Supporting Information

Facile detection of latent fingerprints on various substrates based on perylene probe excimer emission

Fangyuan Wang,^{a,b} Jian Chen,^a Huipeng Zhou,^a Wenying Li,^{a,b} Qingfeng

Zhang,^{*a,b*} and Cong Yu*^{*a,b*}

^aState Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, Jilin, 130022, P. R. China ^bUniversity of Chinese Academy of Sciences, Beijing, 100049, P. R. China

E-mail: congyu@ciac.jl.cn

Fax: (+86) 431-8526-2710

EXPERIMENTAL SECTION

Materials

Water was purified with a Milli-Q system (Millipore, Billerica, MA, USA). All reagents were analytical grade and used without further purification. The perylene probes were prepared as previously described.^{S1-S3} PVDF transfer membrane (0.45 μm) was obtained from Pall Gelman Laboratory, USA. Other substrates were all commercially available or daily used. Ground glass was prepared by the treatment of a glass surface with a grinding wheel. Substrates such as glass slide, aluminum foil, stainless steel, porcelain, coin, and plastic were cleaned with a soft brush to remove the dust. Adhesive tape, electrical tape (green color), nitrocellulose microporous filtering film (0.45 μm), and PVDF membrane were used without any pretreatment. 20 mM Tris-HCl buffer solution (100 mM NaCl, 5 mM MgCl₂, pH 7.4) was used throughout.

Instrumentation

UV-vis absorption spectra were determined with a Cary 50 Bio spectrophotometer (Varian Inc., CA, USA). Fluorescent spectra were measured using a Fluoromax-4 spectrofluorometer (Horiba Jobin Yvon Inc., USA). A PB-10 pH meter (Sartorius Scientific Instrument Co., Ltd., Beijing) was used to adjust the buffer pH. A Nikon FinePix HS22EXR digital camera was used to record the fingerprint images.

Fingerprint Development Procedures

The development solution was prepared by dissolving 0.2 mM Probe 1 in 20 mM Tris-HCl buffer (100 mM NaCl, 5 mM MgCl₂, pH 7.4) solution. Before fingerprint samples were collected, volunteers cleaned their fingers briefly with soap, then rubbed their fingers over their forehead or nosewing to leave fingermarks that contain both eccrine and sebaceous materials (sebum) on the substrates. One hour later, substrates were submerged into the development solution and swayed for an appropriate period of time, took out, and gently rinsed with water for two to three times. The LFP images arose under 365 ultraviolet illumination, and the images were recorded with a common digital camera.

The fingerprint samples used for UV-vis and emission measurements were prepared on glass slides. An undeveloped fingerprint glass slide sample was used as the background/baseline. The glass slides containing the developed LFPs were dried in air, placed in the instruments and the spectra were taken. All experiments were carried out at an ambient temperature. The development time was defined as the period that a fingerprint was immersed in the developer solution. The rinsing time is very short and could be ignored.

Throughout the investigation, some of the fingerprint images were recorded with a bandpass filter (light passing window at 510 - 610 nm) to remove the 365 nm background UV light. Figures S1-a and S1-c show that the color of the fingerprint

shifts slightly to green, clear fingerprint images could be observed, and no changes of the image quality were observed.



Fig. S1 (a) Fingerprint image on aluminium foil. Left section: half of the fingerprint was developed with probe 1; right section: not developed. (b) and (c): Fingerprint images on adhesive tape. Left side (with red circle) was the undeveloped fingerprints for easy comparison. (a) and (c): with a bandpass filter. Conditions: 365 nm UV light

illumination. (d) and (e): Enlarged images of Figure 1-a and Figure S1-a with some details of the fingerprint marked with red circle.

Some of the ridges shown in Figures 1-a and S1-a are discontinuous. It seems that the discontinuous observed is a result of fingerprint sample quality, and not a result of our development method used. In addition, it is worth noting that the LFPs in Figures 1a and S1 show clear details including islands, terminations, bifurcations and other secondary details (Figure S1-d and S1-e, supporting information), which are clear enough for individual identification.

The developed and undeveloped fingerprints on adhesive tape were prepared following exactly the same procedures, and gave satisfactory results. The paths of individual ridges can be accurately assessed, and the quality of the clarity is not lower than level-2.^{S4} The similar non-split comparison approach has also been used by a number of literature publications.^{S5-S8}



Fig. S2 Normalized UV-vis absorption spectra. (a): Probe 1 aqueous solution; (b) Probe 1 fingerprint; (c): Probe 1 powder.



Fig. S3 Normalized emission spectra (443 nm excitation) of Probe 1 in an aqueous buffer solution (20 mM Tris-HCl, 100 mM NaCl, 5 mM MgCl₂, pH 7.4) at different concentrations. Please note that at 200 μ M concentration, the emission spectrum shifts slightly to the red, indicating that there was a low degree of Probe 1 aggregation.



Fig. S4 Structures of Probe 2 and Probe 3.



Fig. S5 Fingerprint images on glass slide. Different concentrations of Probe 1 and development times were used. (a) 50 μ M Probe 1, 10 min development time; (b) 0.2 mM Probe 1, 5 min development time; (c) 1 mM Probe 1, 2.5 min development time. Conditions: 365 nm UV light illumination. The color of the developed fingerprints gradually changed from green to green/light yellow, and brown. The results suggest that at a higher Probe 1 concentration, more extended Probe 1 aggregation occurred.



Fig. S6 Fingerprint images on various substrates. (a) glass slide, (b) adhesive tape, (c) plastic, (d) stainless steel, (e) electrical tape, (f) aluminium foil, (g) coin, (h) some details of the fingerprint on stainless steel. Conditions: 365 nm UV light illumination.

Please note that the fingerprint images on glass slide, adhesive tape, and aluminium foil were already given in the previous section, they are shown here again for easy comparison.



Fig. S7 Fingerprint image on rough surface (ground glass). Conditions: 365 nm UV light illumination.



Fig. S8 Fingerprint image on nitrocellulose microporous filtering film (0.45 μ m). Conditions: 365 nm UV light illumination.



Fig. S9 Fingerprint images on porcelain. (a): Under natural light; (b): Under 365 nm UV light illumination.



Fig. S10 Images of fingerprints aged for different times on PVDF membrane. (a): Aged for 48 hours; (b): Aged for 1 week.



Fig. S11 LFP images on PVDF membrane transferred from (a) aluminum foil, (b) computer screen, (c) curved surface of a glass cup, (d) stainless steel, (e) porcelain surface, (f) some details of the fingerprint on porcelain surface. Conditions: 365 nm UV light illumination.



Fig. S12 LFP images on PVDF membrane transferred from (a) and (b) coin, (c) porcelain cup handle, (d) ground glass, (e) stainless steel door handle, (f) rough plastic surface. Conditions: 365 nm UV light illumination.



Fig. S13 LFP Images on PVDF membrane transferred from (a) claw hammer wooden handle, (b) skin, (c) wooden cabinet, (d) banknote, (e) A4 paper, (f) A4 paper (aged for 5 hours). Conditions: 365 nm UV light illumination.



Fig. S14 Normalized UV-vis absorption and emission spectra of Probe 2 (c, d) and Probe 3 (a, b). Buffer solution (20 mM Tris-HCl, 100 mM NaCl, 5 mM MgCl₂, pH 7.4). UV-vis absorption and emission spectra of Probe 2 on fingerprint, and emission spectra of Probe 2 powder were difficult to obtain. The fingerprints developed with probes 2 and 3 gave no fluorescence images, and the solid sample of probe 2 did not give noticeable emission.



Fig. S15 The location of pores in Fig. 3 and Fig. S10-a.

References

- S1. J. Chen, H. P. Jiao, W. Y. Li, D. L. Liao, H. P. Zhou, C. Yu, Chem. Asian J., 2013,
 - **8**, 276.
- S2. B. Wang, C. Yu, Angew. Chem. Int. Ed., 2010, 49, 1485.

- S3. Y. J. Xu, S. W. Leng, C. M. Xue, R. K. Sun, J. Pan, J. Ford, S. Jin, Angew. Chem. Int. Ed., 2007, 46, 3896.
- S4. R. A. Hicklin, J. A. Buscaglia, M. A. Roberts, *Forensic Sci. Int.*, 2013, 226, 106-117.
- S5. R. M. Brown, A. R. Hillman, Phys. Chem. Chem. Phys., 2012, 14, 8653-8661.
- S6. K. H. Cheng, J. Aijmo, L. Ma, M. Yao, X. Zhang, J. Como, L. J. Hope-Weeks, J. Huang, W. Chen, J. Phys. Chem. C, 2008, 112, 17931–17939.
- S7. A. Parkinson, M. Colella, T. Evans, J. Forensic Sci., 2010, 55, 728-734.
- S8. J. Almog, A. Hirshfeld, A. Frank, J. Sterling, D. Leonov, *J. Forensic Sci.*, 1991, 36, 104-110.