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The second near-infrared fluorescence concealed imaging for identifying smuggled baggage

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ABSTRACT

Smuggling methods are renovating with more diversified, complicated means, thereby developing concealed and non-sensitive luggage identification technology is of great significance. Herein, for the first time, the second near-infrared (NIR-II, 1000–2500 nm) concealed imaging for identifying smuggled baggage based on organic small molecule luminescent material was studied. A small molecule luminescent material (Y6) with the excitation in invisible near-infrared (NIR) light was used to generate fluorescence-emission in NIR-II region. The traceless Y6 sprayed on the surface of criminal luggage does not emit light under visible light irradiation, but shows hidden NIR-II signs under NIR excitation that can prevent the suspects to find abnormality and lose their luggage. The Y6 organic luminescent material has invisibility, low toxicity, long-term fluorescence stability and high transparency. This NIR-II fluorescence imaging technology can be used as a new type of concealed baggage marking, which is of great significance to help the customs combat smuggling crimes.

1. Introduction

In recent years, smuggling methods have been constantly renovated with more concealed, diversified, complicated means, and the difficulty of smuggling and drug inspection is increasing [1–4]. The limitations of the traditional inspection mode have been constantly revealed, which brings great difficulties to the collection and identification of evidence in customs security inspection. Smuggling suspects generally hide prohibited items in their luggage in an attempt to get through [5–7]. When customs officers detect luggage carrying suspicious or prohibited items through X-ray machines or other means, they will paste a seal on the suspicious luggage and lock the customs [8–11]. Traditional suspicious baggage tracking system includes customs lock tracking mode, radio frequency identification technology (RFID) tracking intelligent identification bayonet system mode. The customs locks need to be manually locked, which is a tedious process with obvious objectives. If the suspect finds abnormal marks on the appearance of the luggage when picking up the luggage, the suspects will give up the luggage in order to escape the guilt, and the customs staff will not be able to catch the suspect in time. Although the contraband can be detected, catch the suspect will be not in time [12–14]. For RFID tracking system,

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luggage tags contain sensitive information such as the passenger's name and destination, which could be stolen. And, RFID technology is not shared with customs, which cannot identify suspicious baggage owners.

Therefore, it is urgent to develop concealed and non-sensitive luggage identification technology, which does not emit light under ordinary light but can emit light under the excitation of invisible near-infrared (NIR) light [15–17]. When the luggage containing drugs or other prohibited items is found to be abnormal after going through detection machines or other security checks, customs officers can mark the suspicious luggage with hidden marks. The hidden marks are not likely to arouse the alert of the suspects, so as to avoid the malicious destruction of the explicit marks. After the suspect gets the luggage, the latent image of a specific pattern will be revealed by excited light under the NIR light irradiation environment. Customs staff will take the suspect and his luggage away after identifying the hidden mark for further bag opening inspection, and the stolen goods are found on the spot, which is of great significance to customs security and anti-smuggling work. The second near-infrared (NIR-II, 1000–2500 nm) is further located in the non-visible region, which has the advantages of simple operation, less tissue damage, low absorption and scattering in all kinds of materials, and no spontaneous fluorescence [18–22]. NIR-II imaging can greatly improve the temporal and spatial resolution of imaging, and has broad application prospects in various fields, which is in line with the customs supervision activities in the non-sensory, hidden, identifiable target demand.

Herein, we researched an organic small molecule (Y6) based invisible NIR-II luminescent material [23–25], which shows excitation in NIR region, and the emission in NIR-II region. Therefore, it does not emit light under ordinary light irradiation, but shows hidden signs under the excitation of NIR light, which prevents the suspects from losing their luggage if they find the luggage is abnormal (Scheme 1). The organic luminescent material has invisibility, low toxicity, long-term fluorescence stability and high transparency. NIR-II fluorescence imaging of Y6 on different materials was systematically studied and analyzed to prepare a stable luminous system and select an appropriate dispersion system to be used as a new type of concealed baggage marking. This NIR-II fluorescence imaging technology is of great significance to help the customs combat smuggling crimes.

Scheme 1. The progress of fluorescence concealed identification for customs baggage.

2. Results and discussion

The NIR-absorbed Y6 molecule (Fig. 1a) has a narrow band gap with an electron-deficient core and a multi-fused ring of ladder type that possesses the conjugation along the length of the molecule and makes more electron affinity. The *J*-aggregative [26,27] Y6 nanoparticles (NPs) formed by nanoprecipitation with weak blue color for excellent water dispersibility (Fig. 1b), and present bathochromic shift in both absorption and emission spectra. As shown in Fig. 1c and d, Y6 NPs have the maximal absorption at 825 nm and the maximal emission peak at 946 nm, which is redshift than the Y6 molecule in organic solvent (Fig. S1, the maximal absorption at 688 nm and the maximal emission peak at 780 nm). Therefore, Y6 NPs are able to be excited by NIR light and ideal NIR-II fluorescence imaging ability. In this nearly transparent state, Y6 NPs showed excellent potential for the application of fluorescence concealed identification. As shown in Fig. 1e, Y6 NPs possess an average diameter of ~127 nm according to dynamic light scattering (DLS), which is in accordance with the results of transmission electron microscopy (TEM, Fig. 1f). The typical physical properties of Y6 NPs are summarized in Table 1.

In order to verify the actual NIR-II detection effect of Y6 NPs, we firstly carried out the tests with different materials. As shown in Fig. 2a, Y6 can be well sprayed on different materials like paper, metal, glass plastic textile etc. common luggage materials at rather low concentrations (2, 5, 10 μg/mL), and present subtle light blue color, which is imperceptible by human eyes and can be used in the situation of customs. As shown in Fig. 2b, under the excitation of invisible 808 nm light, bright NIR-II fluorescence signal can be detected on these different materials by an InGaAs camera even at a rather low concentration Y6 NPs of 2 μg/mL thin film. Thus, Y6 NPs can be used for excellent the fluorescence concealed identification ability on different materials.

Customs inspection also faces the questions about the distance of inspection, thereby we further tested the fluorescence imaging of Y6 NPs at different distance. As shown in Fig. 3, different drawn patterns (cinquefoil and dirachmaceae) of Y6 film were prepared on

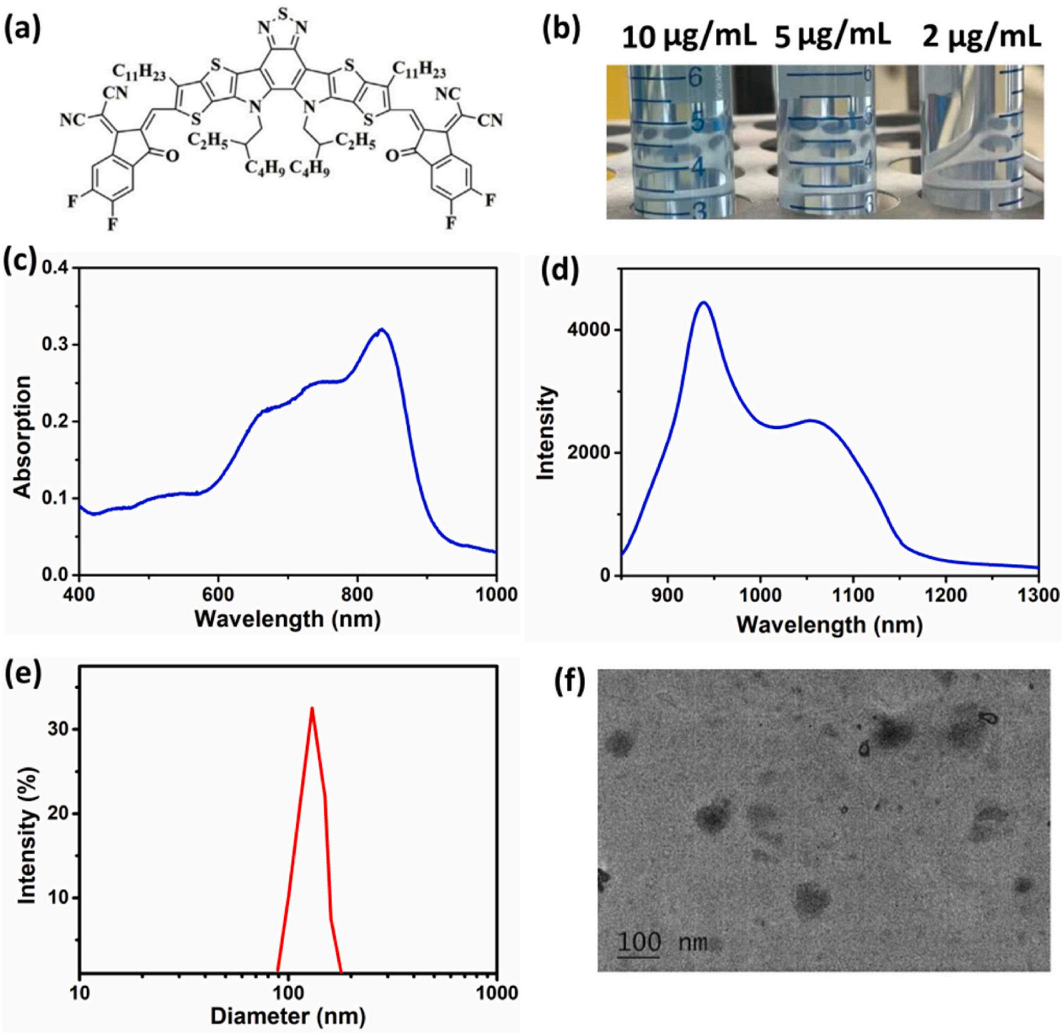

Fig. 1. (a) Molecular structure of Y6. (b) Y6 NPs in water at different concentration. (c) UV–vis–NIR absorption spectra and (d) fluorescence emission spectra of Y6 NPs (40 μg/mL) in water. (e) Size distribution of Y6 NPs. (f) TEM image of Y6 NPs.

Table 1
Physical properties of Y6 NPs.

Absorption peak	Emission peak	Average diameter	Morphology	Solution state
825 nm	946 nm	127 nm	Sphere	Transparent

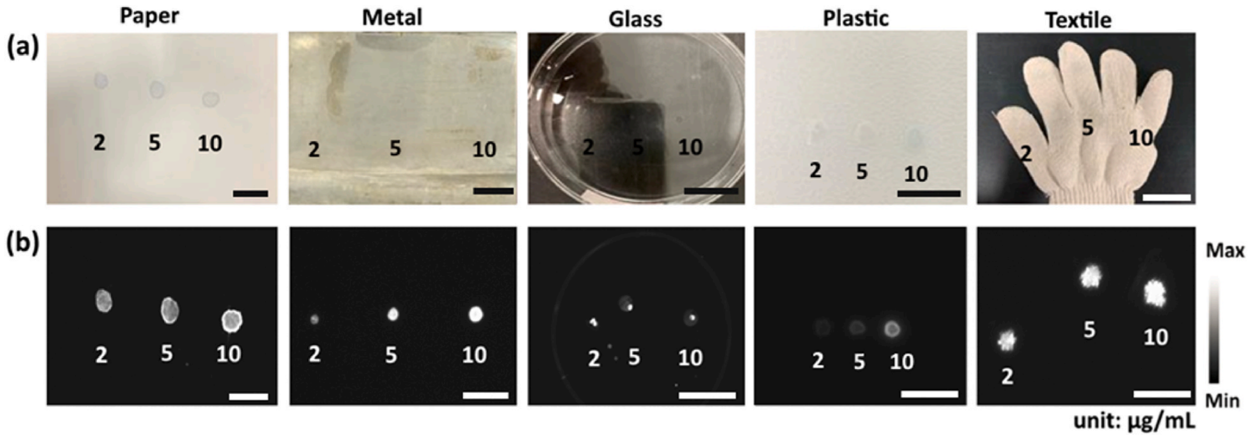

Fig. 2. (a) Y6 sprayed on different materials. (b) NIR-II fluorescence concealed identification on different materials. (Scale bar: 5 cm).

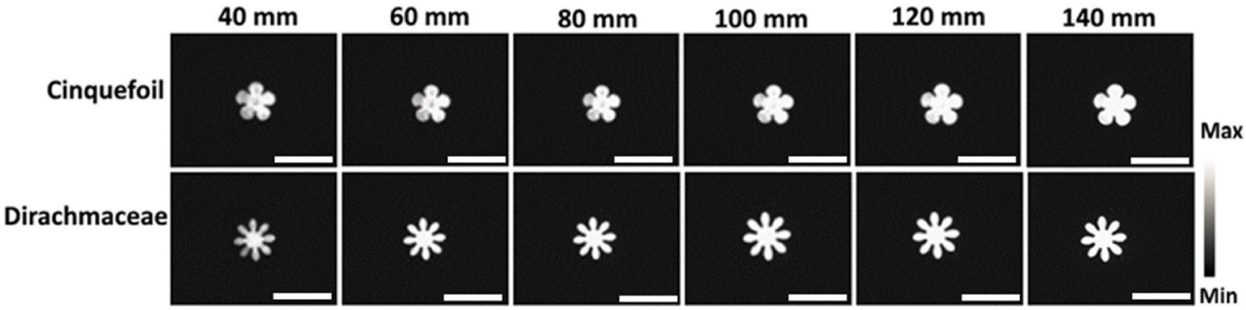

Fig. 3. Different drawn patterns of Y6 and the detection effect at different distances. (Scale bar: 5 cm).

paper and detected at different distances. The imaging effect was barely affected by the distance, and petal of both drawn patterns can be clearly distinguished. These results further confirmed the flexibility and high efficiency of NIR-II fluorescence concealed identification.

In order not to alarm the criminals, the marker needs to be valid for a long time for later detection. Thus, the long-term stability is very important for NIR-II fluorescence concealed identification. Fig. 4a showed the fluorescence emission spectrum of Y6 NPs (40 μg/mL) in water for 14 days, and there was only a slight reduction of the intensity, which indicated the excellent photostability of Y6 NPs. As shown in Fig. 4b, Y6 NPs was sprayed on the customs logo for 14 days, and showed excellent stability in day 7 and day 14. In addition, we used red false color to observe the images and found that it was identical to the white imaging effect of Y6 NPs (40 μg/mL), which has good imaging effect and stability under different pseudo-color imaging effect for 14 days. Besides, misjudgment can be avoided under different pseudo-color imaging. As a contrast, the absorption of the common indocyanine green (ICG) with bovine serum albumin (BSA) showed slightly decreased in 7 days, which indicated ICG NPs also has favourable stability in water (Fig. 5). Thus, Y6 NPs possess excellent stability and show good NIR-II fluorescence concealed identification effect for long-term tracking.

The biosafety of materials is also a very important indicator in the application process. Finally, the biosafety of Y6 NPs was tested by CCK8 method in Human Umbilical Vein Endothelial (HUVEC) Cells. As shown in Fig. 6, Y6 NPs presented no obvious toxicity to the cells at the concentration from 10 μg/mL to 60 μg/mL. Therefore, it is biosafe to use Y6 NPs at a rather low concentration of 2–10 μg/mL in a luggage surface.

3. Conclusions

In summary, a NIR-II concealed imaging for identifying smuggled baggage based on organic small molecule Y6 luminescent material was studied (a simulation experiment is shown in Fig. 7). Y6 NPs does not emit light under ordinary light irradiation, but shows

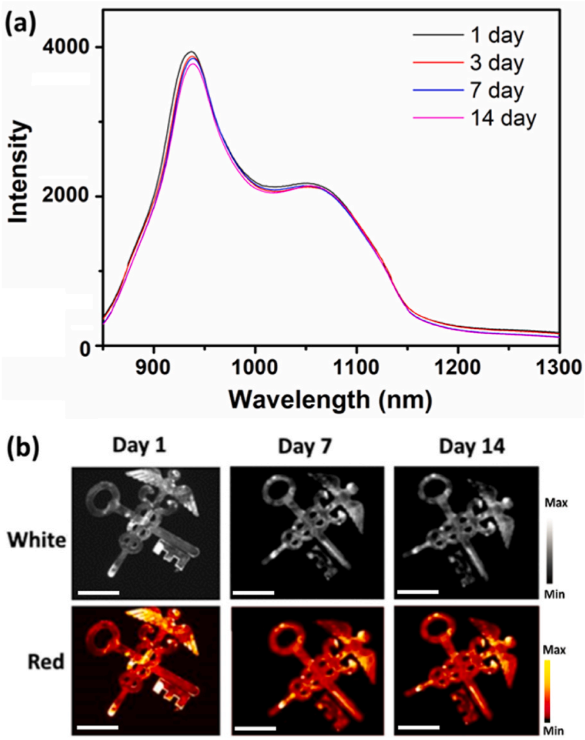

Fig. 4. (a) Fluorescence emission spectrum of Y6 NPs (40 μg/mL) in water for 14 days. (b) Y6 NPs sprayed on the customs logo in different fake colors for 14 days. (Scale bar: 5 cm). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

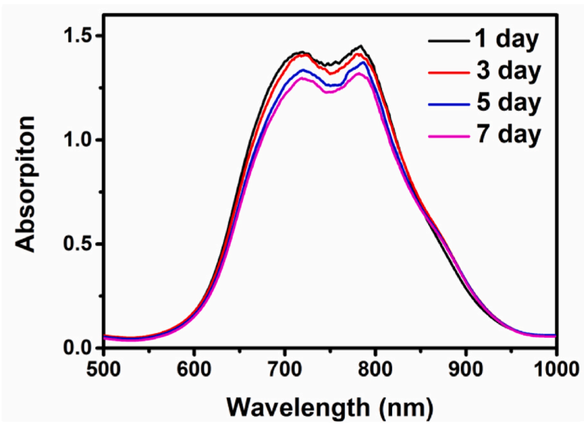

Fig. 5. Absorption spectrum of ICG (40 μg/mL) with BSA in water for 7 day.

hidden signs under the excitation of NIR light, which prevents the suspects from losing their luggage if they find the luggage is abnormal. The organic luminescent material has invisibility, low toxicity, long-term fluorescence stability and high transparency. However, the current design involves excessive manual operation. We aim to incorporate more automated processes in our future designs, such as material spraying and suspect locking systems. In general, NIR-II fluorescence imaging can be used as a new type for concealed baggage marking, which is of great significance to help the customs combat smuggling crimes.

3.1. Experimental section

Materials and characterization. Y6 was purchased from Derthon (Shenzhen, China). Tetrahydrofuran (THF) was purchased from Admas-Beta (Shanghai, China). Cell Counting Kit (CCK8) was purchased from Yeasen Science & Technology Co., Ltd (Shanghai, China). Ultraviolet–visible–near-infrared (UV–vis–NIR) absorbance spectra was collected on a UV–vis–NIR spectrophotometer

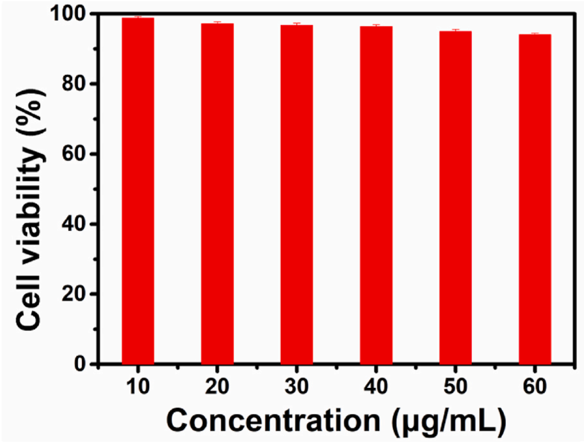

Fig. 6. Cell viability of HUVEC cells against Y6 NPs with different concentration (Mean ± S.D., n = 3).

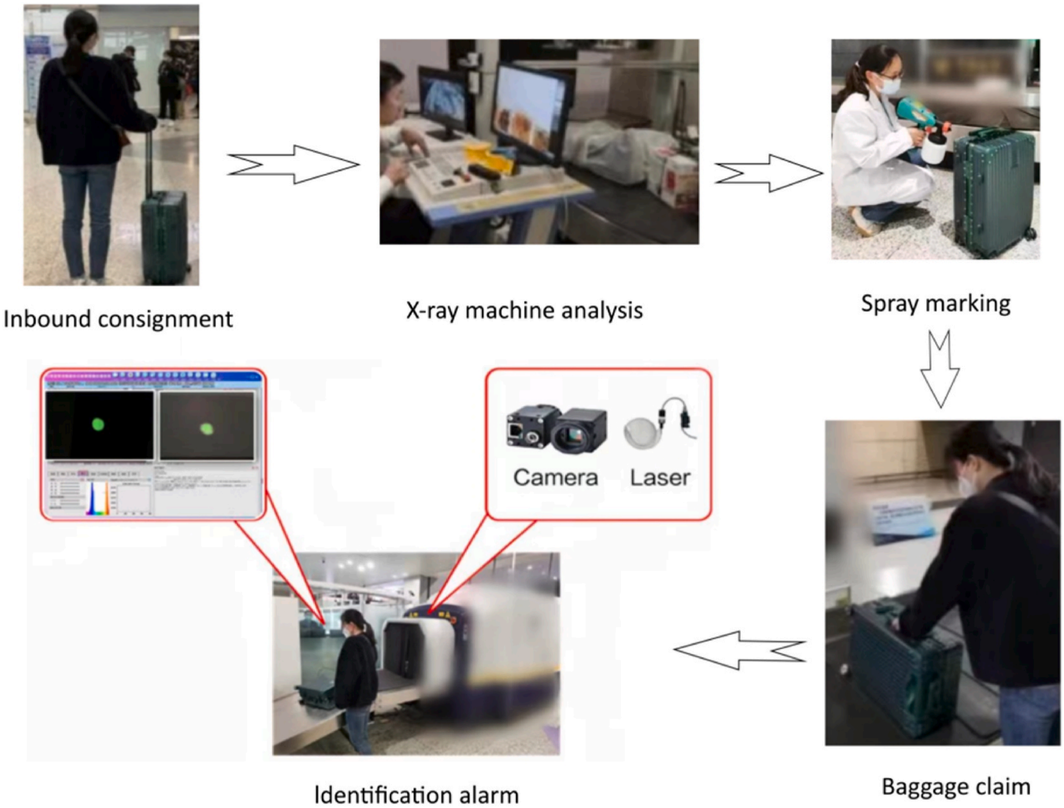

Fig. 7. A simulation experiment of fluorescence concealed identification with Y6 NPs for customs baggage.

(PerkinElmer Lambda 750). Fluorescence spectrum spectra were measured on photoluminescence spectrometer (FLS980, Edinburgh Instruments, UK). The morphology of NPs was observed by using a transmission electron microscope (TEM, HT7700, Hitachi). The hydrodynamic diameter was detected by DLS measurement (Zetasizer Nano ZS, Malvern Instrument, UK). Yingrui Series III 900/1700 (Suzhou, China) NIR-II fluorescence imaging system was used to detect the NIR-II signal.

Preparation of Y6 NPs. 1 mL of Y6 solution (200 μg/mL, THF) was slowly added into H_2O drop by drop (one drop every 10 s) under violent stirring for 5 min, and THF was then removed by rotary evaporation, and water was removed by ultracentrifugation to get the NPs.

NIR-II fluorescence imaging. Yingrui Series III 900/1700 (Suzhou, China) NIR-II fluorescence imaging system was used to detect the NIR-II signal generated by Y6 films (formed with 2, 5, 10 μg/mL of Y6 NPs in water, 50 μL) under different situations (different materials or patterns, excitation laser: 808 nm, power density is 2 W/cm^2). The images were observed using both white and red false color during the long-term stability experiments.

Stability test. 5 mL Y6 NPs (40 μg/mL) in water were stand for 14 days and their fluorescence emission spectra were recorded at day 1, 3, 7 14, respectively.

Cell culture and cytotoxicity experiments. HUVEC cells were cultured in RPMI-1640 medium (Biological Industries) with 21 % O_2 and 5 % CO_2 at 37 °C. CCK-8 assay was used to detect cytotoxicity of Y6 NPs. Briefly, HUVEC cells were seeded into 96-well plates at 5 × 10^3 cells per well and cultured for 24 h. Then, the cells were treated with various concentrations of Y6 NPs for 24 h. After being washed with PBS and the medium was replaced with a fresh medium, the cells were cultured for another 24 h. Subsequently, cell viability was measured through CCK-8 detection.

Author contribution statement

Yu Cai: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper. Jinling Wang: Changjin Ou: Yuanyuan Zhu: Jing Fang: Performed the experiments. Ying Hong: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data.

Data availability statement

Data included in article/supp. Material/referenced in article.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.heliyon.2023.e20815.

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