the visualization of the fingerprints (Fig. 1b). A much better visualization was achieved with HPS aggregates than

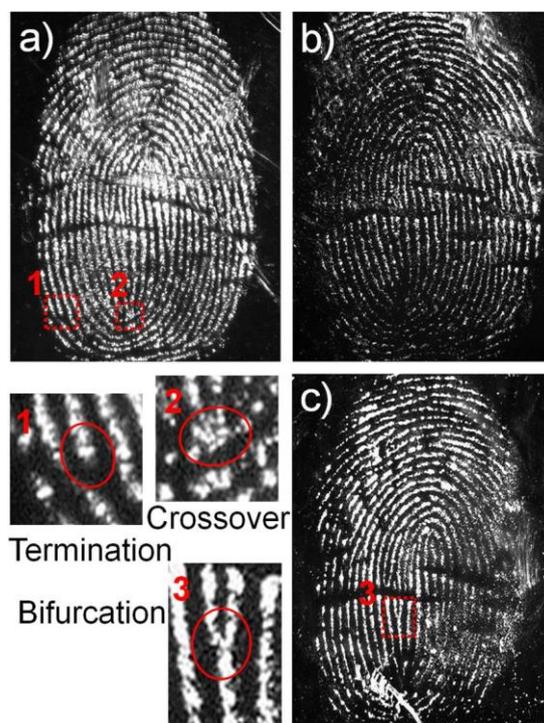
MCSTPS, proving the interaction of AIE aggregates with fingerprint residue is indeed via the hydrophobic-hydrophobic interaction as previously proposed.<sup>27</sup>

HPS is a propeller-shaped non-planar molecule and can be considered as an archetypal AIE-active luminogen. Structurally MCSTPS is similar to HPS but contains a hydrophilic unit of carboxylic acid group which makes it more hydrophilic than HPS and TPE. Silole molecules are virtually non-luminescent when dissolved in good solvents (e.g. acetonitrile, tetrahydrofuran, and chloroform), but become highly emissive when aggregated in poor solvents (e.g. water) or fabricated into thin solid films.<sup>33</sup> Herein, we used ethanol as the good solvent rather than acetonitrile used in our previous work.<sup>27</sup> **Fig. 2** shows the emission spectra of HPS and MCSTPS in ethanol-water mixtures with different volumetric fractions of water ( $f_w$ , vol%). As shown in **Fig. 2a**, HPS is non-luminescent when dissolved in pure ethanol. The AIE effect was activated upon addition of a certain amount of water, leading to the aggregation of the silole molecules and a strong emission. The emission increases rapidly when the water fraction reaches 30% and rises along with the water content. MCSTPS is a weaker emitter than HPS. MCSTPS in ethanol is not emissive until more than 50% of water is added. However, when the water fraction reached 70%, a large amount of block deposit was precipitated and floated on the liquid surface, thereby the solution emission decreased. As reported previously, the restriction of intramolecular rotations is responsible for the AIE effect.<sup>31</sup> In dilute solutions, the intramolecular rotation can serve as a relaxation channel for the excited state to decay. While in the aggregates, it is restricted due to the physical constraint, thus the photonic energy can only be dissipated via the channel of light emission.



**Fig. 2** (a, c) Emission spectra of HPS (a) and MCSTPS (c) in ethanol-water mixtures with different volumetric fractions of water ( $f_w$ , vol%). The concentrations of HPS and MCSTPS are 0.1346 g·L<sup>-1</sup> and 0.1366 g·L<sup>-1</sup>, respectively. (b, d) Variation of the emission peak intensities of HPS (b) and MCSTPS (d) with  $f_w$ .

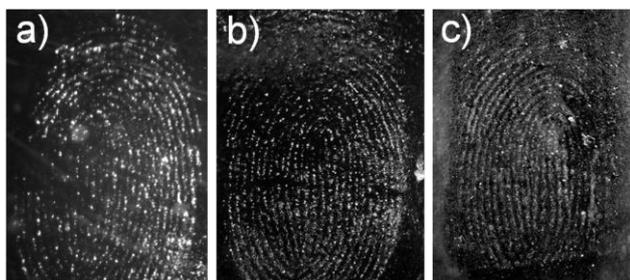
Sebum-rich fingerprint samples were obtained from volunteers by rubbing their fingers over the forehead and stamping them directly onto several different substrates including the glass slides, stainless steel sheets, and aluminium foils. The fingerprints were typically developed by HPS or MCSTPS as follows. The substrates bearing the sebaceous prints were immersed in the ethanol-water mixtures of HPS or MCSTPS with different water contents, under stirring for 5 min. HPS and MCSTPS are lipophilic compounds and therefore their aggregates can preferentially adsorb to the fingerprint ridges via the hydrophobic interaction. Then, the substrates were rinsed with copious amount of water, dried under an argon stream and finally positioned in the dark box of a ChemiScope 2850 fluorescence imaging system (Clinx Science Instruments, Shanghai). The system is equipped with a 365 nm excitation light source, a Model VFA2595H Macro Zoom Iris Megapixel lens (Senko ADL, Japan) and a high sensitive CCD camera (Clinx Clx210, Finger Lakes Instrumentation). The position of the substrate and its distance from the macro lens were adjusted by a three-dimensional translational stage.



**Fig. 3** Fluorescence images of the sebaceous fingerprints on glass slide (a), stainless steel sheet (b) and aluminium foil (c) developed by the AIE of HPS at the concentration of 0.1346 g·L<sup>-1</sup>. The water fraction was 40, 30 and 30% for the three substrates, respectively.

**Fig. 3** displays the representative fluorescence images of the sebaceous fingerprints enhanced by the HPS on different substrate surfaces. Best results were obtained in an ethanol-water mixture with 40%, 30% and 30% of water, respectively for the glass slide, stainless steel sheet, and aluminium foil. These values coincide well with those required in solution systems, in which significant fluorescence was only generated at a water fraction above 30% (**Fig. 2a**). As we previously reported, the water fraction in acetonitrile-water mixture for obtaining best fluorescence images by the TPE was 50%, 40% and 40%, for the glass slide, stainless

steel sheet, and aluminium foil. The result in this paper further affirmed the higher AIE efficiency of HPS than that of TPE. At higher magnifications, clear secondary level details of the ridge pattern of the fingerprint are revealed, such as the termination, crossover and bifurcation, which are the significant features that would enable identification of an individual (Fig. 3).



**Fig. 4** Fluorescence images of the sebaceous fingerprints on glass slide (a), stainless steel sheet (b) and aluminium foil (c) developed by the AIE of MCSTPS at the concentration of  $0.1366 \text{ g}\cdot\text{L}^{-1}$ . The water fraction was 70%, 70% and 50% for the three substrates, respectively.

Sebaceous fingerprints can serve as the hydrophobic surface for the interaction with the lipophilic silole compounds. This leads to the deposition of the AIE luminogens on the ridges and a sufficiently strong fluorescence contrast between the fingerprint and the substrate. To validate the proposed mechanism and test the relationship between the hydrophobicity of the AIE luminogens and the quality of fingerprinting, silole derivative of MCSTPS (Fig. 1a) was synthesized and compared with HPS. As shown in Fig. 4, fluorescence images of fingerprints treated with MCSTPS on different substrates gave poorer resolution and higher background compared to those treated with HPS (Fig. 3). This result suggests that the hydrophilic unit of carboxyl group could weaken the hydrophobic interaction between the MCSTPS aggregates and the sebaceous fingerprints. It is also proved that the hydrophobic interaction between the silole aggregates and the fingerprint residue plays a key role in the development of LFPs.

In summary, two silole compounds with AIE features were applied and compared for the development of LFPs on wet non-porous surfaces. The HPS aggregates adhere preferentially onto the fingerprint material and emit strongly under the UV illumination, thus enhancing the visualization of LFPs with clearly visible secondary level details. However, fluorescence images of LFPs treated with MCSTPS aggregates display a poorer resolution and higher background interference. It is thus proved that the development of LFPs by AIE-active compounds is indeed based on the hydrophobic interaction. The approach is pretty simple and cost-effective, as it can be accomplished in a few minutes upon a single-step treatment and only involves in some simple and portable devices. Moreover, it is user friendly since there is no need to use powder, fume treatment or toxic organic solution. We believe that this AIE strategy can be further improved by adopting many other AIE-active molecules. For instance, other AIE-active molecules such as a phosphorus compounds<sup>34</sup> and a polysilole film<sup>35</sup>, have been investigated for the detection of proteins and explosive compounds. These applications will make them promising to be used for detecting human secretions and metabolites in the fingerprint residue for diagnostic purposes as well as for tracing explosives for security implications.

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## Notes and references

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